# Monograph

## Analysis of water samples and water constituents with Metrohm instruments

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Metrohm

# Preface

## Water is essential for all living organisms – without water no life is possible!

Water is needed for dissolving, transporting, and soaking, making possible the most varied chemical and colloid-chemical cell reactions.

About 71% of the earth's surface are covered by water. The distribution of the water volumes is approximately as follows:

| Occurrence | Percentage |
|---|---|
| Seawater and salt lakes | 97.335% |
| Polar ice and glaciers | 2.04% |
| Groundwater | 0.61% |
| Lakes and rivers | 0.009% |
| Soil humidity | 0.005% |
| Atmosphere (water vapor) | 0.001% |

1% corresponds to 14'000 $km^3$

We all need pure, healthy and clean water. Keeping it clean is not only the task of nature and environmental protection organizations or of the water authorities – each and every individual is concerned. The most diverse regulations and guidelines have been developed worldwide and given rise to an independent branch of analytical science. The aim of this monograph is to show you which parameters and water constituents can be analyzed with Metrohm instruments. No attempt will be made, however, to evaluate the analytical results.

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# 1 – Physical parameters

## 1.1 Temperature



### General remarks

The temperature is required for every water analysis. During sampling, the water temperature and usually also the temperature of the ambient air are measured (the solubility of gases, the pH value and any reaction rates are all temperature-dependent quantities). With all temperature measurements the value is recorded only when the display of the measured value remains stable.

### Relevant accessories

6.1110.100 Pt1000 temperature sensor

### Analysis

#### Water temperature

The temperature sensor has to be immersed at sufficient depth into the sample. If this is not possible, a water sample is taken with a recipient of at least 1 liter volume (which beforehand has assumed the water temperature) and the temperature sensor is immersed (do not expose to direct sunlight).

The temperature is given with an accuracy of 0.1 °C.

#### Air temperature

The air temperature is measured with a dry temperature sensor approximately 1 meter above the water or the ground.
The temperature is given with an accuracy of 0.5 °C.

# 1.2 pH value



## General remarks

Free protons ($H^+$ ions) are not present in solution. They adhere to water forming hydronium ions.

$$H^+ + H_2O \rightarrow H_3O^+$$

The pH value is the negative common logarithm of the concentration of free, dissociated hydronium ions in mol/L:

$$pH = -\log [H_3O^+]$$

The pH scale ranges from 0 to 14 and the neutral point lies at pH = 7.0. Water autodissociates into $H_3O^+$ and $OH^-$ ions. At the neutral point, these ions are present in equal amounts. Acidic pH values are measured if there is an excess of $H_3O^+$ whereas basic pH values are obtained if there is an excess of $OH^-$. As the pH scale is logarithmic, small pH differences correspond to large differences of the $H_3O^+$ concentration. As an example, in a given solution there are twice as many $H_3O^+$ ions at pH = 3.1 than at pH = 3.4.

The pH measurement is done with a pH meter equipped with a combined pH glass electrode. This electrode (pH sensor) has to be calibrated first in order to «inform» the measuring instrument about its properties. For the calibration so-called buffer solutions are used. In practice a two-point calibration is usually sufficient (buffer solutions pH = 7.00 and pH = 4.00 or pH = 9.00).

An ideal pH glass electrode has a slope of 1.00 (100% of the Nernst slope) and an electrode zero point $pH_{as}$ of 7.0 or an $U_{as}$ of 0 mV. In practice, the electrode zero point $U_{as}$ should be situated within ±15 mV (corresponding to $pH_{as}$ = 6.75–7.25) and the slope should be >0.95 (>56.2 mV per pH at 25 °C).

The pH value of water samples is a very important quantity. For example, it is the most important factor in assessing the chemical corrosiveness of water bodies. Knowledge of the pH value also allows to draw conclusions regarding chemical and/or biological processes.

## Relevant accessories

- 6.0257.600 Aquatrode plus with Pt1000
- Ready-to-use buffer solutions pH = 7.00 and pH = 4.00 or pH = 9.00 (Metrohm no. 6.2307.110 and 6.2307.100 or 6.2307.120)



## Calibration

The procedure below describes a two-point calibration.

- Connect the electrode to the measuring instrument, open the electrolyte refilling opening and refill electroyte if necessary.
- Thoroughly rinse the electrode with deionized water.
- Immerse the electrode into buffer pH = 7.0 in a beaker and add a magnetic stirring bar.
- Immerse the electrode.
- While stirring, start calibration with buffer 1 on the measuring instrument. Metrohm instruments are equipped with automatic buffer recognition and «read» the pH values corresponding to the prevailing temperature from tables stored in its memory.
- After the instrument has taken over the measured value, remove the electrode from the buffer solution, rinse thoroughly with dionized water.
- Fill buffer solution pH = 4.00 or pH = 9.00 into a second beaker, add a magnetic stirring bar, immerse the electrode (the second buffer solution must be at the same temperature as the first).
- Continue calibration on the measuring instrument under stirring.
- After the instrument has taken over the measured value, terminate the calibration. Remove the electrode from the buffer solution, rinse thoroughly with dionized water.

## Analysis

The pH value of the sample solution (water) depends on the temperature. This temperature dependence cannot be compensated by the measuring instrument, which only compensates the Nernst slope of the electrode.

For this reason, with each pH value measured the temperature at which it was obtained must also be given.

*Example of a water sample: pH = 6.92 at 15.2 °C*

Immerse the electrode to a sufficient depth into the water sample and gently move the electrode to and fro, or carry out the measurement under stirring. Take over the measured value as soon as the displayed value remains stable.
Record the pH value with an accuracy of 0.01, the temperature with an accuracy of 0.1 °C.

**Metrohm literature**

- Application Bulletin AB-188: «pH measurement technique»
- Metrosensor Electrodes catalog

# 1.3 Redox potential

## General remarks

The redox potential is caused by reducing or oxidizing substances dissolved in the water that are able to exchange electrons on the electrode surface. Changes of the redox potential towards positive values indicate the presence of an excess of oxidizing substances, whereas changes towards negative values indicate an excess of reducing substances. Platinum is generally used as the inert electrode material. The measured potential is referred to the standard hydrogen electrode.

The so-called «loaded» redox systems (e.g., wastewaters containing sulfite or chromate) usually cause no difficulties. With «unloaded» redox systems, however, this is completely different, examples being groundwater, surface water, or even demineralized water. In these cases, one has to expect long to very long adjustment times of the electrode to the point that measurements may make little sense.

Redox potentials depend on temperature and pH value. The pH dependence can be used for certain calculations whereas the effect of temperature is largely unknown or cannot be calculated.

## Recommended accessories

- 6.0451.100 combined Pt ring electrode
- 6.2306.020 redox buffer, +250 mV

## Checking and treatment of the combined Pt electrode

Fill redox buffer solution and a magnetic stirring bar into a beaker. Immerse the combined Pt electrode into the redox buffer and measure under stirring. Record the potential as soon as the measured value is stable. The electrode is suitable for redox measurements if the measured value lies within ±5 mV of the value given in the table, which refers to a reference electrode of type Ag/AgCl/c(KCl) = 3 mol/L.

If the measured value lies outside this range, it must be assumed that the platinum surface is oxidized or otherwise altered, or the reference system is contaminated. In these cases, degrease the electrode with a paper tissue soaked in alcohol and then immerse it under stirring and for approx. 15 min in a solution of approx. 0.5 g $Na_2SO_3$ in 50 mL w(HCl) = 15%. After thorough rinsing with distilled dionized water, control the electrode again using the redox buffer solution.



*Table 1. Redox potential values for 6.2306.020 redox buffer in dependence of the temperature.*

| Temperature °C | Redox potential mV | pH value |
|---|---|---|
| 10 | 265 | 7.06 |
| 20 | 250 | 7.02 |
| 25 | 243 | 7.00 |
| 30 | 236 | 6.99 |
| 40 | 221 | 6.98 |
| 50 | 207 | 6.97 |

## Analysis

If possible, carry out this measurement in a sealed flow-through vessel at a flow rate of approx. 10 mL/s. The measured value is recorded as soon as its drift is below 1 mV/min. This can take up to one hour with «unloaded» systems. Also measure the temperature and the pH value of the water.

### Calculation

The measured value is converted to the potential of the standard hydrogen electrode (defined as 0 mV). As mentioned above, the combined Pt electrode is equipped with an Ag/AgCl/c(KCl) = 3 mol/L reference system. This latter's standard potential is added to the measured value.

*Table 2. Standard potential of Ag/AgCl reference system with c(KCl) = 3 mol/L.*

| Temperature °C | Standard potential mV |
|---|---|
| 0 | 224 |
| 10 | 217 |
| 15 | 214 |
| 20 | 211 |
| 25 | 207 |
| 30 | 203 |

Accordingly, the redox potential is calculated as follows:

$U_H = U_M + U_{ref}$

$U_M$ = measured value in mV

$U_{ref}$ = reference potential from the table in mV (depending on temperature)

### Example

At a water temperature of 15 °C, a potential of 455 mV and a pH value of 7.02 were measured.

$U_H$ = 455 mV + 214 mV = 669 mV, which is rounded to 670 mV as redox potentials are always rounded to the next 10 mV.

### Metrohm literature

- Application Bulletin AB-048: «Check of Silver, Platinum and Gold electrodes»
- Metrosensor Electrodes catalog

# 1.4 Electrical conductivity

## General remarks

The electrical conductivity of a solution depens on:

- The number of ions: the more ions a solution contains, the higher its electrical conductivity.
- In general on the ionic mobility, which in turn depends on:
  - The type of ion: the smaller the ion, the more mobile it is and the better it conducts. $H_3O^+$, $OH^-$, $K^+$ and $Cl^-$ are good conductors. If hydration occurs (the ion surrounds itself with water molecules that make it larger) then the conductivity is reduced.
  - The solvent: the more polar a solvent is, the better the dissolved compounds it contains can ionize. Water is an ideal solvent for ionic compounds.
  - The temperature: in contrast to solids, in solutions the electrical conductivity increases as the temperature increases by 1–9% per K, depending on the ion (water samples: 1.8–2.6% per K).
  - The viscosity: as the viscosity increases, the ionic mobility and therefore the electrical conductivity decreases.

## Definitions

The electrical conductivity γ is equal to the reciprocal value of the electrical resistance (conductance G) multiplied by the cell constant c:



$$\gamma = \frac{1}{R} \times \frac{l}{A} = G \times c$$

| Quantity | Symbol | Unit |
|---|---|---|
| Conductivity | γ | S cm $^{-1}$ (S m $^{-1}$) |
| Resistance | R | Ohm (Ω) |
| Conductance | G = 1/R | S (Siemens) = $\Omega^{-1}$ |
| Distance between measuring electrodes | l | cm (m) |
| Measuring electrode area | A | $cm^2$ ($m^2$) |
| Cell constant | c = l/A | $cm^{-1}$ ($m^{-1}$) |

The electrical conductivity is normally given in µS/cm or mS/cm (1.288 mS/cm = 1288 µS/m; 5 mS/cm = 5000 µS/m). In the United States the terms mho and µho are frequently encountered.

### The cell constant c

In principle most instruments for measuring the electrical conductivity are instruments for measuring the resistance $R_X$ or the conductance $G_X = 1/R_X$ of a measuring cell filled with the sample.

The relationship to the electrical conductivity γ, is provided by the cell constant c, which depends on the geometrical dimensions of the measuring cell:

$$\gamma = c/R_X = c \times G_X \text{ (S/cm)}$$

In a two-plate measuring cell the cell constant c is obtained from the area A and the distance l between the plates:

$$c = l/A \ (cm/cm^2)$$

$$[c] = cm^{-1}$$

Because the distribution of the field lines is not ideal, this calculated value does not agree exactly with the effective cell constant of the measuring cell. The effective value of c can only be determined by calibration with conductivity standards, for example KCl solutions.

## Measuring frequency

For conductivities the measuring frequency has a decisive influence on the correctness of the measured conductance G. Interfering polarization effects can be reduced by increasing the measuring frequency, which equates to extending the usable measuring range. However, at high frequencies the parasitic capacitances of the electrode and electrode cable cause interference, which manifests itself in turn in an increase in measurement error at low conductances. The following basic principles apply, though they are always a compromise:

- At low conductances, measurements are made at a lower frequency. The polarization is normally small, allowing a low measuring frequency. At the same time, the measuring error due to the parasitic capacitances is reduced.
- At high conductances, measurements are made at a higher frequency. As a result, the polarization is reduced; the effect of the parasitic capacitances at high conductances is of minor importance.

## Temperature coefficient

The temperature coefficient depends primarily on the ions contained in the solution and seldom shows a linear behavior. We recommend that you determine the temperature coefficient of your water samples yourself or carry out the measurements at the reference temperature. The temperature coefficient is given in % per °C and is used to convert the measured value to the electrical conductivity at the reference temperature, which for water is usually 25 °C (occasionally 20 °C).

## Conductivity measuring cell

These measuring cells, which are also known as Kohlrausch cells, normally have two platinized platinum electrodes. By selecting the area of and the distance between the two electrodes it is possible to vary the cell constant of such electrodes throughout a wide range. Platinizing the electrodes greatly reduces the risk of obtaining incorrect measured values because of polarization. This also has a favorable effect on the usable measuring range. This means that a conductivity cell with a cell constant of c = 1 $cm^{-1}$ can be used at a measuring frequency of 1 kHz from 10 µS/cm to 100 mS/cm, i.e. in a range spanning four orders of magnitude. Smooth, i.e. non-platinized measuring cells should only be used for low electrical conductivities (<20 µS/cm).

However, platinization also has its disadvantages. Platinized measuring cells are susceptible to encrustation, inclusion, and also growth of algae, bacteria or mold. They also dry out during long storage or the platinization slowly breaks down. As a result of these effects the cell constant changes and has to be redetermined from time to time (and, of course, after every replatinization process).



Some suggestions for treating and preparing platinized conductivity cells:

- Place measuring cells that have been stored dry in acetone for approx. 30 min. Then thoroughly rinse with deionized water and place in deionized water for 2–3 h.
- Frequently used measuring cells should be stored in deionized water.
- Less frequently used measuring cells should be stored in 70% ethanol or stored dry (prevents biological growth).
- Always thoroughly rinse the measuring cell with deionized water after use.

Modern conductivity cells use multielectrode measurement techniques, it is therefore no longer necessary to platinize the measuring cell. Polarization effect becomes minor and moreover, these cell can also be stored dry and do not need a conditioning before the first measurement.

## Relevant accessories

- Conductivity measuring cell, e.g., 6.0915.100 5-ring conductivity cell with Pt1000 temperature sensor
- 6.2301.060 conductivity standard – c(KCl) = 0.1000 mol/L

The cell constant c is chosen according to the expected measuring range:

| **Cell constant** | **Measuring range** |
|---|---|
| 0.1 $cm^{-1}$ | 0.1 µS/cm to 300 µS/cm |
| 1 $cm^{-1}$ | 5 µS/cm to 100 mS/cm |
| 10 $cm^{-1}$ | 10 µS/cm to 1000 mS/cm |

## Calibration

The cell constant c is determined by measurements carried out with conductivity standards. These usually are KCl solutions of exactly defined concentration that should be bought with the corresponding certificate.

The measurement is carried out in a thermostated and closed measuring vessel. The correctly prepared and conditioned measuring cell is pre-rinsed with the conductivity standard and then immersed. The measured value is registered as soon as the temperature is constant.

| **Standard c(KCl)** | **$\gamma$ at 20 °C** | **$\gamma$ at 25 °C** | **TC % per °C** |
|---|---|---|---|
| 0.1000 mol/L | 11.67 mS/cm | 12.88 mS/cm | 2.07 |
| 0.0100 mol/L | 1.28 mS/cm | 1.41 mS/cm | 2.03 |
| 0.0010 mol/L | 133 µS/cm | 147 µS/cm | 2.11 |

The cell constant is obtained by dividing the theoretical value (from the table) by the measured value.

### Example

Standard c(KCl) = 0.0100 mol/L

Measuring temperature = 25 °C

Measured value = 1.535 mS

c = 1.41 / 1.535 = 0.919 $cm^{-1}$

## Analysis

### Waste, ground and surface water, mineral and drinking water

The reference temperature is normally 25.0 °C. In order to avoid errors by incorrectly selecting the temperature coefficient (TC) it is recommended to thermostat the sample solution at 25.0 °C If this is not possible, then a TC can be entered as given in the table below. The table is only to be used for water samples that contain mainly calcium and hydrogen carbonate ions as well as small amounts of magnesium, sulfate, chloride, and nitrate ions, i.e. for drinking, lake, ground, and river water samples.

| **Sample temperature °C** | **TC % per °C** |
|---|---|
| 5–10 | 2.62 |
| 10–15 | 2.41 |
| 15–20 | 2.23 |
| 20–25 | 2.08 |
| 25–30 | 1.94 |
| 30–35 | 1.79 |

Together with the electrical conductivity the measuring temperature and any temperature correction applied (reference temperature) are also documented.

### Example

$\gamma_{25}$ = 485 µS/cm

Measuring temperature = 12.1 °C

Reference temperature = 25 °C

Automatic temperature coefficient (TC = 2.24% per °C)

## Demineralized water

Water has an intrinsic conductivity that cannot be reduced by purification methods. The reason for this is the self-dissociation of water, which is also called autoprotolysis:

$$2\,H_2O \rightleftarrows H_3O^+ + OH^-$$

The self-dissociation of water is strongly temperature-dependent and its temperature coefficients are extremely high between 18 and 25 °C:

| Temperature °C | Conductivity µS/cm | TC % per °C |
|---|---|---|
| 0 | 0.010 | |
| 18 | 0.038 | 9.06 |
| 25 | 0.060 | 8.27 |
| 34 | 0.090 | 5.56 |
| 50 | 0.170 | 5.56 |

Because of possible interferences, a special procedure must be selected for water with a conductivity of <5 µS/cm. The most important interferences result from:

- Absorption of $CO_2$ (or other «conducting» gases) from the atmosphere.
- Leaching of traces of Na and Ca from the glassware used.

Both interferences cause the measured value to drift and finally high-bias conductivities are measured. We recommend the following procedures to eliminate such interferences to as great an extent as possible:

### Version 1

Perform flow-through measurements. Because of the small volume of the measuring setup we recommend to use the 6.0916.040 or 6.0918.040 conductivity cell (stainless steel shaft, built-in Pt1000 temperature sensor) screwed into the 6.1420.100 flow-through vessel. The water is allowed to flow through the measuring setup and the conductivity is determined in the usual way.

### Version 2

The measurement is carried out in a volume as large as possible. Nitrogen or argon should be passed through and over the solution, which should also be stirred. If possible, use a closed or covered setup.

Please note the high temperature coefficient of these water samples (see table above).

### Metrohm literature

- Application Bulletin AB-102: «Conductometry»
- Metrohm Monograph: «Conductometry – Conductivity measurement»
- Metrosensor Electrode catalog

# 1.5 Color

## General remarks

Color gives information about the cleanliness of the water. A yellowish color is an indication that the sample contains decomposition products, while a greenish color indicates algae growth and indirectly a surplus of nutritants.

Besides a visual first impression, most often, the color is compared to a hexachloroplatinate scale at a wavelength of 410 nm. Color can be easily determined with a UV/VIS-spectrophotometer. While Metrohm does not offer such instruments, many can be connected to our software and thus integrated into automated systems.

## Instruments and relevant accessories

UV/VIS-Spectrophotometer with flow-through cell

## Analysis

A calibration with potassium hexachloroplatinate and cobalt(II)-chloride hexahydrate standard solution corresponding to a 100 mg/L Pt concentration is made.

The sample is filtered through a filter with a pore size of 0.45 µm and automatically transferred into the UV/VIS-spectrophotometer using the flow-through cell. There the color is measured and the result is automatically transferred to the control software. After the measurement, the cell is either rinsed with ultrapure water or with the next sample.

### Parameters

Please refer to the measuring parameters recommended by the instrument manufacturer.



### Literature

EN ISO 7887: «Water quality – Examination and determination of colour»

# 1.6 Turbidity

## General remarks

Turbidity is an optical property. It measures the scattering effect that suspended solids have on light. The more suspended matter is present the higher the turbidity. A high turbidity is thus undesirable in drinking water or water for food and beverage processing.
Turbidity is determined by comparing the light scattering of the sample to the scattering of a reference suspension. Turbidity can be easily determined with a turbiditymeter. While Metrohm does not offer such instruments, many can be connected to our software and thus integrated into automated systems.

## Instruments and relevant accessories

Turbiditymeter with flow-through cell

## Analysis

A calibration with NTU standard solutions is made. Calibration standards are provided by the instrument manufacturer or can be obtained from a supplier.

The sample is automatically transferred into the sample cell. The first part of the sample is used to rinse the flow-through cell. After rinsing the cell, the turbidity is measured and the result is automatically transferred to the control software.

### Parameters

Please refer to the measuring parameters recommended by the instrument manufacturer.

## Remarks



- It is important that enough sample is used to pre-rinse the sample cell in order to obtain a stable measuring value. If only a small sample amount is available, it is recommended to use ultrapure water to rinse out the previous sample before transfering the new sample into the sample cell.
- Turbidity measurements among differing technologies are often not consistent.
- For low turbidity values, so-called nephelometers are used, where the scattered light is measured in a 90° angle from the in-coming light. For high turbidity values, various instruments using different technologies are available.

### Literature

ASTM D6855: «Standard Test Method for Determination of Turbidity Below 5 NTU in StaticMode»

ASTM D7315: «Standard Test Method for Determination of Turbidity Above 1 Turbidity Unit (TU) in Static Mode»

# 2 Overall parameters

## 2.1 Permanganate index (PMI)

### General remarks

The permanganate index, given as mg/L $O_2$, is a standard parameter for the determination of the content of organic and inorganic water constituents that are oxidized by permanganate under the test conditions. It cannot be regarded as a measure for the theoretical oxygen demand since many organic compounds are not completely oxidized. Its primary purpose is to evaluate water supplies for human or domestic use (drinking, mineral, source water, water from swimming pools). The procedure is applicable to water samples with a chloride content <300 mg/L. The lower application limit is about 0.5 mg/L $O_2$. Water samples with a permanganate index >10 mg/L $O_2$ must be diluted before the determination.

## Instrument and relevant accessories

- Titrator with DET mode
- Stirrer
- 6.0431.100 Pt Titrode



## Reagents

Deionized water from water purification plants with organic ion exchangers is not suitable for preparing the reagents. Use either distilled water or water from a reverse-osmosis plant.

- Permanganate stock solution: c($KMnO_4$) = 0.02 mol/L (CAS 7722-64-7)
  This solution is commercially available.
- Titrant 1: c($KMnO_4$) = 0.002 mol/L (CAS 7722-64-7)
  The solution can be stored for approx. 3 months.
- Sodium oxalate stock solution: c($Na_2C_2O_4$) = 0.05 mol/L (CAS 62-76-0)
- Titrant 2: c($Na_2C_2O_4$) = 0.005 mol/L (CAS 62-76-0)
  The solution can be stored for approx. 2 weeks.
- Sulfuric acid: c($H_2SO_4$) = 2 mol/L (CAS 7664-93-9)

## Analysis

The determination according to EN ISO 8467 is described here.
Transfer 25 mL water sample into a titration vessel, add 5 mL sulfuric acid and some boiling beads and rapidly heat to boiling for 10 min. Add 5.00 mL c($KMnO_4$) = 0.002 mol/L (titrant 1) and continue heating for exactly 10 min. After the 10 min boiling time, rapidly add 5.00 mL c($Na_2C_2O_4$) = 0.005 mol/L (titrant 2) and wait until the solution is colorless. Titrate the hot solution with c($KMnO_4$) = 0.002 mol/L (titrant 1) past the equivalence point.

Perform a blank the same way, but omit the sample.

## Parameters

| | |
|---|---|
| Mode | DET U |
| Stirring rate | 6 |
| Signal drift | 50 mV/min |
| Min. waiting time | 2 s |
| Max. waiting time | 26 s |
| Measuring point distance | 0 |
| Min. increment | 20 µL |
| Max. increment | 100 µL |
| EP criterion | 50 |

## Calculations

1 mL c($KMnO_4$) = 0.002 mol/L corresponds to 0.316 mg $KMnO_4$.
1 mg $KMnO_4$ corresponds to 7.9 µmol $O_2$ = 0.1264 mg $O_2$.

$$PMI = \frac{(V_{EP1} - Blank) \times V_{Na_2C_2O_4} \times c_{Na_2C_2O_4} \times M_A}{k \times V_S}$$

| | |
|---|---|
| PMI: | Permanganate index in mg/L |
| $V_{EP1}$: | Titrant consumption until the first equivalence point in mL |
| Blank: | Volume for blank in mL |
| $V_{Na_2C_2O_4}$: | Volume of added disodium oxalate standard solution; here 5.5 mL |
| $c_{Na_2C_2O_4}$: | Concentration of disodium oxalate in mmol/L; here 5 mmol/L |
| $M_A$: | Molar mass of oxygen, 15.999 mg/mmol |
| k: | Value of the standardization in mL |
| $V_s$: | Sample size in mL |

## Remarks

- Use only thoroughly cleaned glassware. Detergent residues will falsify the result – it is best to use always the same titration vessels.
- The 10-min boiling time must be strictly adhered to.
- To accelerate the titration, approx. 0.1 g $MnSO_4$ can be added to the solution as a catalyst. The titration can then even be carried out at room temperature.
- To prevent manganese dioxide crystals in the buret, it is recommended to use high, narrow bottles, and the aspiration tip of the buret should not reach the bottom of the bottle. Furthermore, freshly prepared solution should be left to stand for 24 h before using them for the first time.



## Example

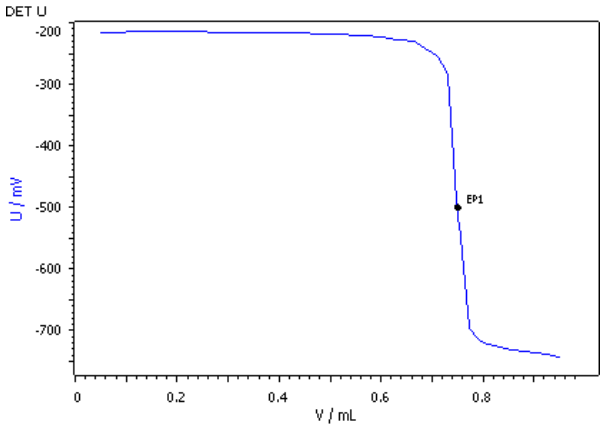


*Figure 1: Example titration curve for the PMI of tap water.*

## Metrohm literature

Application Bulletin AB-178: «Fully automated water analysis»

# 2.2 Acid and base capacity



## General remarks

The acid capacity of a water sample ($K_A$) is equal to the amount of hydronium ions that the sample consumes to reach a given pH value. It is indicated in mmol/L. To obtain the acid capacity to pH 8.2 (p-value), the sample is titrated with HCl to pH = 8.2; to obtain the acid capacity to pH 4.3 (m-value), the sample is titrated to pH = 4.3.

The base capacity of a water sample ($K_B$) is equal to the amount of hydroxide ions that the sample consumes to reach a given pH value. It is indicated in mmol/L. To obtain the base capacity to pH 4.3 ($K_{B4.3}$), the sample is titrated with NaOH to pH = 4.3; to obtain the base capacity to pH 8.2 ($K_{B8.2}$), the sample is titrated to pH = 8.2

## Instrument and relevant accessories

- Titrator with SET mode
- Magnetic stirrer
- 6.0257.600 Aquatrode Plus with integrated Pt1000 temperature sensor

## Reagents

- Titrant 1: c(HCl) = 0.1 mol/L (CAS 7647-01-0)
  This titrant is commercially available.
- Titrant 2: c(HCl) = 0.02 mol/L (CAS 7647-01-0)
  This titrant is commercially available.
- Titrant 3: c(NaOH) = 0.1 mol/L (CAS 1310-73-2)
  This titrant is commercially available.
- Titrant 4: c(NaOH) = 0.02 mol/L (CAS 1310-73-2)
  This titrant is commercially available.
- Buffer solutions pH = 4.00, pH = 7.00, and pH = 9.00,
  e.g., Metrohm no. 6.2307.100, 6.2307.110, and 6.2307.120

## Analyses

Before starting the measurements, calibrate the Aquatrode Plus with buffer solutions pH = 4.00, pH = 7.00, and pH = 9.00.

## Acid capacity (alkalinity)

Transfer 100 mL water sample into the titration vessel. Measure first the pH value under stirring. After this, titrate with c(HCl) = 0.1 mol/L or 0.02 mol/L.



### Parameters

| | |
|---|---|
| Mode | SET pH |
| Stirring rate | 8 |
| Control range pH | 2 |
| Min. dosing rate | 25 µL/min |
| Max. dosing rate | 10 mL/min |
| Endpoint 1 at pH | 8.2 |
| Endpoint 2 at pH | 4.3 |

### Calculations

$$\text{p-value} = \frac{V_{EP1} \times c_{HCl} \times f \times 1000}{V_s}$$

p-value: Amount of carbonate in the sample in mmol/L
$V_{EP1}$: Titrant consumption until the first end point (pH = 8.2) in mL
$c_{HCl}$: Concentration of titrant in mol/L; here c(HCl) = 0.1 mol/L
f: Correction factor («titer») dimensionless
1000: Conversion factor to obtain result in mmol/L
$V_s$: Sample size in mL

$$\text{m-value} = \frac{V_{EP2} \times c_{HCl} \times f \times 1000}{V_s}$$

m-value: Amount of total alkalinity in the sample in mmol/L
$V_{EP2}$: Titrant consumption until the second end point (pH = 4.3) in mL
$c_{HCl}$: Concentration of titrant in mol/L; here c(HCl) = 0.1 mol/L
f: Correction factor («titer») dimensionless
1000: Conversion factor to obtain result in mmol/L
$V_s$: Sample size in mL

The result is given to two decimal places.

## Remarks

- The initial pH value of many water samples is below 8.2 and $K_{A8.2}$ cannot be calculated
- See next chapter for the calculation of the carbonate hardness.



### Example

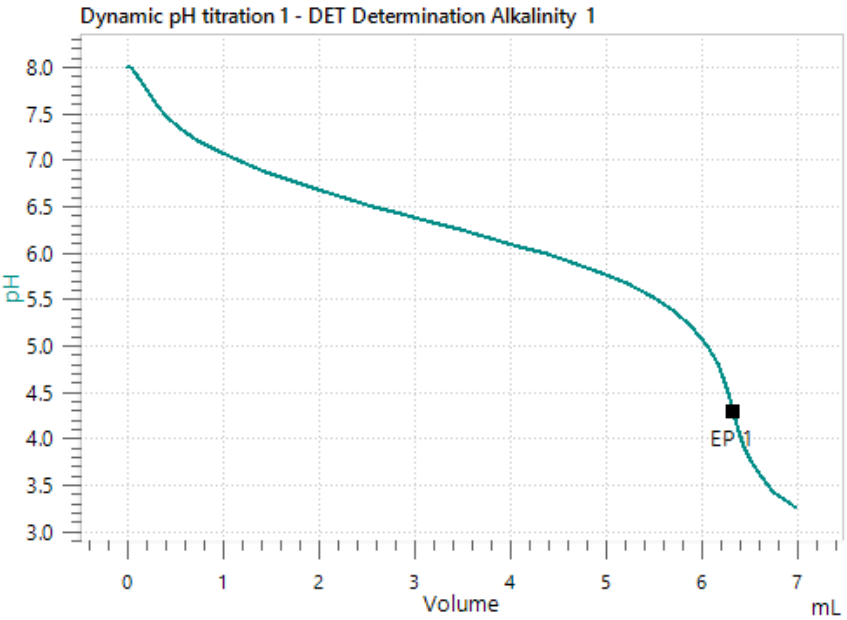


*Figure 2: Example titration curve for the alkalinity of tap water. This example water has an initial pH value lower than 8.2 and thus no p-value.*

### Base capacity (acidity)

Transfer 100 mL water sample into the titration vessel. Measure first the pH value under stirring. After this, titrate with c(NaOH) = 0.1 mol/L or 0.02 mol/L.

## Parameters

| | |
|---|---|
| Mode | SET pH |
| Stirring rate | 8 |
| Control range pH | 2 |
| Min. dosing rate | 25 µL/min |
| Max. dosing rate | 10 mL/min |
| Endpoint 1 at pH | 4.3 |
| Endpoint 2 at pH | 8.2 |

## Calculations

$$K_{B4.3} = \frac{V_{EP1} \times c_{NaOH} \times f \times 1000}{V_s}$$

$K_{B4.3}$: Base capacity of the sample at pH 4.3 in mmol/L
$V_{EP1}$: Titrant consumption until the first endpoint (pH = 4.3) in mL
$c_{NaOH}$: Concentration of titrant in mol/L; here c(NaOH) = 0.02 mol/L
f: Correction factor («titer») dimensionless
1000: Conversion factor to obtain result in mmol/L
$V_s$: Sample size in mL

$$K_{B8.2} = \frac{V_{EP2} \times c_{NaOH} \times f \times 1000}{V_s}$$

$K_{B8.2}$: Base capacity of the sample at pH 8.2 in mmol/L
$V_{EP2}$: Titrant consumption until the second endpoint (pH = 8.2) in mL
$c_{NaOH}$: Concentration of titrant in mol/L; here c(NaOH) = 0.02 mol/L
f: Correction factor («titer») dimensionless
1000: Conversion factor to obtain result in mmol/L
$V_s$: Sample size in mL

The result is given to two decimal places.

## Remarks

- The initial pH value of many water samples is above 4.3 and $K_{B4.3}$ cannot be calculaed.
- Rinse the electrode between runs with dilute HCl followed by deionized water to remove any precipitated $CaCO_3$.



### Example

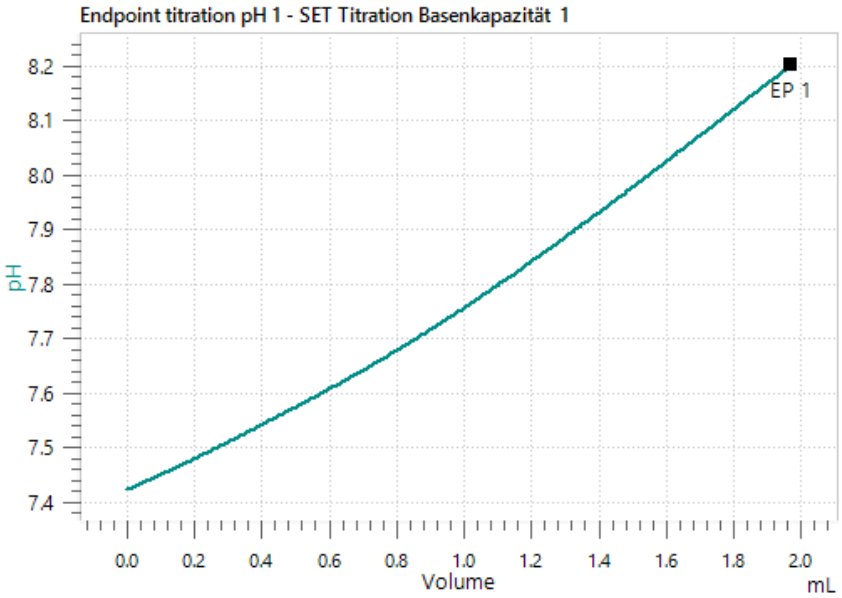


*Figure 3: Example titration curve for the base capacity at pH 8.2 of tap water. This example water has an initial pH value higher than 4.3 and thus no base capacity at pH 4.3.*

# 2.3 Water hardness



## General remarks

Carbon dioxide ($CO_2$) dissolves in water. In calcareous water it is present as carbonate and hydrogen carbonate. In the lime-carbonic acid equilibrium, free carbonic acid and carbonate are in equilibrium with hydrogen carbonate. If there is enough free $CO_2$, calcium remains dissolved as hydrogen carbonate. If there is an excess of free $CO_2$, these waters become aggressive – they leach out calcium from calcareous materials causing, for example, corrosion of concrete. Upon warming up or by plant assimilation (e.g., by algae) $CO_2$ is driven out or consumed and the equilibrium shifts to the carbonate side. The carbonate then precipitates as sparingly soluble $CaCO_3$ (e.g., boiler scale) and the pH value can increase to values above 9.

The total hardness of a water is defined as the sum of the hardness-causing species (Ca, Mg, Ba, Sr), whereas the calcium or magnesium hardness refers to the corresponding ion. The carbonate hardness or temporary hardness is the sum of the carbonates and hydrogen carbonates, which is determined by the acid capacity – m-value. The sulfate hardness or permanent hardness is obtained by subtracting the carbonate hardness from the total hardness. All hardness values are given in mmol/L.

As Al, Ba, Fe, Mn, and Sr ions are present at very low levels in most waters, one only determines calcium and magnesium.

As user information, for example on detergent packages, expressions such as «soft», «hard», «°dH», «°fH» still have a certain importance. The table below informs about the existing relationships:

| mmol/L | mg/L $CaCO_3$ | °fH | °dH | °USH | Hardness |
|---|---|---|---|---|---|
| 0–0.7 | 0–70 | 0–7 | 0–3.92 | 0–3.77 | very soft |
| 0.7–1.5 | 70–150 | 7–15 | 3.92–8.4 | 3.77–8.07 | soft |
| 1.5–2.5 | 150–250 | 15–25 | 8.4–14.0 | 8.07–9.50 | moderately hard |
| 2.5–3.2 | 250–320 | 25–32 | 14.0–17.92 | 9.5–17.22 | rather hard |
| 3.2–4.2 | 320–420 | 32–42 | 17.92–23.5 | 17.22–22.6 | hard |
| >4.2 | >420 | >42 | >23.52 | >22.6 | very hard |

### Conversion factors

mmol/L x 100 → mg/L $CaCO_3$
mmol/L x 10 → °fH (French hardness degrees)
mmol/L x 5.6 → °dH (German hardness degrees)
mmol/L x 5.38 → °USH (US hardness degrees)

## Instrument and relevant accessories

- Titrator with DET mode
- Stirrer
- 6.0510.100 Combined polymer membrane electrode, Ca

## Reagents

- Reagents for the determination of the carbonate hardness: see preceding chapter under «acid capacity».
- Titrant: c($Na_2EDTA$) = 0.1 mol/L (CAS 6381-92-6)
  This solution is commercially available.
- Auxiliary complexing solution:
  c(acetyl acetone) = 0.1 mol/L (CAS 123-54-6) and c(TRIS) = 0.2 mol/L (CAS 77-86-1)
  This solution can only be stored for a few days.

## Analyses

### Carbonate hardness

Use a 100-mL water sample and determine the consumption of HCl in mL to pH = 4.3 (m-value). See above under «acid capacity» in chapter «2.2 Acid and base capacity» for parameters and remarks.

### Calculations

$$\text{carbonate hardness} = \frac{V_{EP1} \times c_{HCl} \times f \times 1000}{V_S}$$

| | |
|---|---|
| carbonate hardness: | Carbonate hardness of the sample in mmol/L |
| $V_{EP1}$: | Titrant consumption until the first end point (pH = 4.3) in mL |
| $c_{HCl}$: | Concentration of titrant in mol/L; here c(HCl) = 0.1 mol/L |
| f: | Correction factor («titer») dimensionless |
| 1000: | Conversion factor to obtain result in mmol/L |
| $V_s$: | Sample size in mL |

The result is given to two decimal places.

## Calcium, magnesium, and total hardness

Pipet 100 mL water sample into the titration beaker, add 15 mL auxiliary complexing solution and titrate with c($Na_2$EDTA) = 0.1 mol/L past the second equivalence point. The first equivalence point corresponds to the calcium content and the difference between the second and first equivalence point corresponds to the magnesium content.



### Parameters

| | |
|---|---|
| Mode | DET U |
| Stirring rate | 8 |
| Signal drift | 50 mV/min |
| Max. waiting time | 26 s |
| Measuring point distance | 4 |
| Min. increment | 10 µL |
| EP criterion | 50 |
| EP recognition | all |

### Calculations

$$\text{Ca hardness} = \frac{V_{EP1} \times c_{EDTA} \times f \times 1000}{V_s}$$

| | |
|---|---|
| Ca hardness: | Amount of calcium in the sample in mmol/L |
| $V_{EP1}$: | Titrant consumption until the first equivalence point in mL |
| $c_{EDTA}$: | Concentration of titrant in mol/L; here c(EDTA) = 0.1 mol/L |
| f: | Correction factor («titer») without unit |
| 1000: | Conversion factor to obtain result in mmol/L |
| $V_s$: | Sample size in mL |

$$\text{Mg hardness} = \frac{(V_{EP2} - V_{EP1}) \times c_{EDTA} \times f \times 1000}{V_S}$$



| | |
|---|---|
| Mg hardness: | Amount of magnesium in the sample in mmol/L |
| $V_{EP2}$: | Titrant consumption until the second equivalence point in mL |
| $V_{EP1}$: | Titrant consumption until the first equivalence point in mL |
| $c_{EDTA}$: | Concentration of titrant in mol/L; here c(EDTA) = 0.1 mol/L |
| f: | Correction factor («titer») without unit |
| 1000: | Conversion factor to obtain result in mmol/L |
| $V_s$: | Sample size in mL |

$$\text{total hardness} = \frac{V_{EP2} \times c_{EDTA} \times f \times 1000}{V_S}$$

| | |
|---|---|
| total hardness: | Total hardness of the sample in mmol/L |
| $V_{EP2}$: | Titrant consumption until the second equivalence point in mL |
| $c_{EDTA}$: | Concentration of titrant in mol/L; here c(EDTA) = 0.1 mol/L |
| f: | Correction factor («titer») without unit |
| 1000: | Conversion factor to obtain result in mmol/L |
| $V_s$: | Sample size in mL |

permanent hardness = total hardness – carbonate hardness

| | |
|---|---|
| permanent hardness: | Permanent hardness of the sample in mmol/L |
| total hardness: | Total hardness of the sample in mmol/L |
| carbonate hardness: | Carbonate hardness of the sample in mmol/L |

## Remarks

- Soft water is best titrated with c($Na_2EDTA$) = 0.05 mol/L.
- Water that contains little Mg besides a high Ca concentration yields a bad separation of the titration curve steps. In these cases we recommend to add Mg standard to the auxiliary complexing solution. This Mg addition must of course be taken into account in the calculations.
- The added volume of the auxiliary solution can be optimized according to the magnesium content. As a rule of thumb, the molar ratio Mg/acetylacetone should be approximately 0.05.



### Example

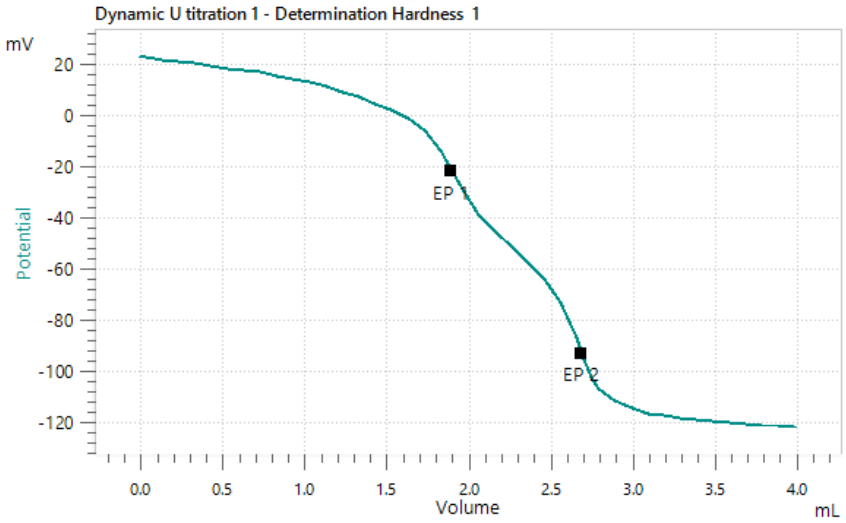


*Figure 4: Example titration curve for the water hardness of tap water.*

### Metrohm literature

Application Bulletin AB-125: «Simultaneous determination of calcium, magnesium, and alkalinity by complexometric titration with potentiometric or photometric indication in water and beverage samples»

# Two alternative titrimetric methods for determining total water hardness

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## Potentiometric titration with Cu ISE

### Instrument and relevant accessories

- Titrator with MET mode
- Stirrer
- 6.0502.140 Ion-selective electrode, Cu
- 6.0750.100 LL ISE reference electrode

## Reagents

- Titrant: c($Na_2$EDTA) = 0.1 mol/L (CAS 6381-92-6)
  This solution is commercially available.
- Cu-complex solution: c[$Cu(NH_4)_2$EDTA] = 0.1 mol/L (CAS 67989-88-2)
  This solution is commercially available.
- Ammonia buffer solution pH = 10

## Analysis

Pipet 100 mL water sample into the titration beaker. Add 5 mL buffer solution pH = 10, followed by 0.5 mL Cu-complex solution, stir for 20 s and titrate with c($Na_2$EDTA) = 0.1 mol/L past the last, clearly pronounced equivalence point.

### Parameters

| | |
|---|---|
| Mode | MET U |
| Pause | 30 s |
| Stirring rate | 8 |
| Signal drift | 50 mV/min |
| Min. waiting time | 5 s |
| Max. waiting time | 26 s |
| Volume increment | 0.1 mL |
| EP criterion | 30 mV |
| EP recognition | all |

### Calculations

$$\text{total hardness} = \frac{V_{EP1} \times c_{EDTA} \times f \times 1000}{V_s}$$

total hardness: Total hardness of the sample in mmol/L
$V_{EP1}$: Titrant consumption until the first equivalence point in mL
$c_{EDTA}$: Concentration of titrant in mol/L; here c(EDTA) = 0.1 mol/L
f: Correction factor («titer») without unit
1000: Conversion factor to obtain result in mmol/L
$V_s$: Sample size in mL

## Remarks

- Soft waters are best titrated with c($Na_2$EDTA) = 0.05 mol/L.
- This method cannot be used for seawater.
- Polish the surface of the Cu ISE with aluminum oxide powder from time to time.

### Example

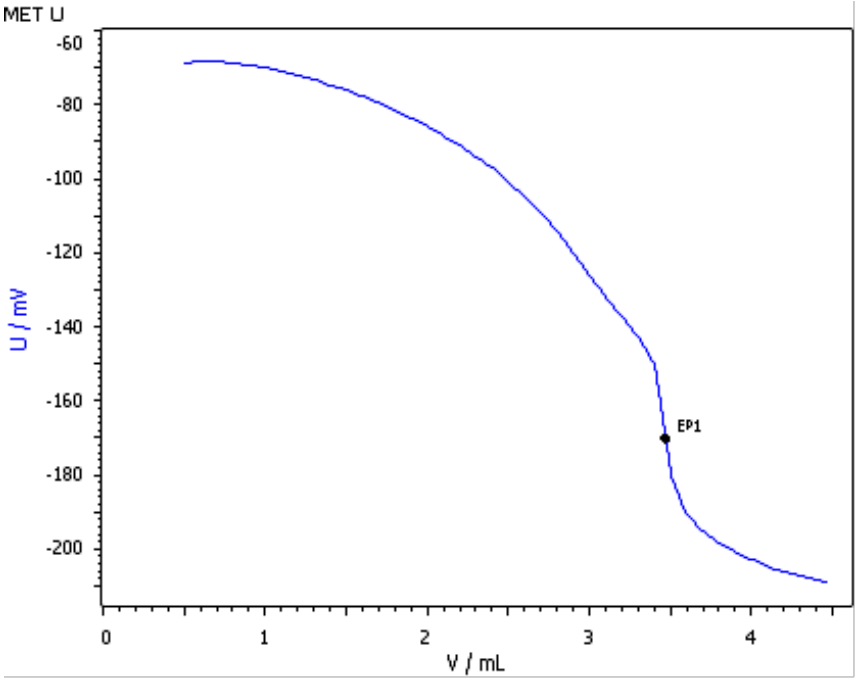



*Figure 5: Example titration curve for the total hardness of tap water by titration with the Cu ISE.*

### Metrohm literature

Application Bulletin AB-101: «Complexometric titrations with the Cu ISE»

Application Note AN-T-131: «Automatic determination of calcium, magnesium and total hardness in water with the Cu ISE»

## Photometric titration with the Optrode

### Instrument and relevant accessories

- Titrator with MET mod
- Stirrer
- 6.1115.000 Optrode

## Reagents

- Titrant: c($Na_2$EDTA) = 0.1 mol/L (CAS 6381-92-6)
  This solution is commercially available.
- Ammonia buffer solution pH = 10
- Mg complex: $K_2$MgEDTA · 2 $H_2O$ (CAS 15708-48-2)
- Indicator solution: Eriochrome Black T (CAS 1787-61-7)

## Analysis

Pipet 100 mL water sample into the titration beaker. Add approx. 0.1 g Mg complex, 10 mL buffer solution pH = 10 and 0.25 mL indicator solution. Degas for approx. 3 min in an ultrasonic bath. Titrate past the first equivalence point with c($Na_2$EDTA) = 0.1 mol/L solution.

| | |
|---|---|
| Mode | MET U |
| Wavelength | 610 nm |
| Pause | 30 s |
| Stirring rate | 8 |
| Signal drift | 50 mV/min |
| Min. waiting time | 5 s |
| Max. waiting time | 26 s |
| Volume increment | 0.1 mL |
| EP criterion | 30 mV |
| EP recognition | greatest |

### Calculations

$$\text{total hardness} = \frac{V_{EP1} \times c_{EDTA} \times f \times 1000}{V_S}$$

| | |
|---|---|
| total hardness: | Total hardness of the sample in mmol/L |
| $V_{EP1}$: | Titrant consumption until the first equivalence point in mL |
| $c_{EDTA}$: | Concentration of titrant in mol/L; here c(EDTA) = 0.1 mol/L |
| f: | Correction factor («titer») without unit |
| 1000: | Conversion factor to obtain result in mmol/L |
| $V_s$: | Sample size in mL |

## Remarks

- Soft water is best titrated with c($Na_2EDTA$) = 0.05 mol/L.
- Make sure that no air bubbles are within the light path of the Optrode during the titration.

### Example

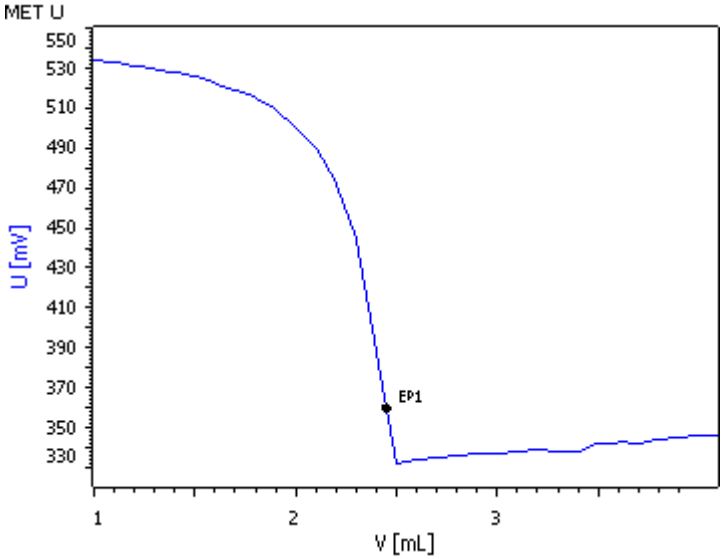



*Figure 6: Example titration curve for the total hardness of tap water by photometric titration with the Optrode.*

### Metrohm literature

Application Note AN-T-084: «Fully automatic determination of the total, calcium and magnesium hardness of water samples using photometric titration»

# 2.4 Kjeldahl nitrogen



## General remarks

Nitrogen is an essential growth nutrient, especially organic and ammoniacal nitrogen are important. Fertilizers can introduce nitrogen into water, stimulating photosynthetic organism growth, for this reason it is important to monitor the nitrogen content in water.

The Kjedahl method determines ammonium nitrogen and a large portion of the organically bound nitrogen of a water sample. The nitrogen present in the following species is not or only partially determined: nitrite, nitrate, azide, cyanide; heterocyclic, nitro, nitroso and diazo compounds.

The sample is digested with sulfuric acid in the presence of a catalyst. This converts organically bound nitrogen to ammonium sulfate. In a distillation apparatus, an excess of NaOH is added to the digestion solution and the liberated ammonia ($NH_3$) distilled into a vessel containing boric acid. The absorbed ammonia is then titrated with $H_2SO_4$ or HCl. In here, the determination based on ASTM D3590 is described.

## Instrument and relevant accessories

- Titrator with SET or DET mode
- Stirrer
- Combined pH glass electrode: 6.0258.600 Unitrode with Pt1000

## Reagents

- Sulfuric acid: $w(H_2SO_4)$ = 98% (CAS 7664-93-9)
- Catalyst:
  5-g tablets of varying composition are commercially available. We recommend to use tablets without Se and/or Hg.
- Sodium hydroxide solution: c(NaOH) = 10 mol/L (CAS 1310-73-2)
- Absorption solution: $w(H_3BO_3)$ = 2% (CAS 10043-35-3)
- Titrant: $c(H_2SO_4)$ = 0.02 mol/L (CAS 7664-93-9)
- Buffer solutions pH = 4.00 and pH = 7.00,
  e.g., Metrohm no. 6.2307.100 and 6.2307.110

## Sample preparation

The sample volume has to be adjusted to the expected nitrogen content. Wastewaters must be homogenized before digestion, e.g., with a high-frequency mixer. Use 500 mL deionized water to determine the blank value of the chemicals. The table below shows the sample volumes to be used when using $c(H_2SO_4)$ = 0.02 mol/L as titrant.

| Nitrogen in mg/L | Sample size in mL |
|---|---|
| 0–5 | 500 |
| 5–10 | 250 |
| 10–20 | 100 |
| 20–50 | 50.0 |
| 50–500 | 25.0 |

Add a catalyst tablet and 20 mL sulfuric acid to the water sample in the digestion flask or digestion tube. Quickly heat to boiling and keep boiling until white $SO_3$ fumes appear and the solution becomes clear and colorless. Heat for another 30 min and leave to cool down.

## Analysis

Before the titration, calibrate the pH electrode with buffer solutions pH = 7.00 and pH = 4.00.

Attach the digestion flask or digestion tube to the distillation apparatus, add 100 mL NaOH solution to the digestion solution and start the distillation. Collect the distillate in 50 mL boric acid solution. Transfer the distillate into a 500 mL volumetric flask and fill it up to the mark with deionized water.
Titrate 250 mL absorption solution with $c(H_2SO_4)$ = 0.02 mol/L.

## Parameters

| | |
|---|---|
| Mode | SET pH |
| EP1 at pH | 6.2 |
| Dynamics | 2 |
| Max. dosing rate | 10 mL/min |
| Min. dosing rate | 25 µL/min |
| Stop criterion | drift |
| Stop drift | 20 µL/min |

## Calculations

1 mL c($H_2SO_4$) = 0.02 mol/L corresponds to 0.56028 mg N

$$\text{Nitrogen} = \frac{(V_{EP1} - \text{Blank}) \times 2 \times c_{H_2SO_4} \times M_N \times 1000}{V_s}$$

| | |
|---|---|
| Nitrogen: | Nitrogen content in the sample in mg/L |
| $V_{EP1}$: | Titrant consumption until the first equivalence point in mL |
| Blank: | Consumption for the blank determination in mL |
| $c_{H_2SO_4}$: | Concentration of titrant in mol/L; here $H_2SO_4$= 0.02 or 0.1 mol/L |
| f: | Correction factor («titer») without unit |
| $M_N$: | Molecular weight of nitrogen in g/mol; 14.007 g/mol |
| 1000: | Conversion factor to obtain result in mg/L |
| $V_s$: | Sample size in mL |

The results are given to one decimal place.

## Example

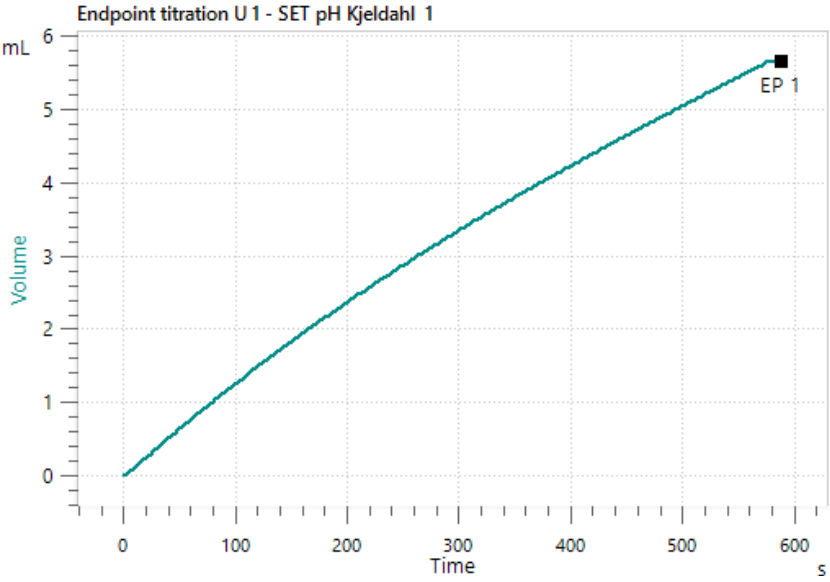



*Figure 7: Example titration curve for the Kjeldahl nitrogen determination of wastewater.*

## Metrohm literature

Application Bulletin AB-053: «Determination of ammonium or Kjeldahl nitrogen»

# 2.5 Hydrogen peroxide and its adducts



## General remarks

Hydrogen peroxide and its adducts (e.g., perborate, percarbonate, peracetic acid) can be present in wastewaters from laundries or after the application of disinfectant solutions. All these compounds can be oxidized by permanganate, whereby the following overall reaction takes place:

$$2\ MnO_4^- + 5\ H_2O_2 + 6\ H_3O^+ \rightarrow 2\ Mn^{2+} + 5\ O_2 + 14\ H_2O$$

## Instrument and relevant accessories

- Titrator with MET mode
- Stirrer
- 6.0451.100 Combined Pt ring electrode

## Reagents

- Titrant 1: $c(KMnO_4)$ = 0.02 mol/L (CAS 7722-64-7)
  This titrant is commercially available.
  It is used for mass concentrations $\beta(H_2O_2)$ = 10–100 mg/L.
- Titrant 2: $c(KMnO_4)$ = 0.001 mol/L (CAS 7722-64-7)
  This titrant is used for mass concentrations $\beta(H_2O_2)$ = 0.4–10 mg/L.
- Acid-catalyst solution: $\beta(MnSO_4 \cdot H_2O)$ = 15 g/L (CAS 10034-96-5) and 80 mL conc. $H_2SO_4$ (CAS 7664-93-9).

## Analysis

Pipet 100 mL water sample into the titration beaker and add 10 mL acid-catalyst solution. Titrate with $KMnO_4$ solution past the first equivalence point. If $c(KMnO_4)$ = 0.001 mol/L is used as the titrant, a polarization current of +1 µA is applied to the Pt electrode.

## Parameters

For c($KMnO_4$) = 0.02 mol/L the titration is carried out in MET U mode. The parameters specified in the table below are used, except for the parameter I(pol), which is not available in this mode.



| | |
|---|---|
| Mode | MET Ipol |
| Stirring rate | 8 |
| Pause | 20 s |
| Signal drift | 50 mV/min |
| Max. waiting time | 26 s |
| Volume increment | 0.05 mL |
| I(pol) | 1 µA |
| EP criterion | 30 mV |
| EP recognition | greatest |

## Calculations

1 mL c($KMnO_4$) = 0.02 mol/L corresponds to 1.701 mg $H_2O_2$.
1 mL c($KMnO_4$) = 0.001 mol/L corresponds to 0.085 mg $H_2O_2$.

$$H_2O_2 = \frac{V_{EP1} \times c_{KMnO_4} \times f \times M_{H_2O_2} \times 1000 \times 2.5}{V_s}$$

| | |
|---|---|
| $H_2O_2$: | Hydrogen peroxide content in the sample in mg/L |
| $V_{EP1}$: | Titrant consumption until the first equivalence point in mL |
| $_{cKMnO_4}$: | Concentration of titrant in mol/L; here c($KMnO_4$) = 0.02 or 0.001 mol/L |
| f: | Correction factor («titer») without unit |
| $M_{H_2O_2}$: | Molecular weight of hydrogen peroxide in g/mol; 34.0147 g/mol |
| 1000: | Conversion factor to obtain result in mg/L |
| 2.5: | Stoichiometric factor (5 $H_2O_2$ react with 2 $MnO_4$) |
| $V_s$: | Sample size in mL |

## Remarks

- $H_2O_2$ and its adducts are determined together.
- The conversion is complete even at room temperature if Mn(II) ions are added as a catalyst.
- By polarizing the Pt electrode one obtains, even with a diluted titrant, titration curves that can be evaluated without any problems.



### Example

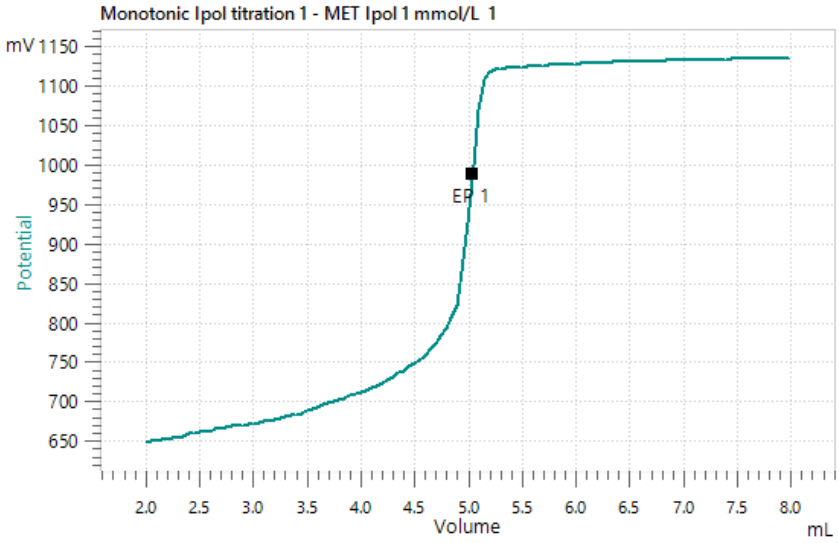



*Figure 8: Example titration curve for the hydrogen peroxide determination in water.*

### Metrohm literature

Application Note AN-T-025: «Hydrogen peroxide in aqueous solutions»

# 2.6 Chemical oxygen demand (COD)



## General remarks

The chemical oxygen index, given as mg/L $O_2$, is an indication for the amount of oxidizable organic and inorganic water constituents. Here, the determination according to DIN 38409-44 is described. This standard is suitable for ground, surface and cooling water with a COD in the range of 5 to 50 mg/L.

Oxidizable constituents react with potassium dichromate in a strongly acidic solution, while heating the sample under defined conditions. The excess of potassium dichromate is then titrated with a ferrous iron solution. The herein described analysis is only suitable for water with a chloride content <0.3 g/L.

## Instrument and relevant accessories

- Titrator with DET mode
- Stirrer
- 6.0435.110 Micro Au Titrode

## Reagents

Deionized water from water purification plants with organic ion exchangers is not suitable for preparing the reagents. Use either distilled water or water from a reverse-osmosis plant.

- Sulfuric acid: $w(H_2SO_4)$ = 98% (CAS 7664-93-9)
- Reaction solution: $\beta(K_2Cr_2O_7)$ = 1.471 g/L (CAS 7778-50-9) and $\beta(HgSO_4)$ = 20 g/L (CAS 7783-35-9) in sulfuric acid
- $Ag_2SO_4$ in sulfuric acid: $\beta(Ag_2SO_4)$ = 10 g/L (CAS 10294-26-5)
  This solution should be prepared at least a day in advance.
- Chromium(III) solution: $\beta(KCr(SO_4)_2 \cdot 12\ H_2O)$ = 25 g/L (CAS 7788-99-0)
- Titrant: $c((NH_4)_2Fe(SO_4)_2 \cdot 6\ H_2O)$ = 0.015 mol/L (CAS 7783-85-9)

## Sample preparation

20 mL sample is added into the reaction tube, followed by 0.5 mL of chromium(III) solution and 10 mL of reaction solution. 40 mL of silver(I) sulfate in sulfuric acid are added while the reaction tube is cooled down in a water bath. All prepared COD tubes are then heated according to DIN 38409-44 for 2 hours. After cooling the tubes below 60 °C, each vessel is filled up to 100 mL with ultrapure water. The sample can be titrated when the tubes have reached room temperature.

## Analysis

The prepared sample solution is stirred for 20 s before titration with ammonium iron(II) sulfate solution.



Perform a blank the same way, but omit the sample.

### Parameters

| | |
|---|---|
| Mode | DET U |
| Stirring rate | 10 |
| Signal drift | 10 mV/min |
| Min. waiting time | 5 s |
| Max. waiting time | 20 s |
| Measuring point distance | 2 |
| Min. increment | 25 µL |
| Max. increment | 500 µL |
| EP criterion | 50 |
| EP recognition | greatest |

### Calculations

$$COD = \frac{(Blank - V_{EP1}) \times f \times c_{(NH_4)_2Fe(SO_4)_2} \times EF_2}{V_s}$$

| | |
|---|---|
| COD: | Chemical oxygen demand in mg/L |
| Blank: | Volume for blank in mL |
| $V_{EP1}$: | Titrant consumption until the first equivalence point in mL |
| f: | Titer of the titrant; dimensionless |
| $c_{(NH_4)_2Fe(SO_4)_2}$: | Concentration of disodium oxalate in mmol/L; here 5 mmol/L |
| $EF_2$: | Equivalence factor; here 8000 mg/mol |
| $V_s$: | Sample size in mL |

## Remarks

- Use only thoroughly cleaned glassware. Detergent residues will falsify the result – it is best to use always the same titration vessels.
- Mercury(II) sulfate and potassium dichromate is highly toxic. Handling those substances requires a totally safe and careful operation process.
- To minimize exposure to chemicals an automated system such as the Metrohm Automated Titration system (MATi) No. 12 is recommended.

### Example

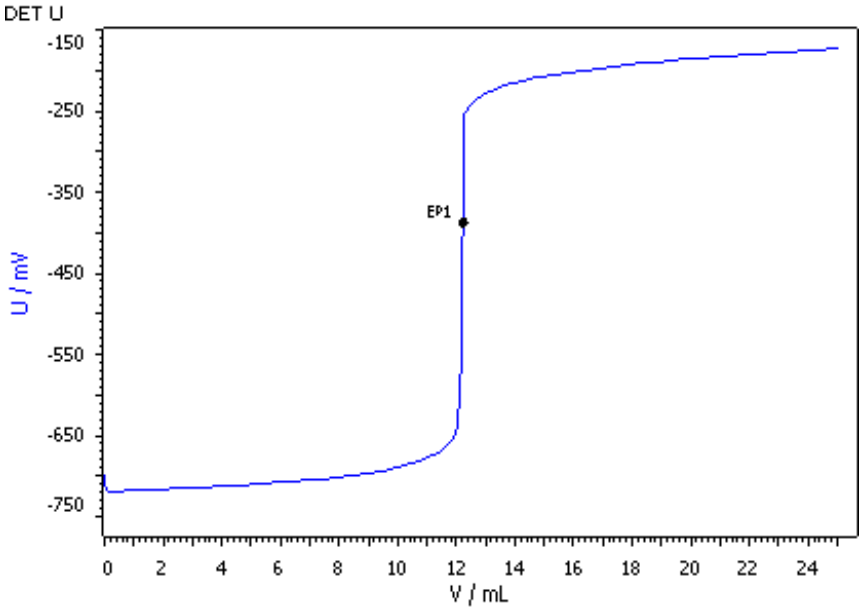



*Figure 9: Titration curves for the COD of wastewater*

### Metrohm literature

Application Bulletin AB-178: «Fully automated water analysis»

# 2.7 Complexing capacity

## General remarks and relevant literature



It is common knowledge that the complexing of metal ions by organic ligands influences the bioavailability as well as the toxicity towards aquatic organisms of metal species. Investigations have shown that generally the bulk, i.e. up to 90%, of the trace metals in surface waters (rivers, lakes, sea) is complexed by organic ligands. These results are important for understanding the biological cycles of water systems.

Metal speciation is the subject of a large number of publications. Many of these describe a type of «voltammetric titration» during which increments of the free metal ion are added to the water sample. After an equilibration time an ASV or CSV run is carried out (ASV = Anodic Stripping Voltammetry, CSV = Cathodic Stripping Voltammetry). The normally V- or L-shaped «titration curves» allow to calculate the stability constants and complexing capacity. As the formation of metal complexes is strongly pH-dependent, the measurements must be carried out at a defined pH to be comparable with each other.

Some publications contain extensive reports concerning the determination of complex formation constants. These latter allow to get further information on the bonding type of the corresponding species. This monograph does not allow an in-depth treatment of this highly interesting subject. The small literature selection appearing below is meant for readers who wish to get additional information.


- Chau, Y. K., Gächter, R., Lum-Shue-Chan, K. Determination of the apparent complexing capacity of lake waters. J. Fish. Res. Board Can. 31 (1974) 1515-1519
- Ruzic ,I. Theoretical aspects of the direct titration of natural waters and its information yield for trace metal speciation. Anal. Chim. Acta 140 (1982) 99-113
- van den Berg, C. M. G. Determination of copper in sea water by cathodic stripping voltammetry of complexes with catechol. Anal. Chim. Acta 164 (1984) 195-207
- Apte, S. C., Gardner, M. J., Ravencroft ,J. E. An evaluation of voltammetric titration procedures for the determination of trace metal complexation in natural waters by use of computer simulation. Anal. Chim. Acta 212 (1988) 1-21
- Campos, L. A., van den Berg, C. M. G. Determination of copper complexation in seawater by cathodic stripping voltammetry and ligand competition with salicylaldoxime. Anal. Chim. Acta 284 (1994) 481-496
- Xue, H. B., Sigg, L. Zinc speciation in lake waters and its determination by ligand exchange with EDTA and differential pulse anodic stripping voltammetry. Anal. Chim. Acta 284 (1994) 505-515

- Van den Berg, C. M. G. Evidence for organic complexation of iron in seawater. Marine Chemistry 50 (1995) 139-157
- Einax, J., Kunze, C. Complexation capacity of aquatic systems in dependance of different ligands and heavy metals – electroanalytical investigations and statistical evaluation. Fresenius,J.Anal.Chem. 354 (1996) 895-899
- Nolting, R. F., Gerringa, L. J. A., Swagerman, M. J. W., Timmermans, K. R., de Baar, H. J. W. Fe(III) speciation in the high nutrient, low chlorophyll Pacific region of the Southern Ocean. Marine Chemistry 62 (1998) 335-352
- Xue, H. B., Sigg, L. Cadmium speciation and complexation by natural organic ligands in fresh water. Anal.Chim.Acta 363 (1998) 249-259
- Ellwood, M. J., van den Berg, C. M. G. Zinc speciation in the Northeastern Atlantic Ocean Marine Chemistry 68 (2000) 295-306
- Jin, L., Gogan, N. J. Copper complexing capacities of freshwaters by adsorptive cathodic stripping voltammetry. Anal.Chim.Acta 412 (2000) 77-88
- Ellwood, M. J., van den Berg, C. M. G. Determination of organic complexation of cobalt in seawater by cathodic stripping voltammetry.
  Marine Chemistry 75 (2001) 33-47
- Xue, H. B., Sigg, L. A review of competitive ligand-exchange-voltammetric methods for speciation of trace metals in freshwater.
  In: Taillefert, M., Rozan, T. F. (eds.) Environmental Electrochemistry – Analysis of Trace Element Biogeochemistry. ACS, Washington (2002) ISBN 0-8412- 3774-3, Chapter 18
- Gardner, M., van Veen, E. Comparability of copper complexation capacity determination by absorption by chelating resin column and cathodic stripping voltammetry. Anal.Chim.Acta 501 (2004) 113-117
- Meylan, S., Odzak, N., Behra, R., Sigg, L. Speciation of copper and zinc in natural freshwater: comparison of voltammetric measurements, diffusive gradients in thin films (DGT) and chemical equilibrium models. Anal.Chim.Acta 510 (2004) 91-100
- Guthrie, J. W., Hassan, N. M. et al. Complexation of Ni, Zn, and Cd by DOC in some metal-impacted freshwater lakes: a comparison of approaches using electrochemical determination of free-metal-ion and labile complexes and a computer speciation model, WHAM V and VI. Anal.Chim.Acta 528 (2005) 205- 218

# 3 Gaseous water constituents

## 3.1 Free and total chlorine



### General remarks

Water chlorination is a worldwide-used method for water disinfection. Being highly toxic, chlorine kills pathogenic microorganisms (e.g., bacteria) but also poses a health risk to humans. The reason for this high toxicity is that chlorine reacts with organic compounds to form disinfection by-products (DBPs), such as trichloromethane and chloroacetic acid. To prevent this, regulatory authorities worldwide impose strict limit values on chlorine concentration.

Chlorine present in water can either be free or bound. *Free chlorine* or *residual chlorine* is the chlorine that is present as hypochloric acid, hypochlorite ion, or as elementary chlorine. *Bound chlorine* is the chlorine that is present as chloroamines[1] or organic chloroamines. *Total chlorine* is the chlorine that is present in free and/or bound form.

All the described species release, when potassium iodide is added to them, a corresponding amount of elementary iodine, which in turn can be titrated with phenyl arsine oxide. As phenyl arsine oxide is toxic, Metrohm does not recommend its use. Instead, the determination according to EN ISO 7393-1 using ferrous ammonium sulfate (FAS) as titrant is described here. The free chlorine can be directly titrated with FAS, while for the total chlorine potassium iodide is added and the liberated iodine is then titrated with FAS.

### Instrument and relevant accessories

- Titrator with MET mode
- Stirrer
- 6.0431.100 Pt Titrode

### Reagents

- Titrant: c[$(NH_4)_2Fe(SO_4)_2 \cdot 6\ H_2O$] = 0.0028 mol/L (CAS 7783-85-9)
  The solution is stored in a brown-glass flask to prevent any decomposition caused by sunlight.
- Phosphate buffer solution pH = 6.5
- Potassium iodide, KI, puriss, 99.0–100.5% (CAS 7681-11-0)

[1] *Derivatives of ammonia; monochloramine ($NH_2Cl$), dichloramine ($NHCl_2$) and nitrogen trichloride ($NCl_3$, also known as trichloramine).*

## Analysis

### Free chlorine

Transfer 100 mL sample to a 250 mL beaker and add 5 mL buffer solution pH = 6.5. After mixing, carry out the titration with $c[(NH_4)_2Fe(SO_4)_2 \cdot 6\ H_2O] = 0.0028$ mol/L until after the equivalence point.

### Total chlorine

Transfer 100 mL sample to a 250 mL beaker and add 5 mL buffer solution pH = 6.5 as well as approx. 1 g KI. Mix and wait for 2 minutes, then carry out the titration with $c[(NH_4)_2Fe(SO_4)_2 \cdot 6\ H_2O] = 0.0028$ mol/L until after the equivalence point.

## Parameters

| | |
|---|---|
| Mode | MET U |
| Stirring rate | 12 |
| Signal drift | 50 mV/min |
| Max. waiting time | 26 s |
| Volume increment | 0.02 mL |
| EP criterion | 50 |
| EP recognition | greatest |

## Calculations

$$\beta_{Cl_2} = \frac{M_{Cl_2} \times V_{EP1} \times f \times c_{(NH_4)_2Fe(SO_4)_2}}{V_S \times 4}$$

$\beta_{Cl_2}$: Mass concentration of (free or total) chlorine in mg/L
$M_{Cl_2}$: Molar mass of chlorine in g/mol, here 70.906 g/mol
$V_{EP1}$: Titrant consumption until the first equivalence point in mL
f: Correction factor («titer») without unit
$c_{(NH_4)_2Fe(SO_4)_2}$: Concentration of titrant in mol/L; here $c[(NH_4)_2Fe(SO_4)_2 \cdot 6\ H_2O] = 0.0028$ mol/L
$V_S$: Amount of sample used for titration in mL
4: Stoichiometric factor (2 mol $ClO^-$ correspond to 1 mol $Cl_2$. 1 mol $Cl_2$ corresponds to 2 mol Fe(II))

## Remarks

- It is possible to determine the free chlorine by titration at pH 3–4 with thiosulfate after the addition of potassium iodide. For this the bivoltametric indication (Double Pt-sheet electrode) is required – potentiometric indication does not yield any useful titration curves.



## Example

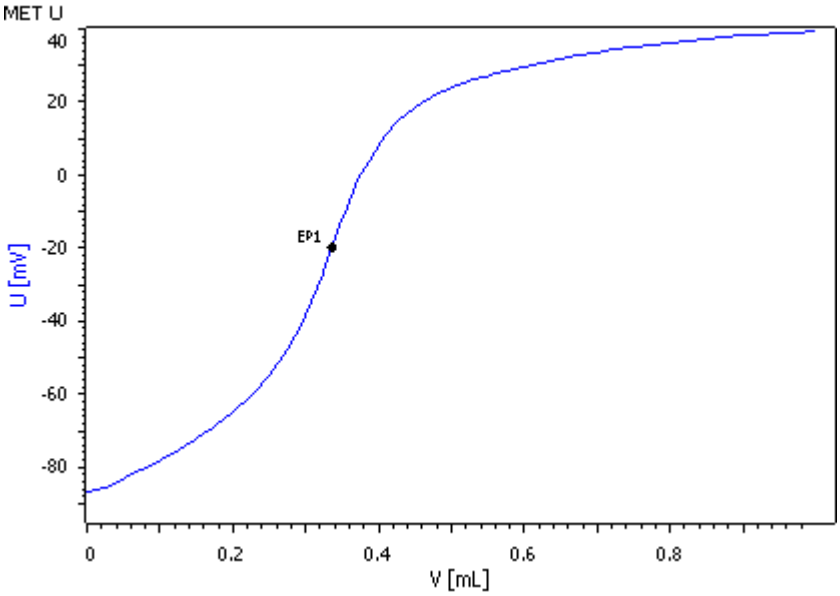



*Figure 10: Determination of free chlorine in 100 mL of a β(Ca(ClO$_4$)$_2$) = 1.28 mg/L solution.*

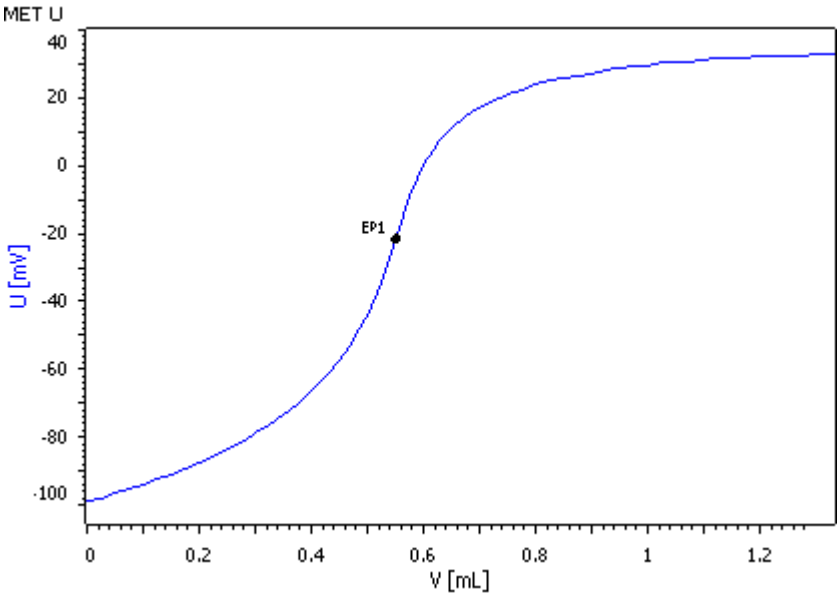



*Figure 11: Determination of total chlorine in 100 mL of a β($Ca(ClO_4)_2$) = 1.28 mg/L solution spiked with 0.3 mL of a β(monochloramine) = 1000 mg/L.*

## Metrohm literature

Application Bulletin AB-249: «Determination of free and residual chlorine based on EN ISO 7393-1 and APHA 4500-Cl»

# 3.2 Dissolved oxygen by Winkler titration



## General remarks

Many aquatic organisms, including fish, require dissolved oxygen for survival. The absence of dissolved oxygen can result in anaerobic decay of organic matter. With an increase of nutrients, e.g., from industrial wastewater, the dissolved oxygen content in water decreases due to plants and algae growth. Knowledge of the dissolved oxygen content thus gives information on the suitability of a water body for aquatic life.

Iodometric titration according to Winkler is a method for determining the oxygen content of water samples in a concentration range of 0.2 mg/L up to double oxygen saturation (approx. 20 mg/L).

Manganese(II) chloride and NaOH are added to the water sample. The oxygen reacts to form manganese(III) hydroxide, which is then dissolved in acid and reduced to Mn(II) by iodide. This latter reaction releases an amount of iodine that is equivalent to the oxygen and can be titrated with thiosulfate. The following reaction equations give an overview:

**Fixation in the alkaline solution:**

$$MnCl_2 + 2\ NaOH \rightarrow Mn(OH)_2 + 2\ NaCl$$

$$4\ Mn(OH)_2 + O_2 \rightarrow 4\ Mn(OH)_3 + 2\ H^+$$

$$(2\ H^+ + 2\ OH^- \text{ (excess)} \rightarrow 2\ H_2O)$$

**After acidification:**

$$2\ Mn(OH)_3 + 6\ HCl \rightarrow 2\ MnCl_3 + 6\ H_2O$$

$$2\ MnCl_3 + 2\ KI \rightarrow 2\ MnCl_2 + 2\ KCl + I_2$$

**During the titration:**

$$2\ Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2\ NaI$$

## Instrument and relevant accessories

- Titrator with MET mode
- Stirrer
- 6.0309.100 Double Pt sheet electrode
- Winkler bottles with wide-neck ground-joint openings plus stoppers

## Reagents

- Titrant: $c(Na_2S_2O_3)$ = 0.05 mol/L (CAS 7772-98-7)
  This titrant is commercially available
- Winkler solution I: $\beta(MnCl_2 \cdot H_2O)$ = 400 g/L (CAS 64333-01-3)
- Winkler solution II: $\beta(NaOH)$ = 500 g/L (CAS 1310-73-2),
  $\beta(NaN_3)$ = 1 g/L (CAS 26628-22-8) and $\beta(KI)$ = 150 g/L (CAS 7681-11-0)
  $NaN_3$ prevents interferences by nitrite ions.
- Acid mixture: 350 mL $w(H_3PO_4)$ = 85% (CAS 7664-38-2) and 350 mL w(HCl) = 36% (CAS 7647-01-0) for 1 L
  $H_3PO_4$ prevents interferences by Fe(III) ions.

## Sample preparation

Fill the water sample into the sample bottle until it flows over. Make sure no bubbles are trapped and seal the bottle. Remove the stopper and immediately add, below the water surface, 2 mL each of Winkler solution I and II, reseal immediately and mix. If the sample contains no $O_2$, the precipitate formed is white. The more $O_2$ the sample contains, the darker brown the precipitate is.

When the precipitate has settled, i.e. after several hours, carefully aspirate approx. 1/3 of the supernatant liquid, add 10 mL acid mixture to the bottle contents, seal the bottle and mix.

## Analysis

If wide-neck bottles are used, add a stirrer bar. Otherwise, transfer the solution quantitatively into a titration beaker with deionized water and titrate immediately with $c(Na_2S_2O_3)$ = 0.05 mol/L to the predefined endpoint.

## Parameters

| | |
|---|---|
| Mode | SET Ipol |
| Stirring rate | 8 |
| I(pol) | 1.0 µA |
| EP1 at U | 30 mV |
| Dynamics | 2 |
| Max. dosing rate | 2 mL/min |
| Min. dosing rate | 10 µL/min |
| Stop criterion | drift |
| Stop drift | 20 µL/min |

## Calculations

1 mL c($Na_2S_2O_3$) = 0.05 mol/L corresponds to 0.40 mg $O_2$.

$$\text{Oxygen} = \frac{V_{EP1} \times c_{Na_2S_2O_3} \times f \times M_{O_2} \times 1000}{(V_{WF} - V_{WS}) \times 4}$$

| | |
|---|---|
| Oxygen: | Dissolved oxygen content in the sample in mg/L |
| $V_{EP1}$: | Titrant consumption until the first end point in mL |
| $c_{Na_2S_2O_3}$: | Concentration of titrant in mol/L; here c($Na_2S_2O_3$) = 0.05 mol/L |
| f: | Correction factor («titer») without unit |
| $M_{O_2}$: | Molecular weight of oxygen in g/mol; 31.9988 g/mol |
| 1000: | Conversion factor to obtain result in mg/L |
| $V_{WF}$: | Volume of the Winkler flask in mL |
| $V_{WS}$: | Total volume of Winkler solutions added in mL |
| 4: | Stoichiometric factor |

If aliquot of sample is used for the titration, then the following formula is required.



$$\text{Oxygen} = \frac{V_{EP1} \times c_{Na_2S_2O_3} \times f \times M_{O_2} \times 1000 \times V_{WF}}{(V_{WF} - V_{WS}) \times 4 \times V_A}$$

| | |
|---|---|
| Oxygen: | Dissolved oxygen content in the sample in mg/L |
| $V_{EP1}$: | Titrant consumption until the first end point in mL |
| $c_{Na_2S_2O_3}$: | Concentration of titrant in mol/L; here $c(Na_2S_2O_3)$ = 0.05 mol/L |
| f: | Correction factor («titer») without unit |
| $M_{O_2}$: | Molecular weight of oxygen in g/mol; 31.9988 g/mol |
| 1000: | Conversion factor to obtain result in mg/L |
| $V_{WF}$: | Volume of the Winkler flask in mL |
| $V_{WS}$: | Total volume of Winkler solutions added in mL |
| 4: | Stoichiometric factor |
| $V_A$: | Volume of the aliquote used for the titration in mL |

## Remarks

The oxygen-uptake capacity of waters depends on three parameters:

- Temperature – increasing temperature reduces the uptake capacity.
- Pressure – increasing pressure increases the uptake capacity.
- Salt content – increasing salt content reduces the uptake capacity. The decrease amounts to approx. 0.554% per g/L salt.

To calculate the oxygen saturation of a water sample, one has to take into account the air pressure, temperature and salt content of the sample. The following tables give an overview:

This table shows the air:
Air pressure as a function height above sea level, 101.325 kPa = 1 atm = 760 mm Hg.

| height above sea level / m | average air pressure / kPa | height above sea level / m | average air pressure / kPa |
|---|---|---|---|
| 0 | 101.3 | 900 | 90.5 |
| 100 | 100.1 | 1000 | 89.4 |
| 200 | 98.8 | 1100 | 88.3 |
| 300 | 97.6 | 1200 | 87.2 |
| 400 | 96.4 | 1300 | 86.1 |
| 500 | 95.2 | 1400 | 85.0 |
| 600 | 94.0 | 1500 | 84.0 |
| 700 | 92.8 | 1600 | 82.9 |
| 800 | 91.7 | 1700 | 81.9 |

This table shows the solubility:
Solubility of oxygen (saturation) in mg/L $O_2$ as a function of temperature and air pressure.

| Temperature / °C | 111.5 kPA | 101.3 kPa | 91.2 kPa | 81.1 kPa | 70.9 kPa |
|---|---|---|---|---|---|
| 0.0 | 16.09 | 14.62 | 13.14 | 11.68 | 10.21 |
| 5.0 | 14.06 | 12.77 | 11.48 | 10.20 | 8.91 |
| 10.0 | 12.43 | 11.29 | 10.15 | 9.00 | 7.86 |
| 15.0 | 11.10 | 10.08 | 9.05 | 8.03 | 7.01 |
| 20.0 | 10.02 | 9.09 | 8.14 | 7.23 | 6.30 |
| 25.0 | 9.12 | 8.62 | 7.40 | 6.56 | 5.70 |
| 30.0 | 8.35 | 7.56 | 6.76 | 5.99 | 5.19 |
| 35.0 | 7.69 | 6.95 | 6.22 | 5.47 | 4.75 |

## Example

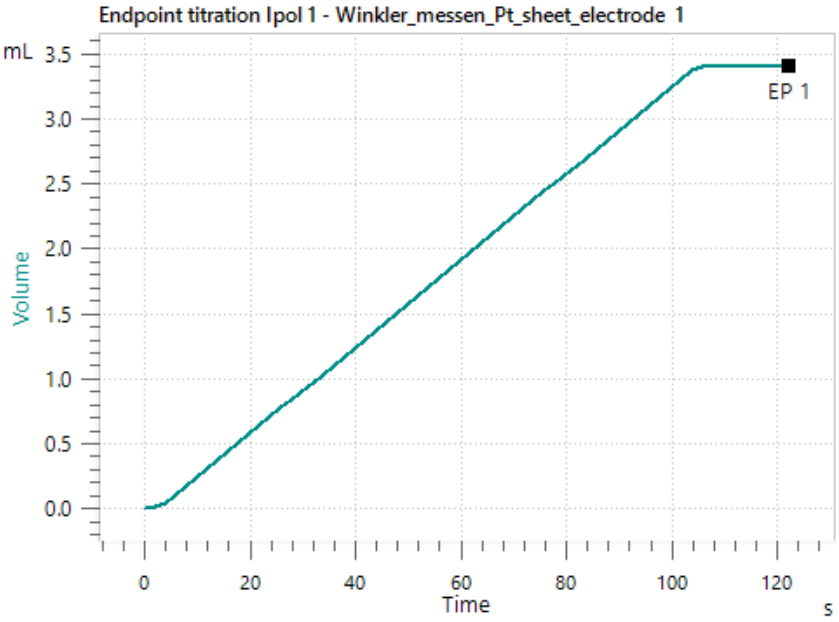



*Figure 12: Titration curve for the dissolved oxygen determination by Winkler titration of tap water.*

# 3.3 Dissolved oxygen with optical sensor

## General remarks

The dissolved oxygen is classically determined using the Winkler method. However, a more modern method with optical sensor and measuring device offers many advantages over the Winkler method. The oxygen content can be measured with the sensor directly on site. There are no errors during sampling or oxygen changes due to storage and transport to the laboratory. Compared to other sensors, the optical sensor also offers the advantage that no oxygen is consumed during measurement and the stirring of the measuring solution is therefore no longer necessary. This is particularly important for laboratory samples and standing waters.

## Instruments and relevant accessories

- Meter able to measure DO
- Optical sensor for dissolved oxygen

## Reagents

- Ready-to-use 0% oxygen calibration solution



## Calibration of a DO sensor

The sensor is very stable and drifts only minimally over time. Therefore, the optical sensor has to be calibrated very rarely. If necessary, the optical sensor can easily be calibrated with a one-point or two-point calibration. The calibration is done first at 100% air saturation and then at 0% air saturation. Metrohm provides a calibration kit for this procedure.

### Two-point calibration

- Connect the sensor to the measuring input
- Moisten the sponge in the calibration vessel
- Insert the sensor into the calibration vessel
- Start the calibration with 100% air saturation
- After the instrument has taken over the measured value, remove the sensor from the calibration vessel
- Open the ready-to-use 0% oxygen calibration solution
- Insert the sensor into the calibration solution immediately
- After the instrument has taken over the measured value, terminate the calibration. Remove the electrode from solution, rinse thoroughly with deionized water and place it in the calibration vessel for storage.

### One-point calibration

- The same procedure as the two-point calibration but only with the 100% air saturation using the calibration vessel.

## Measuring dissolved oxygen

Immerse the sensor in the measuring medium and read off the value. The measuring instrument directly calculates the dissolved oxygen content considering the current temperature, air pressure and salinity (if a corresponding conductivity sensor is connected).

## Remarks

- The sensor works on the principle of luminescence quenching: A luminophore is embedded in the membrane of the sensor cap. Irradiated light puts the luminophore into an excited state. When reverting to the ground state, the luminophore emits light in the NIR range. The time period between excitation and reverting to the ground state (luminescence lifetime) causes a phase shift between irradiated and emitted light and this phase shift is evaluated.

## Example

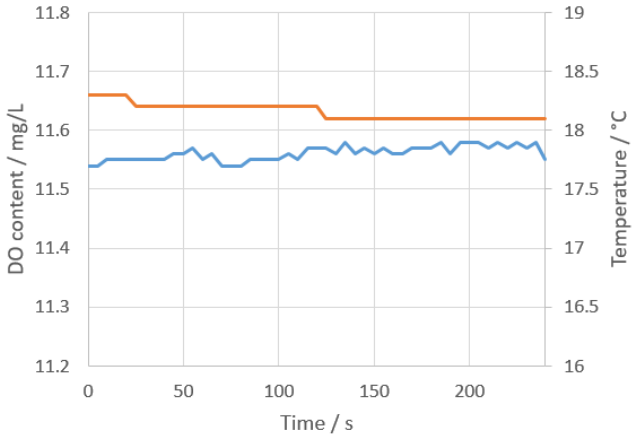



*Figure 13: Measuring curve for the dissolved oxygen measurement in surface water (DO content = blue, Temperature = orange).*

### Literature

Application Note AN-I-028: «Dissolved oxygen in surface water – Fast, in-situ determination based on ISO 17289»

Application Note AN-I-030: «Dissolved oxygen in tap water – Fast, online determination using an optical sensor according to ISO 17289»

# 3.4 Ozone

## General remarks

The iodometric method is suitable for determining higher ozone levels in drinking water and swimming-pool water. Any oxidants present in the water, e.g., chlorine, chlorine dioxide,

hydrogen peroxide, interfere with the determination. Ozone oxidizes iodide to elementary iodine, which latter can be titrated with thiosulfate. To prevent loss of ozone by degassing or decomposition, the water sample is added to a potassium iodide solution.

## Instrument and relevant accessories



- Titrator with MET mode
- Stirrer
- 6.0309.100 Double Pt sheet electrode

## Reagents

- Titrant: $c(Na_2S_2O_3)$ = 0.01 mol/L (CAS 7772-98-7)
  This titrant is commercially available.
- Neutral potassium iodide solution: $\beta(KI)$ = 20 g/L (CAS 7681-11-0), $\beta(Na_2HPO_4 \cdot 2\ H_2O)$ = 7.3 g/L (CAS 10028-24-7) and $\beta(KH_2PO_4)$ = 3.5 g/L (CAS 7778-77-0)
- Dilute sulfuric acid: $w(H_2SO_4)$ = approx. 25% (CAS 7664-93-9)

## Sampling

Transfer 100 mL neutral potassium iodide solution into a 500 mL volumetric flask. Make up to the mark with the water sample and mix.

## Analysis

Transfer 250 mL of the pretreated sample (corresponding to 200 mL original sample) into a titration beaker, add 10 mL dilute sulfuric acid and titrate immediately with $c(Na_2S_2O_3)$ = 0.01 mol/L past the first equivalence point.

## Parameters

| | |
|---|---|
| Mode | MET Ipol |
| Stirring rate | 8 |
| Pause | 0 s |
| Signal drift | 50 mV/min |
| Max. waiting time | 26 s |
| Volume increment | 0.05 mL |
| I(pol) | 1 µA |
| EP criterion | 30 mV |
| EP recognition | greatest |

## Calculations

1 mL c($Na_2S_2O_3$) = 0.01 mol/L corresponds to 0.24 mg $O_3$.

$$O_3 = \frac{V_{EP1} \times c_{Na_2S_2O_3} \times f \times M_{O_3} \times 1000}{V_s \times 2}$$

| | |
|---|---|
| $O_3$: | Ozone content in the sample in mg/L |
| $V_{EP1}$: | Titrant consumption until the first equivalence point in mL |
| $C_{Na_2S_2O_3}$: | Concentration of titrant in mol/L; here c($Na_2S_2O_3$) = 0.01 mol/L |
| f: | Correction factor («titer») without unit |
| $M_{O_3}$: | Molecular weight of ozone in g/mol; 47.997 g/mol |
| 1000: | Conversion factor to obtain result in mg/L |
| $V_S$: | Sample size in mL |
| 2: | Stoichiometric factor |

The ozone mass concentration is rounded to 0.1 mg/L.

## Example

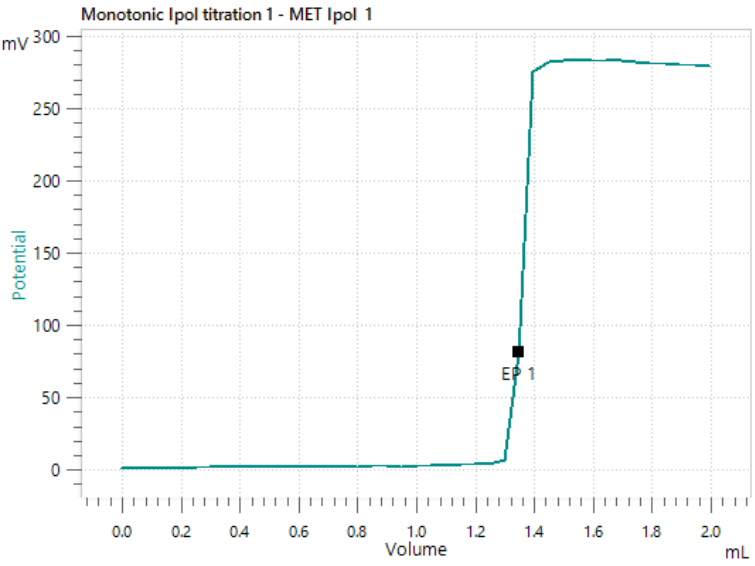



*Figure 14: Titration curve for the ozone determination in tap water.*

**Metrohm literature**

Application Note AN-T-213: «Ozone in water – Easy determination of ozone in water»



# 4 Anions

## 4.1 Chloride by titration

### General remarks

Chloride ions occur in most waters, even in rainwater. Their concentrations range from a few mg/L (ground and drinking water) to g/L (brackishwater, seawater, and wastewater).
The titrimetric determination of chloride ions is carried out with silver nitrate. Interferences occur with any anions forming precipitates with $AgNO_3$ that are less soluble than AgCl. These anions are mainly sulfide, cyanide, iodide, and bromide. The precipitation and titration sequence can be predicted from the solubility product $K_L$. The least soluble precipitate is always titrated first. The table gives an overview:

| Ag salt | $K_L$ / ($mol^2/L^2$) |
|---|---|
| AgBr | $7.7 \cdot 10^{-13}$ |
| $Ag_2CO_3$ | $6.15 \cdot 10^{-12}$ |
| AgCl | $1.56 \cdot 10^{-10}$ |
| AgCN | $2.2 \cdot 10^{-12}$ |
| AgCNS | $1.16 \cdot 10^{-12}$ |
| AgI | $1.5 \cdot 10^{-16}$ |
| $Ag_2S$ | $1.6 \cdot 10^{-49}$ |

Interferences by sulfide can be eliminated by adding $H_2O_2$, which oxidizes sulfide to sulfate. Interferences by carbonate are overcome by titrating in acidic solution (pH value <4).

### Instrument and relevant accessories

- Titrator with DET mode
- Stirrer
- 6.00430.100S Ag Titrode with $Ag_2S$ coating

## Reagents

- Titrant 1: c($AgNO_3$) = 0.1 mol/L (CAS 7761-88-8)
  For chloride contents >300 mg/L. This titrant is commercially available.
- Titrant 2: c($AgNO_3$) = 0.01 mol/L (CAS 7761-88-8)
  For chloride contents <300 mg/L. Store in a dark bottle.
- Nitric acid: c($HNO_3$) = approx. 2 mol/L (CAS 7697-37-2)

## Parameters

| | |
|---|---|
| Mode | DET U |
| Stirring rate | 8 |
| Signal drift | 50 mV/min |
| Max. waiting time | 26 s |
| Measuring point distance | 4 |
| Min. increment | 10 µL |
| EP criterion | 10 |
| EP recognition | greatest |

## Calculations

1 mL c($AgNO_3$) = 0.01 mol/L corresponds to 0.3545 mg chloride.

1 mL c($AgNO_3$) = 0.10 mol/L corresponds to 3.545 mg chloride.

$$\text{Chloride} = \frac{V_{EP1} \times c_{AgNO_3} \times f \times M_{Cl} \times 1000}{V_S}$$

Chloride: Chloride content in the sample in mg/L
$V_{EP1}$: Titrant consumption until the first equivalence point in mL
$c_{AgNO_3}$: Concentration of titrant in mol/L; here c($AgNO_3$) = 0.10 or 0.01 mol/L
f: Correction factor («titer») without unit
$M_{Cl}$: Molecular weight of chloride in g/mol; 35.453 g/mol
1000: Conversion factor to obtain result in mg/L
$V_s$: Volume of the sample in mL

The result is given with three significant digits.

## Example

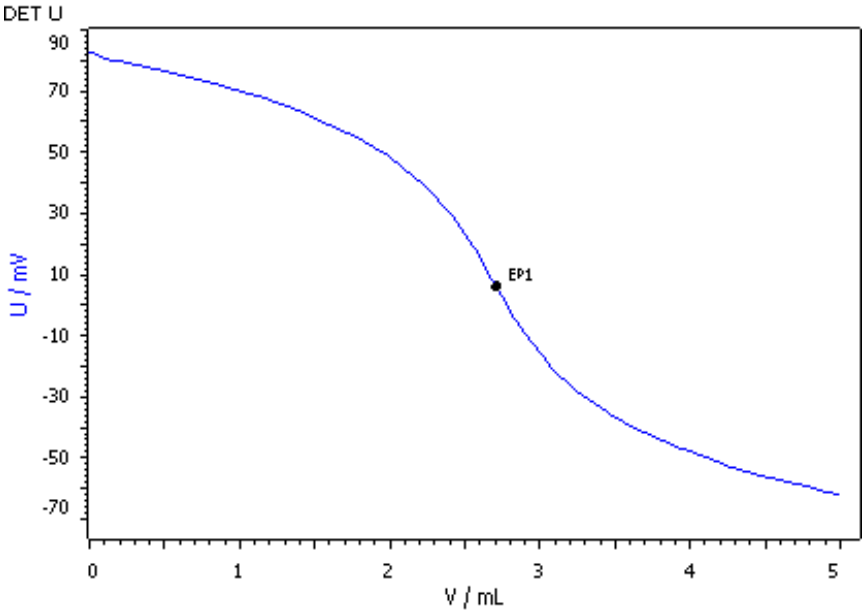



*Figure 15: Titration curve for the chloride determination in tap water.*

### Metrohm literature

Application Bulletin AB-130: «Chloride titrations with potentiometric indication»

# 4.2 – Cyanide by titration

## General remarks

The determination of cyanide in seepage water and electroplating wastewater before and after decontamination is highly important. Concentrations as low as 0.05 mg/L of cyanide can be lethal for fish species.

One has to distinguish between easily released cyanides, e.g. from KCN, and the total cyanide content, which comprises also the CN complexes of heavy metals. The decomposition and separation occurs according to DIN 38405-13. We will use the potentiometric titration with silver nitrate, which is described by the following reactions:

$CN^- + Ag^+ \rightarrow [Ag(CN)_2]^-$ EP 1 (large potential jump)
$[Ag(CN_2)]^- + Ag^+ \rightarrow 2\ AgCN \downarrow$ EP 2 (small potential jump)

EP1 is used for the titration. If $c(AgNO_3)$ = 0.0002 mol/L is used as the titrant, concentrations as low as 0.01 mg/L $CN^-$ can be determined. HCN, as shown by its $pK_A$ of 9.4, is a very weak acid. To prevent losses, the titration is always carried out in strongly alkaline solution (pH = >12).

## Instrument and relevant accessories

- Titrator with DET mode
- Stirrer
- 6.00430.100S Ag Titrode with $Ag_2S$ coating

## Reagents

- Titrant solutions: $c(AgNO_3)$ = 0.01, 0.002 or 0.0002 mol/L (CAS 7761-88-8)
  Store in a dark bottle.
- Sodium hydroxide solution: c(NaOH) = 1 mol/L (CAS 1310-73-2)
- Decomposition chemicals:
  These can be found in Application Bulletin AB-046

## Analysis

The *easily released cyanides* (e.g., from KCN) are determined by driving off HCN at room temperature and a pH value of approx. 4 by means of an air stream and absorbed in c(NaOH) = 1 mol/L.

The determination of the *total cyanide* content, which also comprises the complex heavy metal cyanides, is carried out by driving off the HCN under boiling in the presence of Cu(I) ions and HCl and absorbing the HCN in c(NaOH) = 1 mol/L.

Normally, 100 mL water sample is used. If the water contains less than 0.1 mg/L cyanide, the sample volume is increased to 200 mL.

Rinse the contents of the absorption vessel into a beaker using dionized water. At cyanide concentrations of 0.2–10 mg/L, titrate with $c(AgNO_3)$ = 0.002 mol/L, at cyanide concentrations of 0.01–0.5 mg/L with $c(AgNO_3)$ = 0.0002 mol/L. Higher cyanide concentrations – e.g., in electroplating wastewaters – can be titrated at pH ≥ 12 directly with $c(AgNO_3)$ = 0.01 mol/L.

## Parameters

| | |
|---|---|
| Mode | DET U |
| Stirring rate | 8 |
| Signal drift | 30 mV/min |
| Max. waiting time | 32 s |
| Measuring point distance | 2 |
| Min. increment | 10 µL |
| EP criterion | 5 |
| EP recognition | greatest |

## Calculations

1 mL c($AgNO_3$) = 0.0002 mol/L corresponds to 0.0104 mg cyanide.

1 mL c($AgNO_3$) = 0.002 mol/L corresponds to 0.104 mg cyanide.

1 mL c($AgNO_3$) = 0.01 mol/L corresponds to 0.520 mg cyanide.

$$\text{Cyanide} = \frac{V_{EP1} \times c_{AgNO_3} \times f \times M_{CN} \times 1000}{V_S}$$

Cyanide: Cyanide content in the sample in mg/L
$V_{EP1}$: Titrant consumption until the first equivalence point in mL
$c_{AgNO_3}$: Concentration of titrant in mol/L; here c($AgNO_3$) = 0.01, 0.002, or 0.0002 mol/L
f: Correction factor («titer») without unit
$M_{CN}$: Molecular weight of cyanide in g/mol; 26.018 g/mol
1000: Conversion factor to obtain result in mg/L
$V_S$: Volume of the sample in mL

## Remarks

- Condition the electrode before the first analysis for 20 min in a solution of 0.3 mg/L $CN^-$ in c(NaOH) = 0.4 mol/L.
- The detailed procedure is described in Application Bulletin AB-046: «Potentiometric determination of cyanide»

## Example

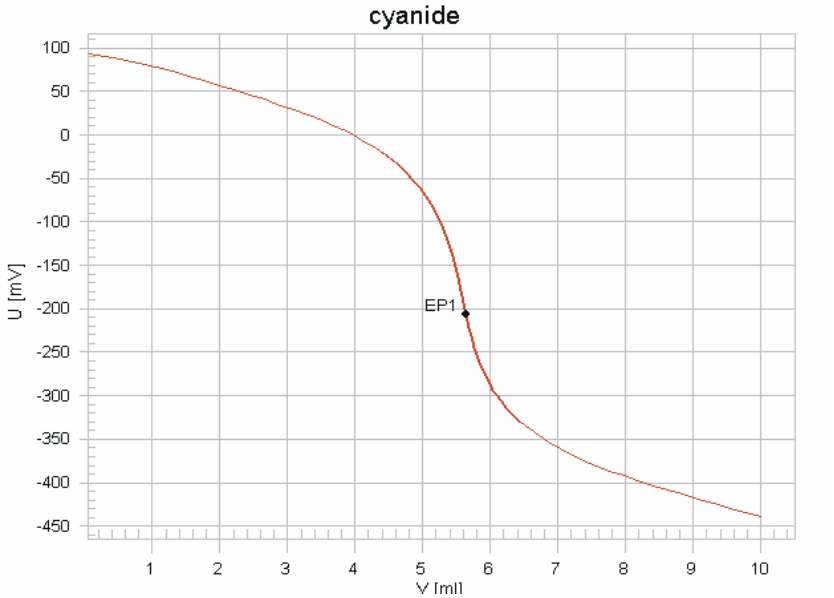



*Figure 16: Determination of cyanide in electroplating wastewater (direct titration)*

### Metrohm literature

Application Bulletin AB-046: «Potentiometric determination of cyanide»

# 4.3 Sulfate by titration



## General remarks

The method allows the interference-free determination of sulfate in the presence of Ca, Mg, and Cl ions. An excess of Ba ions is added to the sample. This causes the sulfate to be precipitated as $BaSO_4$. The portion of the Ba not precipitated with the sulfate is determined by back-titration with EGTA. This titration yields two equivalence points, the first equivalence point corresponds to the Ca and the difference between the second and first equivalence point to the excess Ba. Mg does not interfere, as it is not complexed by EGTA.

The determination limit is approx. 10 mg/L sulfate.

## Instrument and relevant accessories

- Titrator with DET mode
- Stirrer
- 6.0510.100 combined polymer membrane electrode, Ca

## Reagents

- Titrant: c(EGTA) = 0.05 mol/L (CAS 67-42-5)
- Barium chloride solution: c($BaCl_2$) = 0.05 mol/L (CAS 10326-27-9)
- Ammonia buffer solution pH = 10
- Hydrochloric acid: c(HCl) = approx. 2 mol/L (CAS 7647-01-0)

## Blank

Transfer approx. 30 mL deionized water and 5.00 mL c($BaCl_2$) = 0.05 mol/L into the titration beaker. Add 5 mL buffer solution pH = 10, leave to react for 3 min under stirring, then titrate with c(EGTA) = 0.05 mol/L. Store the mean value of the titrant consumption as a common variable.

## Analysis

A water sample containing not more than 20 mg sulfate is pipetted into the titration beaker and brought to a pH value of <4 by the dropwise addition of HCl. Add 5.00 mL c($BaCl_2$) = 0.05 mol/L and leave to react for 3 min under stirring. Add 5 mL buffer solution pH = 10 and leave to react for another 3 min under stirring. Titrate with c(EGTA) = 0.05 mol/L past the second equivalence point.
EP1 corresponds to the Ca and the difference EP1–EP2 to the Ba excess.

## Parameters

| | |
|---|---|
| Mode | DET U |
| Stirring rate | 8 |
| Signal drift | 50 mV/min |
| Max. waiting time | 26 s |
| Measuring point distance | 4 |
| Min. increment | 10 µL |
| EP criterion | 10 |
| EP recognition | greatest |

## Calculations

1 mL c(EGTA) = 0.05 mol/L corresponds to 4.803 mg sulfate or 2.004 mg calcium.

$$\beta_{SO_4^{2-}} = \frac{(\text{Blank} - (V_{EP2} - V_{EP1})) \times c_{EGTA} \times f \times M_{SO_4^{2-}} \times 1000}{V_s}$$

$\beta_{SO_4^{2-}}$: Sulfate content in mg/L
Blank: Blank of the barium chloride solution in mL
$V_{EP2}$: Titrant consumption until the second equivalence point in mL
$V_{EP1}$: Titrant consumption until the first equivalence point in mL
$c_{EGTA}$: Concentration of the selected titrant in mol/L; here c(EGTA) = 0.05 mol/L
f: Titer of the selected titrant without unit
$M_{SO_4^{2-}}$: Molecular weight of the sulfate in g/mol; here 96.063 g/mol
1000: Conversion factor to obtain result in mg/L
$V_S$: Sample volume in mL

$$\beta_{Ca} = \frac{V_{Ep1} \times c_{EGTA} \times f \times M_{Ca} \times 1000}{V_s}$$



$\beta_{Ca}$: Calcium content in mg/L
$V_{EP1}$: Titrant consumption until the first equivalence point in mL
$c_{EGTA}$: Concentration of the selected titrant in mol/L; here c(EGTA) = 0.05 mol/L
f: Titer of the selected titrant without unit
$M_{Ca}$: Molecular weight of the calcium in g/mol; here 40.078 g/mol
1000: Conversion factor to obtain result in mg/L
$V_S$: Sample volume in mL

## Remarks

- The water samples must be acidified with HCl to prevent the precipitation of $BaCO_3$.
- Waters that do not contain Ca must be spiked, e.g., with 0.5 mL c(Ca) = 0.1 mol/L standard.
- The total water hardness cannot be determined with this method, as Mg is not taken into account.

## Example

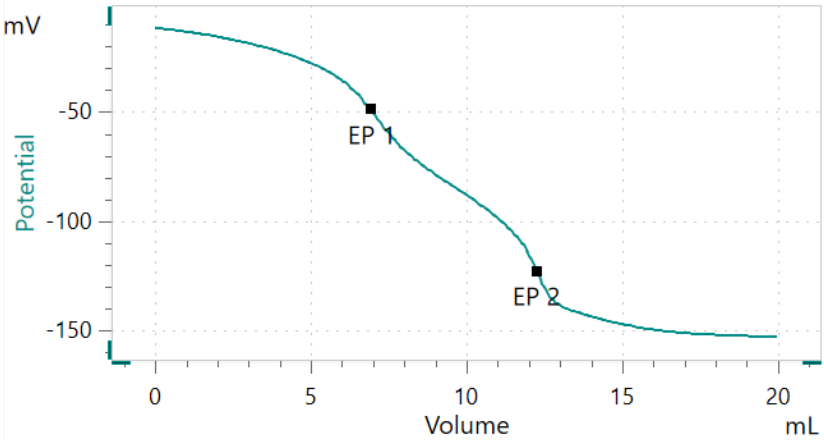



*Figure 17: Titration curve for the sulfate determination in tap water.*

**Metrohm literature**

Application bulletin AB-140: «Titrimetric sulfate determination»



# 4.4 Sulfides and hydrogen sulfide by titration

## General remarks

Sulfides and/or $H_2S$ can be present in reductive groundwater, in seepage water and at the bottom of surface waters (under anaerobic conditions). The addition of silver nitrate produces insoluble precipitates ($K_L = 1.6 \cdot 10^{-49}$).

Sulfides are volatile and easily oxidized by atmospheric oxygen. They are determined by titration with $AgNO_3$ in strongly alkaline solution and under nitrogen purging.

The determination limit is approx. 0.05 mg/L sulfide.

## Instrument and relevant accessories

- Titrator with DET mode
- Stirrer
- 6.00430.100S Ag Titrode with $Ag_2S$ coating

## Reagents

- Titrant: c($AgNO_3$) = 0.001 mol/L (CAS 7761-88-8)
  Store in a dark bottle.
- Sodium hydroxide solution: w(NaOH) = 30% (CAS 1310-73-2)
- Nitrogen: $O_2$-free

## Analysis

Transfer 1 mL NaOH into the titration beaker. Add 100 mL water sample, purge with nitrogen and titrate with c($AgNO_3$) = 0.001 mol/L past the first equivalence point.



## Parameters

| | |
|---|---|
| Mode | DET U |
| Stirring rate | 8 |
| Signal drift | 30 mV/min |
| Max. waiting time | 32 s |
| Measuring point distance | 2 |
| Min. increment | 10 µL |
| EP criterion | 5 |
| EP recognition | greatest |

## Calculations

1 mL c($AgNO_3$) = 0.001 mol/L corresponds to 0.016 mg $S^{2-}$ or 0.017 mg $H_2S$.

$$\text{Sulfide} = \frac{V_{EP1} \times c_{AgNO_3} \times f \times M_S \times 1000}{V_S \times 2}$$

| | |
|---|---|
| Sulfide: | Sulfide content in the sample in mg/L |
| $V_{EP1}$: | Titrant consumption until the first equivalence point in mL |
| $c_{AgNO_3}$: | Concentration of titrant in mol/L; here c($AgNO_3$) = 0.001 mol/L |
| f: | Correction factor («titer») without unit |
| $M_S$: | Molecular weight of sulfide in g/mol; 32.066 g/mol |
| 1000: | Conversion factor to obtain result in mg/L |
| $V_S$: | Volume of the sample in mL |
| 2: | Stoichiometric factor |

If the result should be expressed as hydrogen sulfide, then a molecular weight of 34.080 g/mol should be used.

## Remarks

- Sulfides and hydrogen sulfide are very volatile compounds. We therefore recommend alkalinizing the samples immediately after sampling.
- The $Ag_2S$ coating on the Ag Titrode ensures the fast response and stable adjustment of this electrode.

## Example

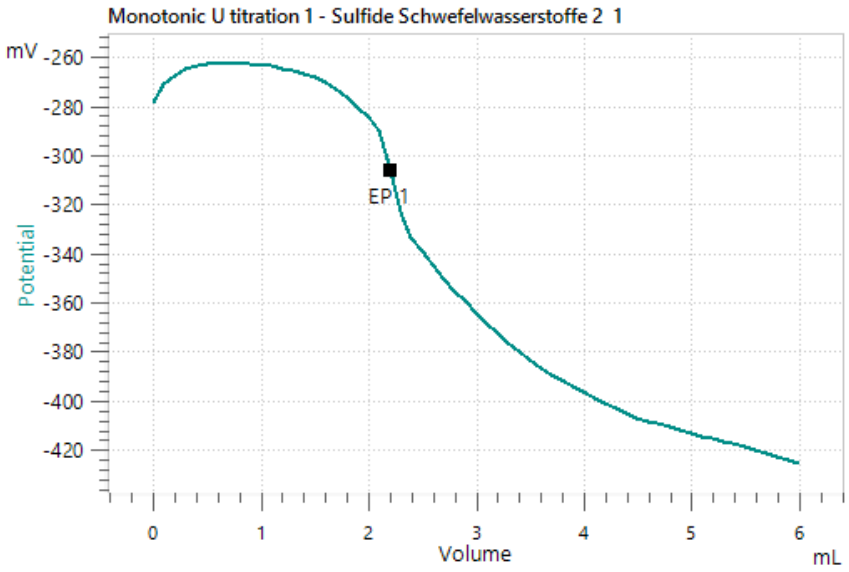



*Figure 18: Titration curve for the sulfide and hydrogen sulfide determination in wastewater.*

## Metrohm literature

Application Note AN-T-032: «Hydrogen sulfide or sulfide in water»

# 4.5 Bromide by ion measurement



## General remarks

Bromide occurs naturally in seawater in a concentration of about 65 mg/L and commonly in a concentration not higher than 0.5 mg/L in drinking water. A higher bromide value may indicate a contamination of groundwater with fertilizers, road salt, or industrial wastewater.

This section describes the determination according to ASTM D1246 for ground and drinking water with a bromide content in the range of 0.5 to 1000 mg/L bromide.

## Instrument and relevant accessories

- Ion meter or instrument with ion measurement mode
- Stirrer
- 6.0502.100 Ion-selective electrode, Br
- 6.0750.100 LL ISE reference electrode

## Reagents

- Ionic strength adjuster (ISA): $\beta(NaNO_3)$ = 425 g/L (CAS 7631-99-4)

## Calibration

Carry out a calibration with at least 3 different standard concentrations. Use the same ratio of calibration standard to ISA as for the sample measurement. Measure the calibration standards without stirring. In between each measurement, condition the electrode in deionized water for 1 min.

## Analysis

Transfer 100 mL water sample into a sample beaker. Add 2 mL ISA and stir vigorously for 1 min. Then place the electrodes in the sample solution. After stirring for additional 2 min, measure the bromide concentration without stirring. In between each measurement, condition the electrode in deionized water for 1 min.

## Parameters

| | |
|---|---|
| Mode | MEAS CONC |
| Stirring rate | 0 |
| Signal drift | 1 mV/min |
| Min. waiting time | 60 s |
| Max. waiting time | 200 s |
| Measuring interval | 2 s |

## Remarks

- If the sample has an ionic strength higher than 0.1 mol/L, the calibration standards should be prepared with a similar sample composition. For samples with a lower ionic strength, the addition of the ISA should be sufficient.
- Chloride and hydroxide do not interfere, as long as their concentration is not higher than 400 and 30'000 times that of bromide.

## Example

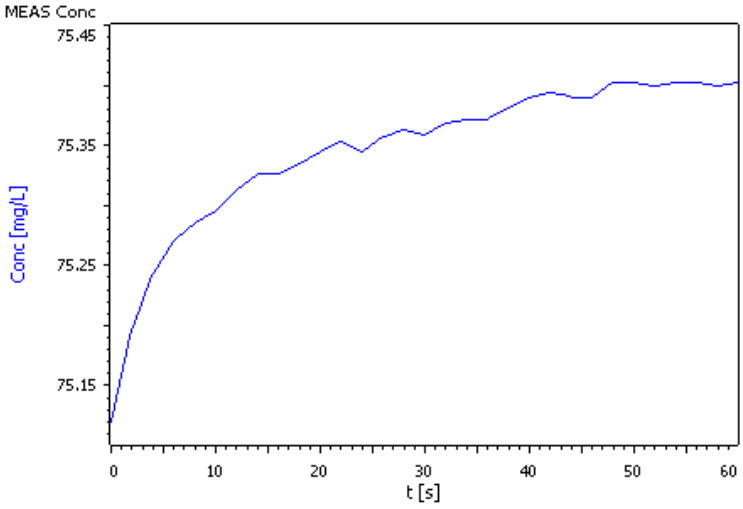



*Figure 19: Measuring curve for the bromide determination in spiked tap water.*

## Metrohm literature

Application Note AN-I-014: «Bromide in water in accordance with ASTM D1246»



# 4.6 Cyanide by ion measurement

## General remarks

The determination of cyanide in seepage water and electroplating wastewater before and after decontamination is highly important. Concentrations as low as 0.05 mg/L of cyanide can be lethal for fish species.

The herein described procedure provides information on the total amount of cyanides after distillation. It does not distinguish between free cyanide ions and metallocyanide compounds.

## Instrument and relevant accessories

- Ion meter or instrument with ion measurement mode
- Stirrer
- 6.0502.130 Ion-selective electrode, CN
- 6.0750.100 LL ISE reference electrode

## Reagents

- Collecting solution: c(NaOH) = 1 mol/L (CAS 1310-73-2)
- Sulfuric acid: w($H_2SO_4$) = 49% (CAS 7664-93-9)
- Magnesium chloride solution: β($MgCl_2 \cdot 6\ H_2O$) = 510 g/L (CAS 7791-18-6)
- Dilution solution: c(NaOH) = 0.04 mol/L (CAS 1310-73-2)

## Sample preparation

Add 10 mL c(NaOH) = 1 mol/L into the collecting vessel and dilute it with deionized water to obtain an adequate liquid level in the collecting vessel. Transfer 500 mL sample into a 1 L three-neck round bottom flask. Connect the round bottom flask to the distillation apparatus. Turn on the vacuum, which is connected to the collecting vessel.

Add 20 mL magnesium chloride solution to the round bottom flask. Wash down any remaining solution. After waiting for 3 min, carefully add 50 mL sulfuric acid to the round bottom flask. Turn on the cooling water and heat the distillation apparatus. Reflux the solution for 1 h. Turn off the heating but maintain the airflow for an other 15 min.

Quantitatively transfer the collected solution into a 250 mL volumetric flask. Fill up the flask to the mark with deionized water.

## Calibration

Carry out a calibration with at least 3 different standard concentrations. Use a commercially available cyanide standard and make up to a total volume of 100 mL with c(NaOH) = 0.04 mol/L. In between each measurement, condition the electrode in dilution solution for 1 min.

## Analysis

Transfer 100 mL absorption solution into a sample beaker. Place the electrodes into the sample solution and measure the cyanide concentration. In between each measurement, condition the electrode in dilution solution for 1 min.

## Parameters

| | |
|---|---|
| Mode | MEAS CONC |
| Stirring rate | 6 |
| Signal drift | 0.05 mV/min |
| Min. waiting time | 360 s |
| Max. waiting time | 600 s |
| Measuring interval | 2 s |

## Remarks

- To avoid loss of volatile free cyanide in neutral or acidic solutions add 10 mL c(NaOH) = 10 mol/L to the sample bottle (1 L) prior to sampling.
- For large cyanide contents, reduce the sample volume. The round bottom flask should not contain more than 5 mg cyanide. Dilute to 500 mL with deionized water.
- Not all cyanocomplexes are completely recovered by this test method.
- Smaller sample volumes can be used. In this case, dilute the accurately measured aliquot to 100 mL with c(NaOH) = 0.04 mol/L.



## Example

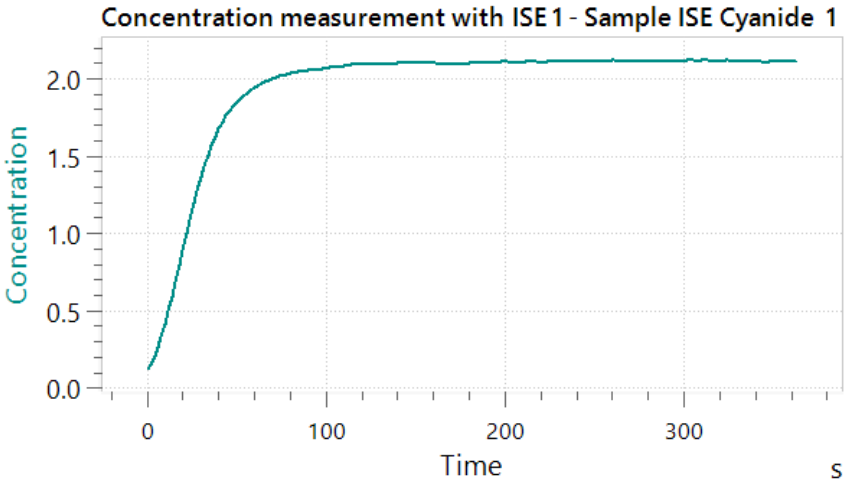



*Figure 20: Measuring curve for the cyanide determination in spiked tap water.*

### Metrohm literature

Application Note AN-I-009: «Cyanide in water – Inexpensive determination according to APHA Method 4500-CN and ASTM D2036»

# 4.7 Fluoride by ion measurement



## General remarks

Too high fluoride concentrations in water may cause tooth damage, growth disorders and bone deformation. According to the World Health Organization (WHO), concentrations above 1.5 mg/L are critical.

One possible source of fluoride in water are landfills. Rain washes out the fluoride from landfills, which can enter the groundwater. The leachate of landfills should thus be monitored for the fluoride concentration.

This section describes the direct measurement with the fluoride-selective electrode for leachate samples.

## Instrument and relevant accessories

- Ion meter or instrument with ion measurement mode
- Stirrer
- 6.0502.150 Ion-selective electrode, F
- 6.0750.100 LL ISE reference electrode

## Reagents

- Diluted total ionic strength adjustment buffer (diluted TISAB IV): β(NaCl) = 29 g/L (CAS 7647-14-5), β(complexon IV) = 2.5 g/L (CAS 482-54-2), glacial acetic acid = 27.5 mL (CAS 64-19-7), adjusted to pH 5.5 with NaOH (CAS 1310-73-2)

## Calibration

Carry out a calibration with at least 3 different standard concentrations. Use the same ratio of calibration standard to diluted TISAB IV as for the sample measurement. In between each measurement, condition the electrode in diluted TISAB IV for 5 min.

## Analysis

Pipette 20 mL leachate into the sample beaker. Add 20 mL diluted TISAB IV. Stir the solution for 10 s. Afterwards, measure the concentration of the sample. In between each measurement, condition the electrode in diluted TISAB IV for 5 min.

## Parameters

| | |
|---|---|
| Mode | MEAS CONC |
| Stirring rate | 4 |
| Signal drift | 0.5 mV/min |
| Min. waiting time | 10 s |
| Max. waiting time | 215 s |
| Measuring interval | 2 s |

## Remarks

- Before determining fluoride concentrations below 1 mg/L, condition the electrode in deionized water for approximately 30 min.

## Example

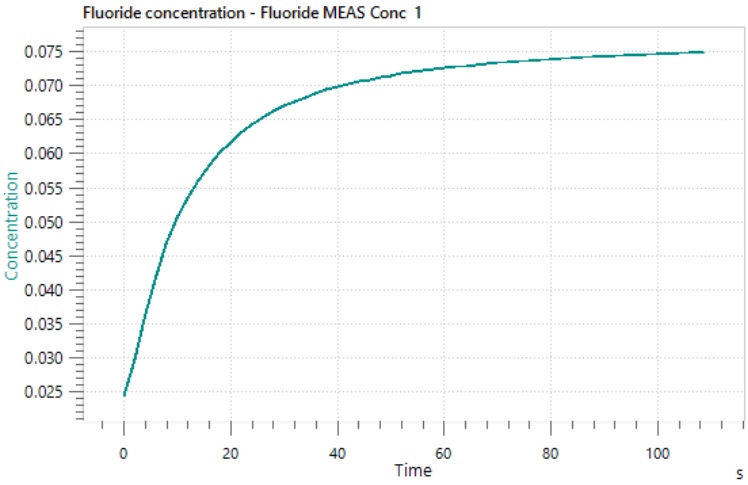



*Figure 21: Measuring curve for the fluoride determination in leachate.*

### Metrohm literature

Application Note AN-I-026: «Fluoride in leachate – Fast determination of fluoride using direct measurement»

# 4.8 Nitrate by ion measurement



## General remarks

Nitrate is naturally present in the environment. However, excessive concentrations of nitrate in surface and groundwater are problematic as such concentrations have a negative effect on the water quality. Usually, excessive levels of nitrate are a direct result of extensive usage of fertilizers in agriculture. Nitrate is easily washed from soils and can end up in surface or groundwater. As the nitrate content is regulated in many countries, a quick and inexpensive assessment of its concentration is required to monitor the water quality.

This section describes the direct measurement with the nitrate-selective electrode for surface water samples.

## Instrument and relevant accessories

- Ion meter or instrument with ion measurement mode
- Stirrer
- 6.00510.120 combined polymer membrane electrode, $NO_3$

## Reagents

- Ionic strength adjustor (ISA): $c(Al_2(SO_4)_3)$ = 0.1 mol/L (CAS 10043-01-3)
- Conditioning solution: $c(KNO_3)$ = 0.01 mol/L (CAS 7757-79-1)

## Calibration

Carry out a calibration with at least 3 different standard concentrations. Use 50 mL calibration standard and 2 mL ISA. In between each measurement, condition the electrode in conditioning solution for 30 s.

## Analysis

Pipette 50 mL sample into the sample beaker. Add 2 mL ISA. Afterwards, measure the concentration of the sample. In between each measurement, condition the electrode in conditioning solution for 30 s.

## Parameters

| | |
|---|---|
| Mode | MEAS CONC |
| Stirring rate | 8 |
| Signal drift | 0.2 mV/min |
| Min. waiting time | 10 s |
| Max. waiting time | 300 s |
| Measuring interval | 2 s |

## Remarks

- Before the first use, the $NO_3$-ISE is conditioned for 30 min in c($KNO_3$) = 0.01 mol/L.
- The $NO_3$-ISE is stored dry with some moisture residue (some drops of deionized water) in the storage vessel as otherwise the polymer membrane is leached out.

## Example

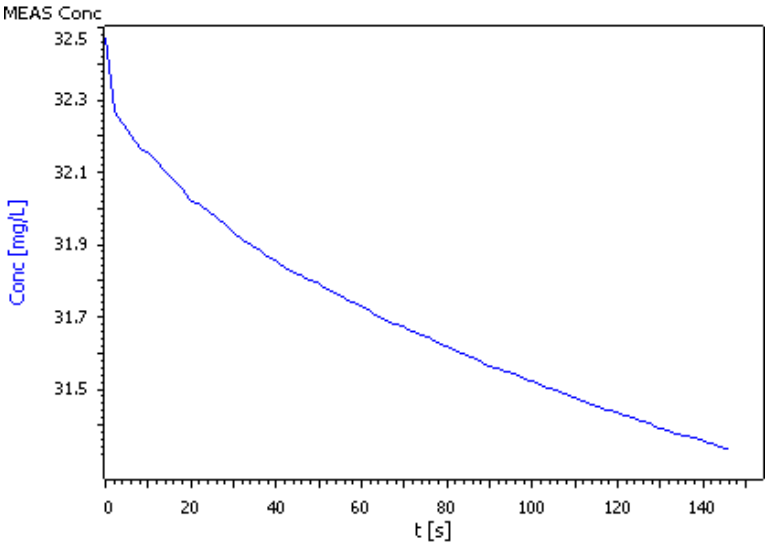



*Figure 22: Measuring curve for the nitrate determination in surface water.*

### Metrohm literature

Application Note AN-I-024: «Nitrate in surface water – Fast and inexpensive determination by direct measurement»

# 4.9 Sulfide by ion measurement



## General remarks

Sulfide ions are present in groundwater and wastewater. They cause odor and corrosion problems. In acidified water, they can form hydrogen sulfide, which is extremely toxic even at low levels.

This section describes the determination according to ASTM D4658 for a sulfide content in the range of 0.04 to 4000 mg/L sulfide.

## Instrument and relevant accessories

- Ion meter or instrument with ion measurement mode
- Stirrer
- 6.0502.180 Ion-selective electrode, Ag/S
- 6.0750.100 LL ISE reference electrode

## Reagents

- Sulfide antioxidant buffer (SAOB): c(NaOH) = 2 mol/L (CAS 1310-73-2), c(ascorbic acid) = 0.2 mol/L (CAS 50-81-7), and c(EDTA) = 0.2 mol/L (CAS 6381-92-6)
- Zinc acetate solution: $c(Zn(C_2H_3O_2)_2)$ = 2.0 mol/L (CAS 557-34-6)
- Sodium hydroxide solution: c(NaOH) = 6 mol/L (CAS 1310-73-2)
- Bridge electrolyte: $c(KNO_3)$ = 1 mol/L (pH = 13.5) (CAS 7757-79-1)

## Sample preparation

The samples must be preserved because sulfide is highly volatile. For preservation add 200 µL $c(Zn(C_2H_3O_2)_2)$ = 2.0 mol/L (equivalent to 128 mg/L $S^{2-}$) and 50 µL c(NaOH) = 6.0 mol/L to 100 mL water.

## Calibration

Carry out a calibration with at least 3 different standard concentrations. Use the same ratio of calibration standard to SAOB as for the sample measurement. Measure the calibration standards without stirring. In between each measurement, condition the electrode in SAOB/deionized water (1:1) for 1 min.



## Analysis

Transfer 50 mL water sample into a sample beaker. Just before the measurement, add 50 mL SAOB and stir the solution vigorously for 15 s. After a waiting for 3 min, place the electrodes into the sample solution and measure the sulfide concentration without stirring. In between each measurement, condition the electrode in SAOB/deionized water (1:1) for 1 min.

## Parameters

| | |
|---|---|
| Mode | MEAS CONC |
| Stirring rate | 0 |
| Signal drift | 1 mV/min |
| Min. waiting time | 200 s |
| Max. waiting time | 1000 s |
| Measuring interval | 2 s |

## Remarks

- The SAOB fixes the pH value at a high alkaline level. This ensures that the sulfide is mainly present as $S^{2-}$ ion rather than $HS^-$ or $H_2S$, which are present at lower pH values.
- Furthermore, SAOB contains ascorbic acid greatly reducing the oxidation of the present $S^{2-}$ by air.
- To preserve the sulfide, zinc acetate is added to the sample, forming insoluble zinc sulfide. The EDTA present in the SAOB reacts with the zinc sulfide, redissolving the sulfide. Therefore, it is necessary to wait after the addition of the SAOB to the sample and before the measurement.

## Example

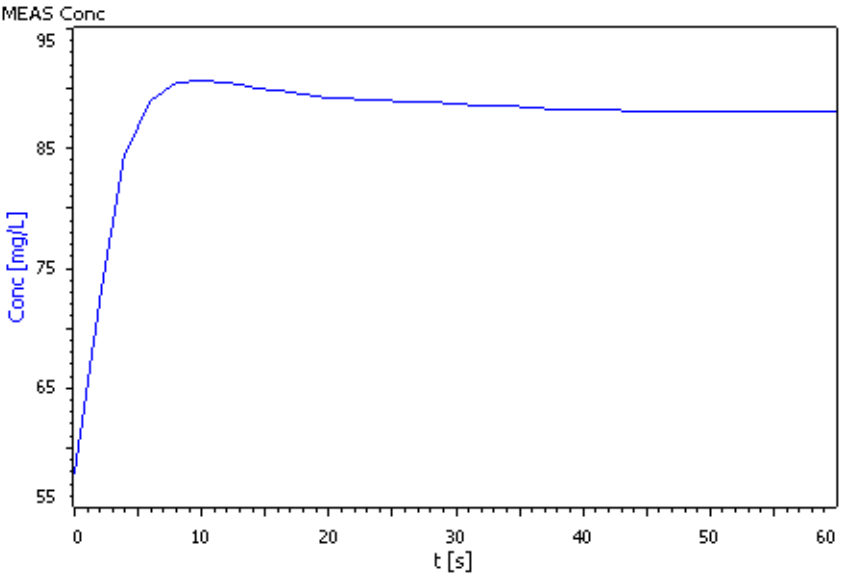



*Figure 23: Measuring curve for the sulfide determination in spiked tap water.*

### Metrohm literature

- Application Note AN-I-013: «Sulfide in water in accordance with ASTM D4658»

# 4.10 Ion chromatography – Introduction



Ion chromatography (IC) is the method of choice for water analysis. It almost seems to have been invented especially for this field. Its advantages are obvious:

- Multicomponent analysis – several species (e.g. anions, cations) can be determined simultaneously in one run.
- High selectivity – optimized columns and eluents improve separation – perfectly separated peaks.
- Low detection limits; preconcentration allows to reach the ng/L (ppt) range.
- High precision and accuracy thanks to software programs for linear and nonlinear calibration curves and automated peak evaluation.
- High degree of automation allows large sample series and monitoring.
- High sample throughput.
- Metrohm Inline Sample Preparation for less manual work and improved reproducibility and accuracy of the results.

As a support to its customers Metrohm publishes a wide range of Application Notes and monographs. Please search for Application Notes and a list of monographs on our website and order those that interest you free of charge from your Metrohm distributor.

Of course one has to consider which ions have to be determined at which concentration in which type of water (wastewater, groundwater, drinking water, lake, river or seawater, cooling and rainwater). These questions are treated in a large number of publications in scientific journals.

# 4.11 Instrumentation

Metrohm Ion Chromatography are separated in to three levels*:

- 940 Professional IC Vario: High-end ion chromatograph for research applications and method development.
- 930 Compact IC Flex: Compact ion chromatograph for routine analysis.
- Eco IC: Entry-level ion chromatograph for water analysis and utilization as a training tool.

** at the time of publication. Further instrument generations apply accordingly.*

Most applications shown below can be performed with a Professional or a Compact instrument. The entry-level ICs are recommended in the medium µg/L and mg/L range only. Especially due to the limitation to chemical suppression.

All Metrohm ion chromatographs can be automated. Inline Sample Preparation methods are reserved to the Professional IC Vario and the Compact IC Flex instruments. The latter are restricted to Inline Ultrafiltration and Inline Dialysis.

There is a large variety of IC columns available from Metrohm. The «Column Finder» on the Metrohm website (https://www.metrohm.com) gives an overview on the available columns and helps to find the right column for your application.

Typically several columns may be applied for a certain application. In this monograph only a selection is shown.

# 4.12 Reagents

Reagents for eluents, standards, and regeneration solutions need to be highest purity (minimum p.a.). The most important reagent is ultrapure water. It needs to have at least Grade I (ISO 3696/ASTM D1193), recommended is a resistivity at 25 °C of ≥ 18.2 MΩ·cm and a TOC of < 5 µg/L. We strongly recommend to avoid any other type of purified water. The bottled "Water for IC" is an option. But, for trace analysis and long-term use we recommend to invest in a proper water purification system.

Eluent concentrates and dedicated single and multi-ion standards are commercial available from different manufacturers. We recommend the products from Fluka/Merck. Especially for cation standard solutions it is important to use dedicated IC standard solutions. The respective ICP standards are too acidic for IC purposes.

# 4.13 Anion determination with IC

## General remarks

The determination of fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulfate is of great importance to assess for example the quality of drinking as well as mineral water, for example. The ion chromatographic determination of these anions is therefore the subject of regulations and standard methods.

## Sample preparation



The samples have to be filtered, for example using Minisart (Sartorius) or disposable filter supports (Whatman, formerly Schleicher & Schuell) with a pore size of 0.2 µm. Even seemingly clear solutions can contain very fine particles that damage the column. The samples can be filtered automatically applying Inline Ultrafiltration. At higher concentrations, it may be necessary to dilute the samples. Intelligent Inline Dilution enables a fully automated sample dilution as well as a one-standard calibration. As alternative, lower sample volumes may be injected by applying intelligent Partial-Loop Injection Technique or intelligent Pick-up Technique. Both methods are fully automated and enable one standard calibration.

For water samples containing a high proportion of organic substances we recommend to apply Inline Dialysis as a sample preparation step that is completely automated.

Metrohm offers fully automated IC systems that carry out Inline Ultrafiltration, Inline Dialysis, as well as Inline Dilution. The MISP systems (Metrohm Inline Sample Preparation) simplify and improve sample preparation significantly.

## Analysis

When working in the concentration range 10 ppb to 100 ppm, one normally injects 20–100 µL sample, which is separated on the anion exchanger column and undergoes chemical or sequential suppression (chemical and $CO_2$ suppression) followed by conductivity detection.

If lower detection limits need to be achieved, the sample volume must be increased markedly. Consider, however, that larger sample volumes mean a larger water peak, which affects the evaluation of the early-eluting peaks.

Sample preconcentration is a simple method for lowering the detection limit by several orders of magnitude. The sample loop is replaced by a preconcentration column. An increased sample volume, e.g. 10 mL, is passed over the preconcentration column, which contains essentially the same material as the separation column. This ensures that all anions to be analyzed in the sample solution (e.g., ultrapure water) are kept back on the column and are preconcentrated. The preconcentrated analyte ions are then carried to the separation column by the eluent flowing counter-current.

Quantification is performed by means of an external calibration in the respective concentration range. Thereby, at least a five-point calibration is recommended for the determination of anions with suppression.

# Examples

## Anions in drinking water with chemical suppression



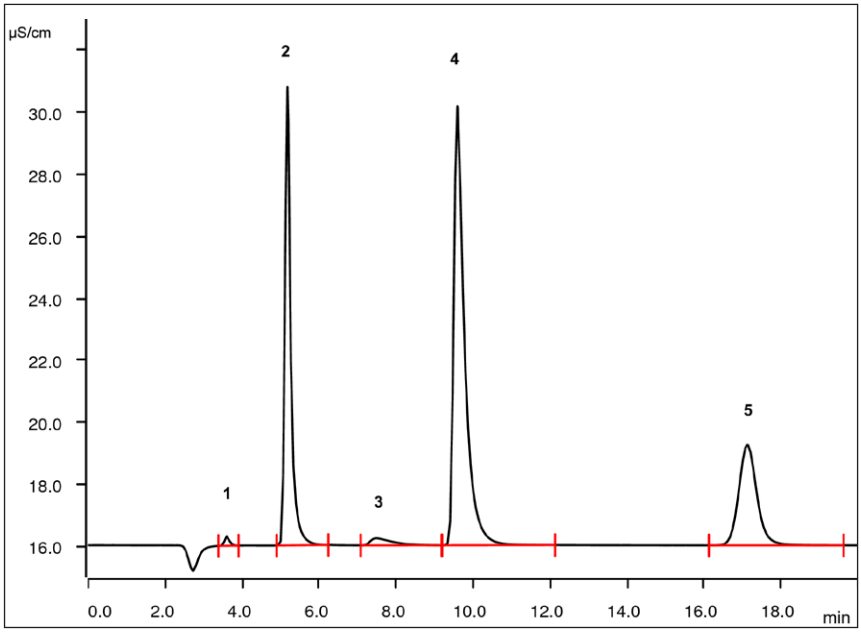



*Figure 24: Anions in drinking water with sequential suppression*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/L] |
|---|---|---|---|
| 1 | Fluoride | 3.6 | n.q. |
| 2 | Chloride | 5.2 | 7.9 |
| 3 | System peak | 7.5 | – |
| 4 | Nitrate | 9.6 | 26.9 |
| 5 | Sulfate | 17.1 | 7.8 |

*n.q. = not quantified*

| | |
|---|---|
| Instrument | Any IC instrument |
| Column | 6.01032.420 Metrosep A Supp 17 - 150/4.0 |
| Eluent | $c(Na_2CO_3)$ = 5.0 mmol/L (CAS 497-19-8)<br>$c(NaHCO_3)$ = 0.6 mmol/L (CAS 144-55-8) |
| Flow | 0.6 mL/min |
| Suppressor regenerant | $c(H_2SO_4)$ = 100 mmol/L (CAS 7664-93-9) |
| Suppressor rinsing | STREAM |
| Injection volume | 20 µL |



## Anions in drinking water with sequential suppression

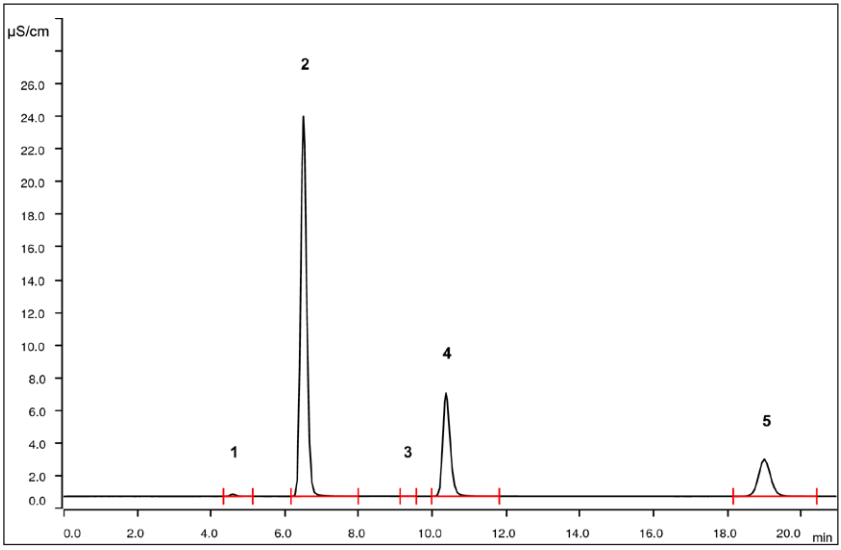



*Figure 25: Anions in drinking water with chemical suppression*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/L] |
|---|---|---|---|
| 1 | Fluoride | 4.6 | 0.07 |
| 2 | Chloride | 6.5 | 12.4 |
| 3 | Bromide | 9.3 | 0.02 |
| 4 | Nitrate | 10.4 | 7.60 |
| 5 | Sulfate | 19.0 | 3.88 |

| | |
|---|---|
| Instrument | Compact or Professional IC instruments |
| Column | 6.1006.420 Metrosep A Supp 5 - 150/4.0 |
| Eluent | $c(Na_2CO_3)$ = 3.2 mmol/L (CAS 497-19-8)<br>$c(NaHCO_3)$ = 1.0 mmol/L (CAS 144-55-8) |
| Flow | 0.7 mL/min |
| Suppressor regenerant | $c(H_2SO_4)$ = 100 mmol/L (CAS 7664-93-9) |
| Suppressor rinsing | STREAM |
| Injection volume | 20 µL |

## Metrohm literature

IC Application Note AN-S-353: «Anions in drinking water with the Eco IC»

IC Application Note AN-S-354: «Anions in wastewater with the Eco IC»

IC Application Note AN-S-235/236: «Determination of anions and oxyhalides by US EPA method 300.1 A and B in a single analysis»

IC Application Note AN-S-364: «Dissolved anions in water according to EN ISO 10304-1 applying Inline Ultrafiltration»

IC Application Note AN-S-348: «Anions in drinking water on the Metrosep A Supp 5-150/2.0 column»

IC Application Note AN-S-367: «Ultratrace-level perchlorate in water containing 3000 mg/L of total dissolved solids (US EPA method 314.0) applying Inline Ultrafiltration»

White Paper WP-009: «Determination of anions in tap water in accordance with US EPA Method 300»

### Additional literature

US EPA Method 300.1: «Determination of inorganic anions in drinking water by ion chromatography»



EN ISO 10304-1: «Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate»

ASTM D6581: «Standard Test Methods for Bromate, Bromide, Chlorate, and Chlorite in Drinking Water by Suppressed Ion Chromatography»

# 4.14 Oxyhalides with IC: Chlorate, chlorite, bromate

## General remarks

Chlorate, chlorite, and bromate are disinfection by-products that have to be monitored in water types such as drinking water and mineral water. The determination of bromate is especially important as bromate affects the thyroid gland and is a suspected carcinogenic. Bromate is formed by the oxidation of bromide, whose determination is therefore also very important.

The US EPA Method 300.1 part A and B is a standard method for the determination of inorganic anions including oxyhalides in water. If this method is applied, dichloroacetate (DCA) must be added as an internal standard. The IC column Metrosep A Supp 7 - 250/4.0 fulfills the method's requirements.

## Sample preparation

All water samples should be filtered through a filter with 0.2 µm pore size (preferably applying Inline Ultrafiltration).

## Analysis

The determination needs an external multipoint calibration in the concentration range concerned. The required concentrations are obtained by diluting the above-mentioned standards with ultrapure water.

## Examples

### Anions in drinking water spiked with chlorite, bromate, and chlorate



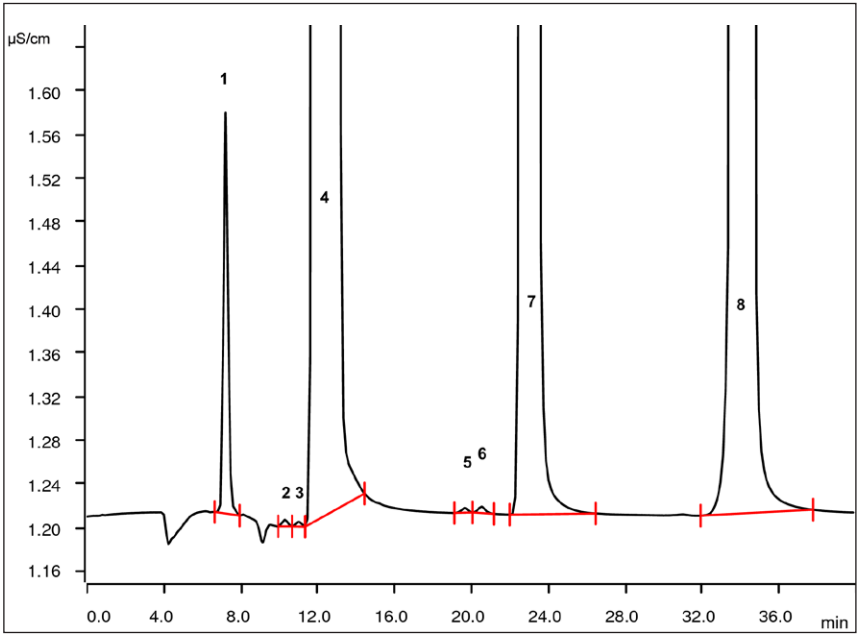



*Figure 26: Drinking water spiked with 5 µg/L of bromide and the oxyhalides*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/L] |
|---|---|---|---|
| 1 | Fluoride | 7.2 | 0.07 |
| 2 | Chlorite | 10.3 | 5.00 |
| 3 | Bromate | 11.0 | 5.00 |
| 4 | Chloride | 12.2 | 12.53 |
| 5 | Bromide | 19.6 | 5.00 |
| 6 | Chlorate | 20.5 | 5.00 |
| 7 | Nitrate | 22.8 | 7.90 |
| 8 | Sulfate | 34.1 | 3.91 |

| | |
|---|---|
| Instrument | Compact or Professional IC instruments |
| Column | 6.1006.630 Metrosep A Supp 7 - 250/4.0 |
| Eluent | c($Na_2CO_3$) = 3.6 mmol/L (CAS 497-19-8) |
| Flow | 0.7 mL/min |
| Suppressor regenerant | c($H_2SO_4$) = 100 mmol/L (CAS 7664-93-9) |
| Suppressor rinsing | STREAM |
| Injection volume | 20 µL Column |
| Column temperature | 45 °C |

## Anions in drinking water (Houston) spiked with chlorite, bromate, and chlorate

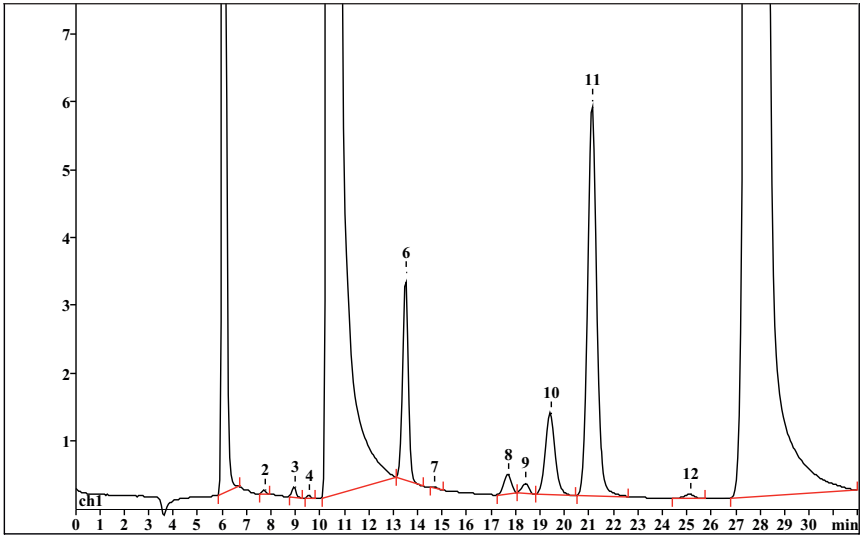



*Figure 27: Anions in drinking water (Houston) spiked with chlorite, bromate, and chlorate*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/L] |
|---|---|---|---|
| 1 | Fluoride | 6.09 | 0.640 |
| 2 | not identified | 7.72 | – |
| 3 | Chlorite | 8.94 | 0.013 |
| 4 | Bromate | 9.56 | 0.006 |
| 5 | Chloride | 10.50 | 21.400 |
| 6 | N as nitrite | 13.50 | 0.079 |
| 7 | not identified | 14.69 | – |
| 8 | Bromide | 17.68 | 0.050 |
| 9 | Chlorate | 18.41 | 0.045 |
| 10 | DCA | 19.41 | 0.873 |
| 11 | N as nitrate | 21.13 | 0.264 |
| 12 | P as phosphate | 25.12 | 0.171 |
| 13 | Sulfate | 27.85 | 23.400 |

| | |
|---|---|
| Instrument | Compact or Professional IC instruments |
| Column | 6.1006.630 Metrosep A Supp 7 - 250/4.0 |
| Eluent | $c(Na_2CO_3)$ = 3.6 mmol/L (CAS 497-19-8) |
| Flow | 0.8 mL/min. |
| Suppressor regenerant | $c(H_2SO_4)$ = 100 mmol/L (CAS 7664-93-9) |
| Suppressor rinsing | STREAM |
| Injection volume | 20 µL |
| Column temperature | 45 °C |

## Metrohm literature

IC Application Note AN-S-16: «Detection limits of bromate in drinking water»

IC Application Note AN-S-170: «Oxyhalides in drinking water»

IC Application Note AN-S-235: «Determination of anions and oxyhalides by US EPA method 300.1 A and B in a single analysis (standard solution)»

IC Application Note AN-S-236: «Determination of anions and oxyhalides by US EPA method 300.1 A and B in a single analysis (sample)»

IC Application Note AN-S-312: «Disinfection by-products and standard anions according to EPA 300.1 A & B on 930 Compact IC Flex»

### Additional literature

US EPA Method 300.1: «Determination of inorganic anions in drinking water by ion chromatography»



# 4.15 Bromate with IC

## General remarks

Bromate affects the thyroid gland and is a potential carcinogen. It is formed by oxidation of bromide traces during the disinfection of water, for example by ozonization.

The limiting values prescribed by the pertinent laws differ from one country to the other. As example the German Drinking Water Regulation prescribes a limit of 10 µg/L in 2011. For mineral water a limiting value of 3 µg/L has been in force in Germany since 2004.

The internationally accepted standards stipulate different methods for determining bromate. Four of them will be described below:

- Bromate determination after separation on an anion-exchange column (see 4.15 Oxyhalides) conductivity detection can be used to determine additional anions in the same run (US EPA 300.1).
- Bromate determination by means of post-column derivatization with o-danisidine followed by VIS detection. The separation occurs on an anion-exchange column. The post-column reaction with o-danisidine, which is highly selective for bromate, can be applied after conductivity detection. This allows to determine additional anionic constituents (US EPA 317). Due to the toxicity of o-dianisidine, this method is only rarely applied.
- Bromate determination by means of post-column derivatization with acidic potassium iodide (triiodide method) followed by UV detection. The separation occurs on an anion-exchange column (US EPA 326, ISO 11206).
- Bromate determination using an anion-exchange column followed by MS detection. The coupling of ion chormatographic separation and MS detection opens up another possibility to increase the selectivity and sensitivity of bromate determination.

The following limits of detection LOD (according to DIN 32645) can be reached

| Method | Injected volume µL | LOD in ultrapure water µg/L | LOD in drinking water matrix* µg/L |
|---|---|---|---|
| Determination using conductivity detection after chemical suppression | 100 | 0.13 | 0.39 |
| Post-column derivatization with o-dianisidine and VIS detection | 100 | 0.21 | 0.64 |
| Determination by means of post-column derivatization with KI (triiodide method) and UV detection | 1000 | 0.032 | 0.066 |
| Determination using MS detection | 100 | 0.0064 | 0.0067 |

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

## Sample preparation

All water samples should be filtered through a filter with 0.2 µm pore size.

## Analysis

The determination needs an external multipoint calibration in the concentration range concerned. The required concentrations are obtained by diluting the standard solution with ultrapure water.

## Examples

### a) Bromate determination using post-column derivatization with potassium iodide (triiodide method) and UV/VIS detection (ISO 11206)



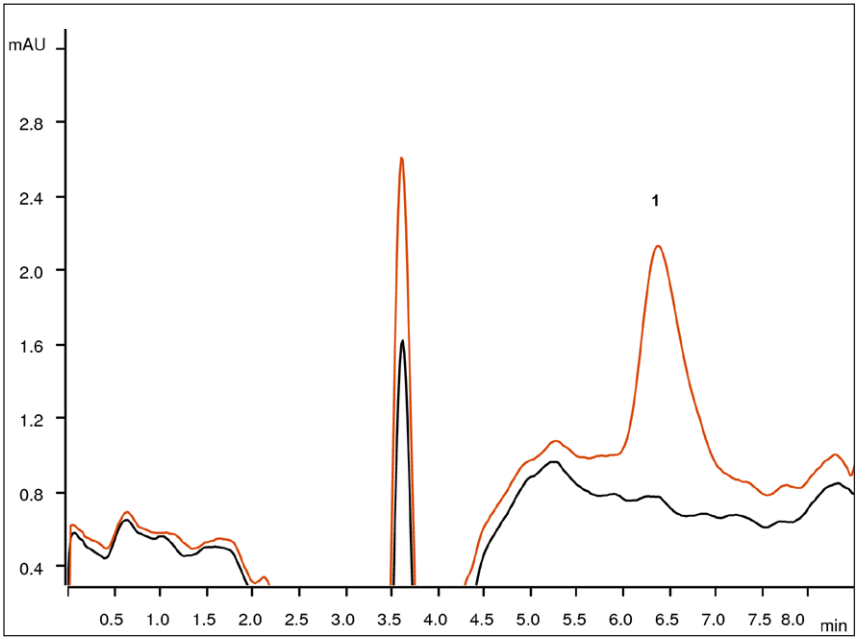



*Figure 28: Drinking water direct (black) and spiked with 1 µg/L (red) of bromate*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/L] |
|---|---|---|---|
| 1 | Bromate | 7.2 | 1.0 |

| | |
|---|---|
| Instrument | Compact or Professional IC instruments |
| Column | 6.1031.420 Metrosep A Supp 16 - 150/4.0 |
| Eluent | c($H_2SO_4$) = 100 mmol/L (CAS 7664-93-9)<br>c($(NH_4)_6Mo_7O_{24}$ x 4 $H_2O$) = 19.3 µmol/L (CAS 12054-85-2, ammonium heptamolybdate) |
| PCR reagent | c(KI) = 0.27 mol/L (CAS 7681-11-0) |
| Flow (eluent) | 0.8 mL/min |
| Flow (PCR, Dosino) | 0.2 mL/min |
| Lamp | UV |
| Wavelength | 352 nm |
| Injection volume | 1325 µL |
| Column temperature | 45 °C |

## b) Bromate determination using IC-MS

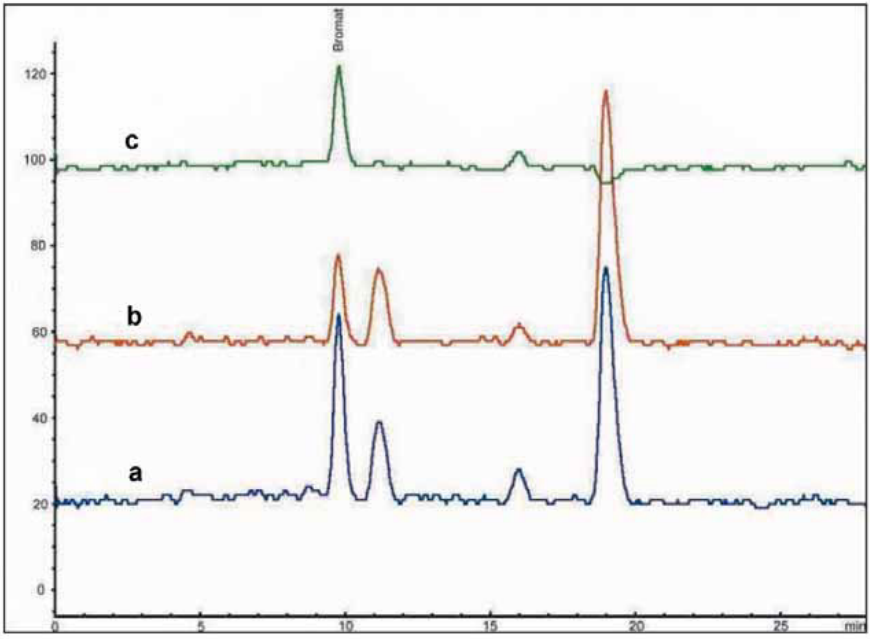



*Figure 29: Analysis of drinking water applying IC-MS. Displayed traces: a) m/z 127 + 129, b) m/z 127, c) m/z 129*

| Peak no. | Component | $t_R$ [min] | Conc. [µg/L] |
|---|---|---|---|
| 1 | Bromate | 9.5 | 0.32 |



| | |
|---|---|
| Instrument | Compact or Professional IC instruments + MS detector |
| m/z | a) 127 + 129; b) 127; c) 129 |
| SIM | negative |
| Fragmentor voltage | 70 V |
| Eluent | $c(Na_2CO_3) = 3.2$ mmol/L (CAS 497-19-8)<br>$c(NaHCO_3) = 1.0$ mmol/L (CAS 144-55-8) |
| Flow | 0.7 mL/min |
| Injection volume | 100 µL |

## Metrohm literature

IC Application Note AN-S-169: «Bromate determination using post column reaction (o-dianisidine method)»

IC Application Note AN-N-47: «Bromate determination using post-column reaction (triiodide method)»

IC Application Note AN-M-004: «Traces of bromide and bromate in drinking water by IC-MS, determination of the Method Detection Limit (MDL)»

IC application Note AN-U-51: «Trace bromate in drinking water according to ISO 11206»

Poster 8.000.6074: «Influence of pH, temperature, and molybdate concentration on the performance of the triiodide method for the trace-level determination of bromate (US EPA 326)»

Poster 8.000.6005: «Hyphenated techniques as modern detection systems in ion chromatography»

Metrohm White Paper WP-039: «Current applications in water and environmental analysis»

### Additional literature



US EPA Method 300.1: «Determination of inorganic anions in drinking water by ion chromatography»

US EPA Method 317: «Determination of inorganic oxyhalide disinfection by-products in drinking water using Ion Chromatography with the addition of a post-column reagent for trace bromate analysis»

US EPA Method 326: «Determination of inorganic oxyhalide disinfection by-products in drinking water using Ion Chromatography incorporating the addition of a suppressor-acidified post-column reagent for trace bromate analysis»

Metrohm White Paper WP-039: «Current applications in water and environmental analysis»

# 4.16 Perchlorate with IC

## General remarks

Perchlorate salts are used as oxidants in rocket propellants, in explosives and in the electroplating industry. Investigations have shown that perchlorate accumulates in water. Accordingly, perchlorate contamination is found in surface waters in regions adjacent to former or actual rocket testing sites for example in California, Nevada, and Arizona.

The effects of perchlorate on humans are still not sufficiently known. One knows for sure, however, that perchlorate slows down the uptake of iodine into the thyroid gland. The determination of perchlorate in different types of water (drinking water, groundwater, surface water, wastewater) is therefore of paramount importance.

The determination of perchlorate is the subject of various international methods.
An example is US EPA Method 332, which describes the determination of perchlorate using IC-MS coupling. The detection limits are given as 0.02 µg/L. The IC-MS coupling has the advantage of significantly reducing matrix effects.

US EPA Method 314.0 describes perchlorate determination using a system based entirely on ion chromatography.

EN ISO 19340 describes trace perchlorate determination by ion chromatography with three different approaches. Here we will show the re-injection technique (Appendix B), the method with no additional sample preparation and a single channel IC system with one additional injector.

In more detail the three methods comprise:

- Perchlorate determination in the µg/L range (US EPA 314) after separation on a high-capacity anion-exchange column using conductivity detection after chemical suppression. With increasing matrix concentrations of chloride, carbonate, and sulfate, the determination of perchlorate using conductivity detection becomes increasingly difficult below 5 µg/L.
- Perchlorate determination using conductivity detection after chemical suppression followed by mass detection. Also here, the separation is carried out on an anion-exchange column. This method allows to determine perchlorate reliably in the ppt range. The IC-MS coupling reduces matrix effects significantly (US EPA 332).
- Perchlorate determination applying the re-injection technique (EN ISO 19340, Appendix B) improves the separation of perchlorate from the matrix anions (chloride, carbonate, and sulfate) by matrix elimination after the first injection. Quantification of 1 µg/L with high anionic matrix load can be easily achieved.



## Sample preparation

All water samples should be filtered through a filter with 0.2 µm pore size.

## Analysis

The determination is carried out by means of an external multipoint calibration covering the concentration range concerned. To obtain the required concentrations, the standard solution is diluted with ultrapure water.

## a) Perchlorate determination using conductivity detection after sequential suppression

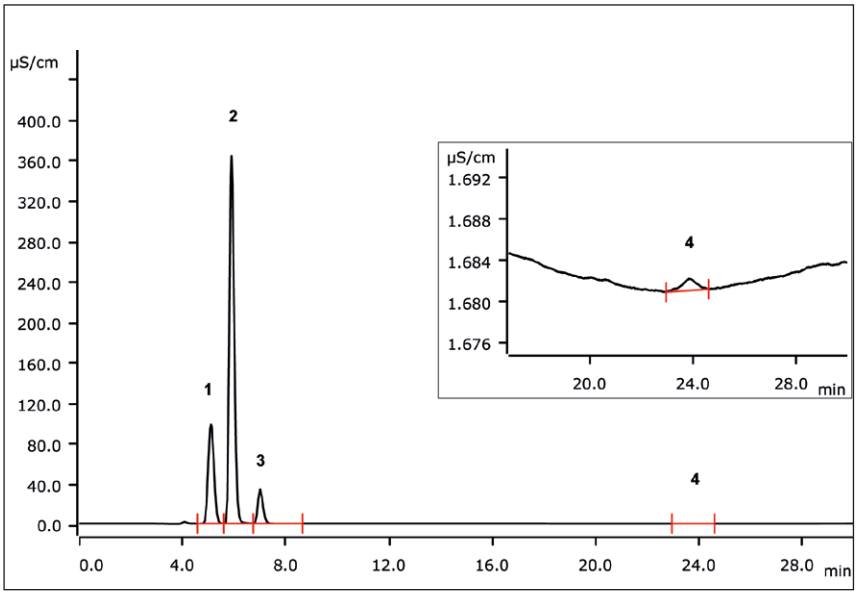



*Figure 30: Perchlorate in drinking water by IC with conductivity detection after sequential suppression*

| Peak no. | Component | $t_R$ [min] | Conc. [µg/L] |
|---|---|---|---|
| 1 | Chloride | 5.1 | n.q. |
| 2 | Sulfate | 5.9 | n.q. |
| 3 | Nitrate | 7.0 | n.q. |
| 4 | Perchlorate | 23.8 | 1.2 |

| | |
|---|---|
| Instrument | Compact or Professional IC instruments |
| Column | 6.1006.620 Metrosep A Supp 7 - 150/4.0 |
| Eluent | c($Na_2CO_3$) = 20 mmol/L (CAS 497-19-8) |
| Flow | 0.7 mL/min. |
| Suppressor regenerant | c($H_2SO_4$) = 100 mmol/L (CAS 7664-93-9) |
| Suppressor rinsing | STREAM |
| Injection volume | 250 µL |
| Column temperature | 60 °C |

**b) Perchlorate determination using conductivity detection after sequential suppression according to US EPA method 314.0 applying Inline Ultrafiltration**

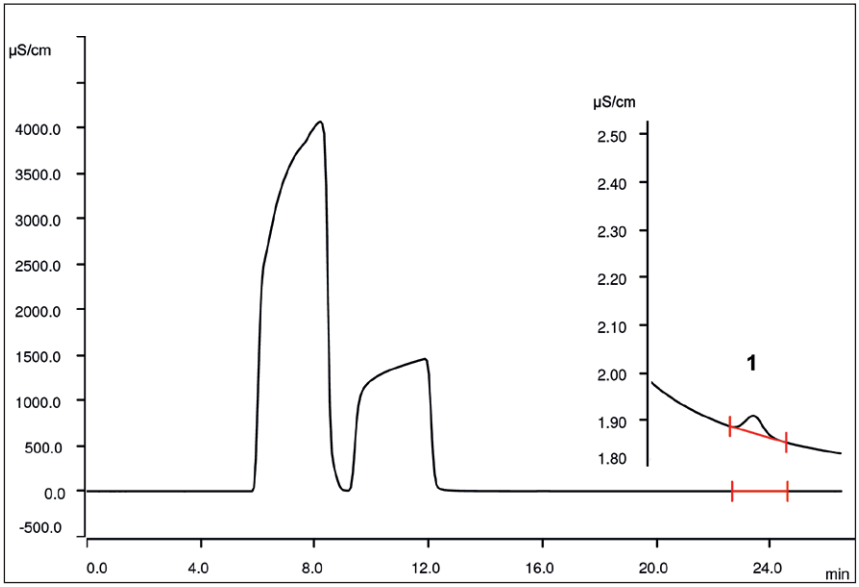



*Figure 31: Perchlorate in high matrix water by IC with conductivity detection after sequential suppression according to US EPA method 314.0. Matrix: 1000 mg/L of chloride, carbonate, and sulfate each.*

| Peak no. | Component | $t_R$ [min] | Conc. [µg/L] |
|---|---|---|---|
| | Chloride | – | 1,000,000 |
| | Sulfate | – | 1,000,000 |
| | Nitrate | – | 1,000,000 |
| 1 | Perchlorate | 23.8 | 1.2 |

| | |
|---|---|
| Instrument | Compact or Professional IC instruments |
| Column | 6.1006.630 Metrosep A Supp 7 - 250/4.0 |
| Eluent | $c(Na_2CO_3)$ = 9.6 mmol/L (CAS 497-19-8)<br>c(NaOH) = 3.0 mmol/L (CAS 1310-73-2)<br>c(acetonitrile) = 25% v/v (CAS 75-05-8) |
| Flow | 0.8 mL/min. |
| Suppressor regenerant | $c(H_3PO_4)$ = 250 mmol/L (CAS 7664-38-2)<br>c(acetonitrile) = 10% v/v (CAS 75-05-8) |
| Suppressor rinsing | STREAM |
| Injection volume | 1250 µL |
| Column temperature | 50 °C |

### c) Perchlorate determination using conductivity detection after sequential suppression according to EN ISO 19340 Appendix B: Re-injection technique

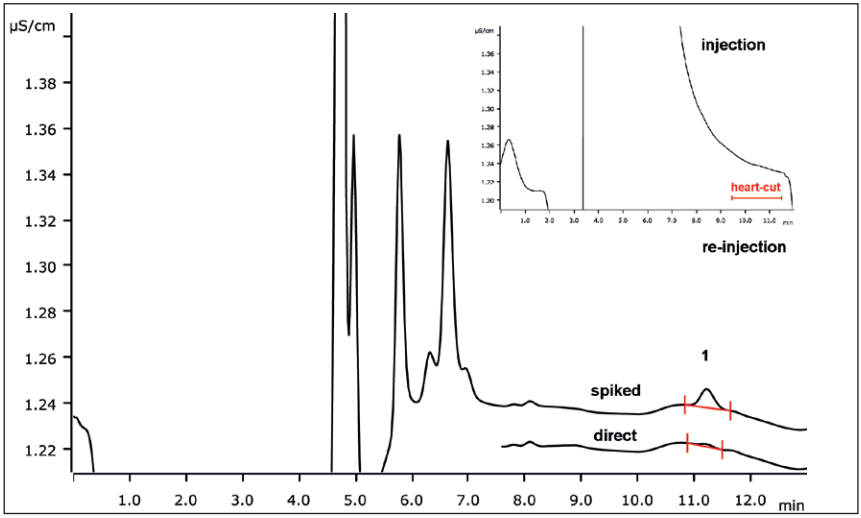



*Figure 32: Perchlorate in drinking water. Determination according to EN ISO 19340. Overlay of a sample injected directly and after spiking with 1 µg/L perchlorate.*

| Peak no. | Component | $t_R$ [min] | Conc. [µg/L] |
|---|---|---|---|
| 1 | Perchlorate (direct) | 11.2 | 0.07* |
| 1 | Perchlorate (spiked) | 11.2 | 1.04 |



* result below the calibration range

| | |
|---|---|
| Instrument | Professional IC instruments |
| Column | 6.1006.510 Metrosep A Supp 5 - 100/4.0 |
| Eluent | c($Na_2CO_3$) = 10 mmol/L (CAS 497-19-8) |
| Flow | 0.8 mL/min |
| Suppressor regenerant | c($H_2SO_4$) = 100 mmol/L (CAS 7664-93-9) |
| Suppressor rinsing | STREAM |
| Injection volume | 1000 µL |
| Re-injection volume | 2200 µL |
| Column temperature | 60 °C |

## Re-injection setup

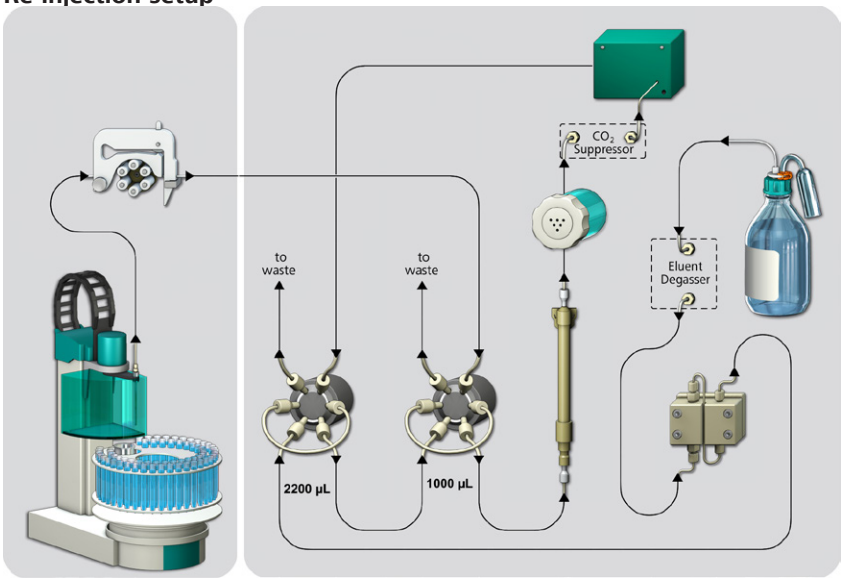



*Figure 33: Setup of the re-injection system according to EN ISO 19340. The re-injection valve is equipped with a 2200 µL loop. Alternatively a preconcentration column may be used.*

The water sample is injected to the chromatographic system with a 1000 µL loop. While the first separation is performed, the re-injection valve (2200 µL loop) is set in the injection position. The effluent from the conductivity detector therefore goes to waste. Shortly before the elution of perchlorate, the re-injection valve is switched to the fill position. The perchlorate is moved into the loop and is subsequently injected for the second time to the same column. The switching times as well as the loop size have to be optimized for the actual eluent/column combination.

## Metrohm literature

IC Application Note AN-S-367: «Ultratrace-level perchlorate in water containing 3000 mg/L of total dissolved solids (US EPA method 314.0) applying Inline Ultrafiltration»

IC Application Note AN-M-002: «Chlorite, chlorate and perchlorate in explosion residue applying IC/MS coupling»

IC Application Note AN-S-342: «Trace perchlorate in drinking water according to ISO 19340 applying Annex B»

IC Application Note AN-S-346: «Perchlorate traces in drinking water»

Metrohm White Paper WP-039 «Current applications in water and environmental analysis»

Reprint LC-GC, The Application Notebook, 2006, February. p. 33: «Determination of Ultra-Trace Level Perchlorate by Ion Chromatography Tandem with Single Quad Mass Spectrometer», Jay Gandhi, Sheher Mohsin»

## Additional literature

Agilent Application Note 5989-0816EN: «The Analysis of Perchlorate by Ion Chromatography/ Mass Spectrometry»

US EPA Method 314.0: «Determination of Perchlorate in Drinking water using Ion Chromatography»

US EPA Method 332.0: «Determination of Perchlorate in Drinking water by Ion chromatography with suppressed conductivity and Electrospray Ionization Mass Spectrometry»

EN ISO 19340: «Water quality – Determination of dissolved perchlorate – Method using ion chromatography (IC)»

# 4.17 Chromate – Cr(VI) with IC



## General remarks

Chromium is considered as an essential trace element. Only the compounds of hexavalent chromium (Cr(VI)) are toxic because of their oxidative effect on cell constituents. Cr(VI) has mutagenic and carcinogenic properties and can cause skin allergies. It is therefore important to know the chromium content of the different types of water.

The chromium content of surface waters ranges from 0.2 to 20 µg/L. The requirements for drinking water depend on local legislation, the limiting values range from <1 µg/L Cr(VI) as a single component parameter to 50 µg/L total chromium i.e. the sum of non-toxic Cr(III) and toxic Cr(VI).

We are going to describe three methods for the determination of Cr(VI):

- Separation on an anion exchange column followed by chemical suppression and conductivity detection. The generally applicable conductivity detection can take advantage to determine additional anions in the same run.
- Separation on an anion exchange column, post-column derivatization with diphenyl carbazide and VIS detection (US EPA 218.6). The post-column derivatization with diphenyl carbazide, which is highly selective for chromate, can be carried out after the conductivity measurement. This allows to determine further ionic species besides chromate combined with high sensitivity and selectivity for chromate.
- Chromate determination with IC-ICP/MS. The combination of ion chromatography with ICP/MS detection separates chromate from possible interferences and enables the determination of Cr(VI) at very low detection limits. The Cr(III) cation is eluted in the injection peak in anion chromatography. Furthermore, the use of an complexing eluent or complexation of Cr(III) enables speciation of Cr(III) as a complex anion and chromate. The individual peaks are detected by ICP/MS.

## Sample preparation

All water samples should be filtered through a filter with 0.2 µm pore size.

## Analysis

The determination is carried out by means of an external multipoint calibration covering the concentration range concerned. To obtain the required concentrations, the standard solution is diluted with ultrapure water.

## Examples

### a) Chromate determination using conductivity detection after chemical suppression (recommended)



The example chromatogram has been recorded with chemical suppression. We recommend to apply sequential suppression to minimize the injection peak (water dip) and the system peak.

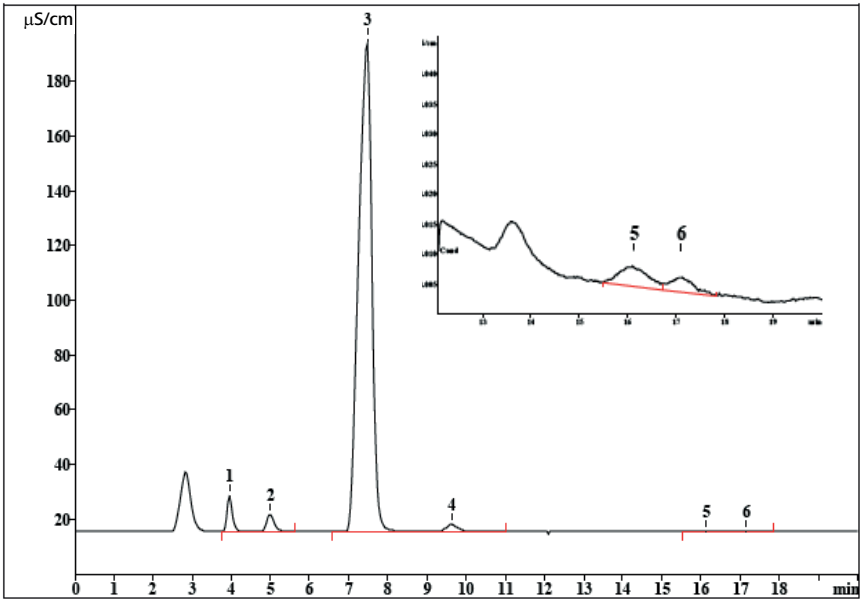



*Figure 34: Determination of chromate besides standard anions in a wastewater sample.*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/L] |
|---|---|---|---|
| 1 | Chloride | 4.0 | 84.3 |
| 2 | Nitrite | 5.0 | 105 |
| 3 | Nitrate | 7.5 | 3652 |
| 4 | Sulfate | 9.6 | 53.0 |
| 5 | Unknown | 16.1 | – |
| 6 | Chromate | 17.1 | 0.1 |

| | |
|---|---|
| Instrument | Compact or Professional IC instruments |
| Column | 6.1006.510 Metrosep A Supp 5 - 100/4.0 |
| Eluent | $c(Na_2CO_3)$ = 3.2 mmol/L (CAS 497-19-8)<br>$c(NaHCO_3)$ = 1.0 mmol/L (CAS 144-55-8) |
| Flow | 0.7 mL/min |
| Suppressor regenerant | $c(H_2SO_4)$ = 100 mmol/L (CAS 7664-93-9) |
| Suppressor rinsing | STREAM |
| Injection volume | 20 µL |
| Column temperature | ambient |

## b) Chromate determination using post-column derivatization with diphenyl carbazide and VIS detection

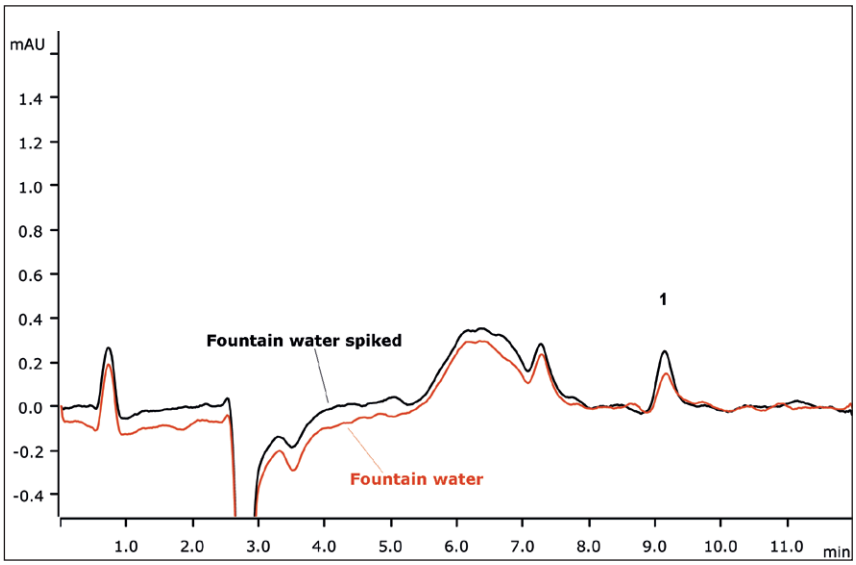



*Figure 35: Trace chromate in fountain water. Large volume injection on to a 2 mm column.*

| Peak no. | Component | $t_R$ [min] | Conc. [µg/L] |
|---|---|---|---|
| 1 | Chromate (direct, red) | 9.1 | 0.032 |
| 1 | Chromate (spiked black) | 9.1 | 0.055 |

| | |
|---|---|
| Instrument | Compact or Professional IC instruments with a UV/VIS detector |
| Column | 6.1020.230 Metrosep A Supp 10 - 250/2.0 |
| Eluent | $c((NH_4)_2CO_3)$ = 100 mmol/L (CAS 506-87-6)<br>$c(NH_4OH)$ = 100 mmol/L (CAS 1336-21-6) |
| PCR reagent | c(1,5-diphenylcarbazide) = 2.0 mmol/L (CAS 140-22-7) |
| Flow | 0.3 mL/min |
| Flow (PCR) | 0.2 mL/min |
| Injection volume | 1000 µL |
| Column temperature | 50 °C |
| PCR temperature | 50 °C |
| Wavelength | 530 nm |

### c) for chromium speciation wit IC-ICP/MS

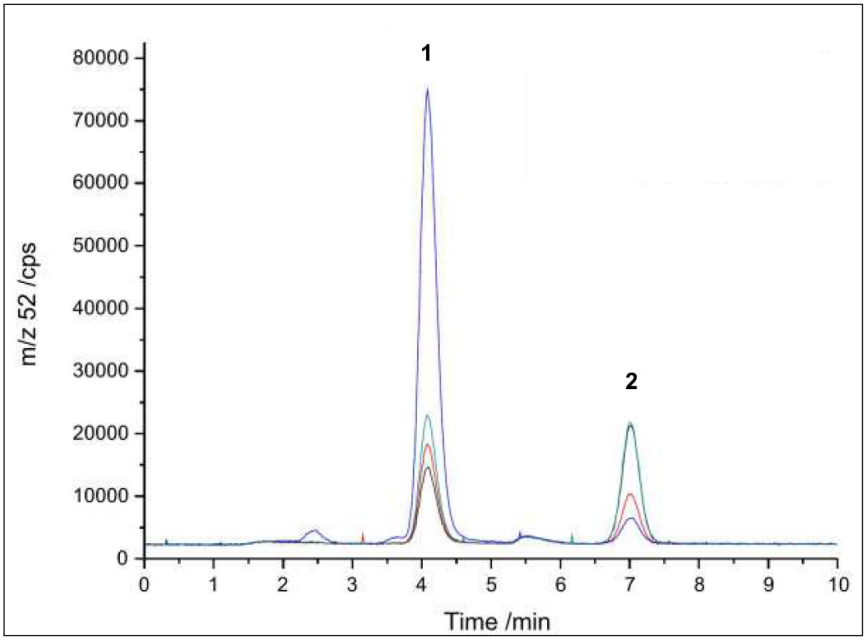



*Figure 36: Overlay of four standard solutions injected to the IC-ICP/MS system. EDTA is added to samples and standards for pre-column complexation of Cr(III). The respective Cr(III)-EDTA complex anion is detected.*

| Peak no. | Component | $t_R$ [min] | Std. 1 [µg/L] | Std. 2 [µg/L] | Std. 3 [µg/L] | Std. 4 [µg/L] |
|---|---|---|---|---|---|---|
| 1 | Cr(III) as EDTA complex | 4.1 | 1.0 | 0.8 | 4.0 | 0.6 |
| 2 | Cr(VI) as chromate | 7.0 | 1.0 | 0.4 | 0.2 | 1.0 |

| | |
|---|---|
| Instrument | Compact or Professional IC instruments with an ICP/MS detector |
| Column | 6.01090.210 Metrosep Carb 2 - 100/2.0 |
| Eluent | $c(NH_4NO_3)$ = 100 mmol/L (CAS 6484-52-2) |
| Sample preparation | Cr(III) complexation with EDTA (CAS 60-00-4) |
| Flow | 0.2 mL/min |
| Injection volume | 20 µL |
| Column temperature | ambient |
| m/z | 52 |

## Metrohm literature

IC Application Note AN-U-057: «Chromate in drinking water by ion chromatography with PCR and UV/VIS detection according to EPA Method 218.7»

IC Application Note AN-U-069: «Chromate using PCR and UV/VIS detection according to EPA 218.7»

IC Application Note AN-M-008: «Determination of chromate in water using IC-ICP/MS detection»

IC Application Note AN-M-013: «Chromium(III) and chromium(VI) speciation analysis via Microbore column and IC-ICP/MS»

## Additional literature

US EPA Method 218.7: «Determination of Hexavalent Chromium in Drinking Water by Ion Chromatography with Post-Column Derivatisation and UV-Visible Spectroscopic Detection»

ASTM D5257: «Standard Test Method for Dissolved Hexavalent Chromium in Waterby Ion Chromatography»

# 4.18 Silicate – dissolved silicic acid with IC



## General remarks

Silicates are salts of silicic acid and form a large group of minerals. The earth's crust consists to more than 90%, the earth's mantle almost completely of silicates. The silicates occur in dissolved form in virtually all types of water and their determination, for example in drinking water, is of considerable interest.

The silicate ion is also an indicator of the quality of ultrapure water as it is one of the first ions that appear in the purified water when the ion exchangers used for water purification becomes exhausted. The determination at very low concentration levels is therefore very important, for example in thermal power plants.

Silicate cannot be determined by standard suppressed IC. With a first $pK_s = 9.51$ the silicic acid will be totally protonated during suppression. Therefore, there will be no conductivity signal. Applying non-suppressed IC with alkaline eluents, silicate is at least partially deprotonated and a peak can be observed and quantified.

Another method for ion chromatographic silicate determination is the use of a PCR-UV/VIS detection after the separation. Silicate is separated with an alkaline eluent. An acidic molybdate solution is added. The molybdosilicic acid is then detected at 410 nm. In the same run phosphate can be determined as well.

## Sample preparation

All water samples should be filtered through a filter with 0.2 µm pore size.

## Analysis

Quantified is carried out by means of an external multipoint calibration covering the concentration range concerned. To obtain the required concentrations, the above-mentioned standard is diluted with ultrapure water. If one works in the low ppb range using preconcentration, it is recommended to apply inline calibration.

# Examples

## a) Silicate determination using non-suppressed conductivity detection



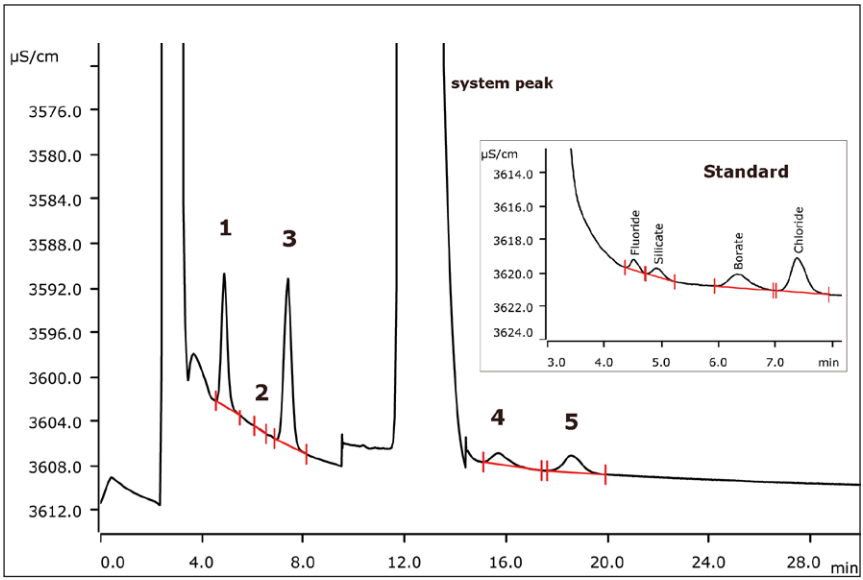



*Figure 37: Determination of silicate besides borate, chloride, nitrate, and sulfate in drinking water applying non-suppressed conductivity detection. The inlay shows a standard injection of fluoride (0.1 mg/L), silicate (0.3 mg/L), borate (1.0 mg/L), and chloride (1.0 mg/L) indicating the separation of these four anions.*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/L] |
|---|---|---|---|
| | Fluoride | 4.5 | -* |
| 1 | Silicate | 4.9 | 6.0 |
| 2 | Borate | 6.3 | n.d. |
| 3 | Chloride | 7.4 | 7.9 |
| | System peak | 12.3 | – |
| 4 | Nitrate | 15.7 | 7.0 |
| 5 | Sulfate | 18.6 | 5.1 |

** No fluoride in the sample*

| | |
|---|---|
| Instrument | Compact or Professional IC instruments non-suppressed |
| Column | 6.1031.430 Metrosep A Supp 16 - 250/4.0 |
| Eluent | c(NaOH) = 20 mmol/L (CAS 1310-73-2)<br>c($NaHCO_3$) = 1.5 mmol/L (CAS 144-55-8) |
| Flow | 0.3 mL/min |
| Injection volume | 250 µL |
| Column temperature | 45 °C |

## b) Trace silicate determination using non-suppressed conductivity detection with preconcentration

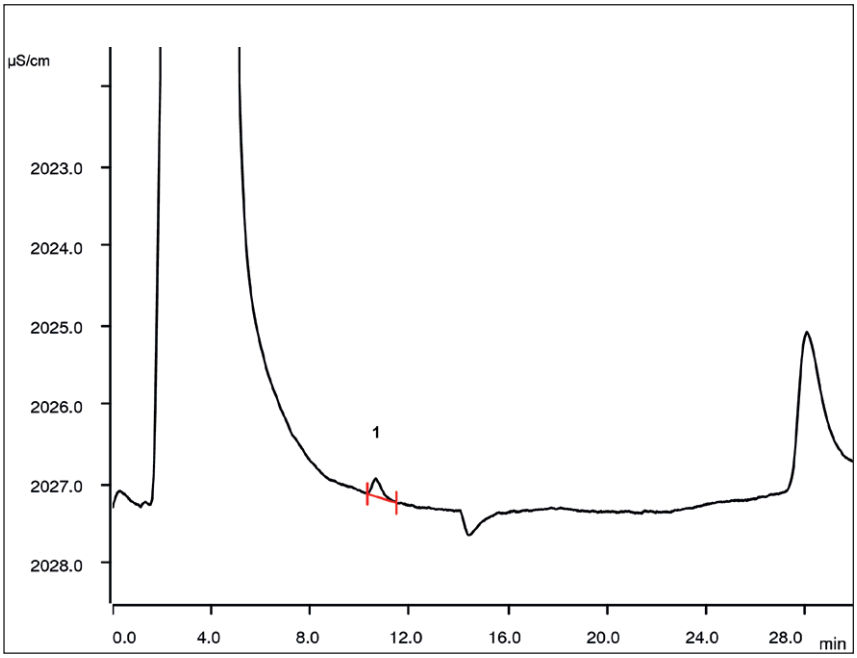



*Figure 38: Silicate in boiler feed water*

| Peak no. | Component | $t_R$ [min] | Conc. [µg/L] |
|---|---|---|---|
| 1 | Silicate | 10.6 | 22.4 |

| | |
|---|---|
| Instrument | Professional IC instruments non-suppressed |
| Column | 6.1031.430 Metrosep A Supp 16 - 250/4.0 +<br>6.1005.000 Hamilton PRP-X 100 - 125/4.0 |
| Preconcentration column | 6.1006.310 Metrosep PCC 1 HC |
| Eluent | c(NaOH) = 2.0 mmol/L (CAS 1310-73-2)<br>c($NaHCO_3$) = 0.25 mmol/L (CAS 144-55-8) |
| Flow | 1.0 mL/min |
| Injection volume | 1500 µL |
| Column temperature | 40 °C |

### c) Silicate determination applying post-column derivatization followed by UV/VIS detection

This example of silicate determination is part of an analysis system for anions, cations, and silicate for a reverse osmosis system. In the anion channel, the conductivity detector and the post-column derivatization as well as the UV/VIS detector are connected in series. The molybdate reagent reacts with phosphate as well. Phosphate therefore is detected in the silicate chromatogram as well. Quantification is done for silicate only.

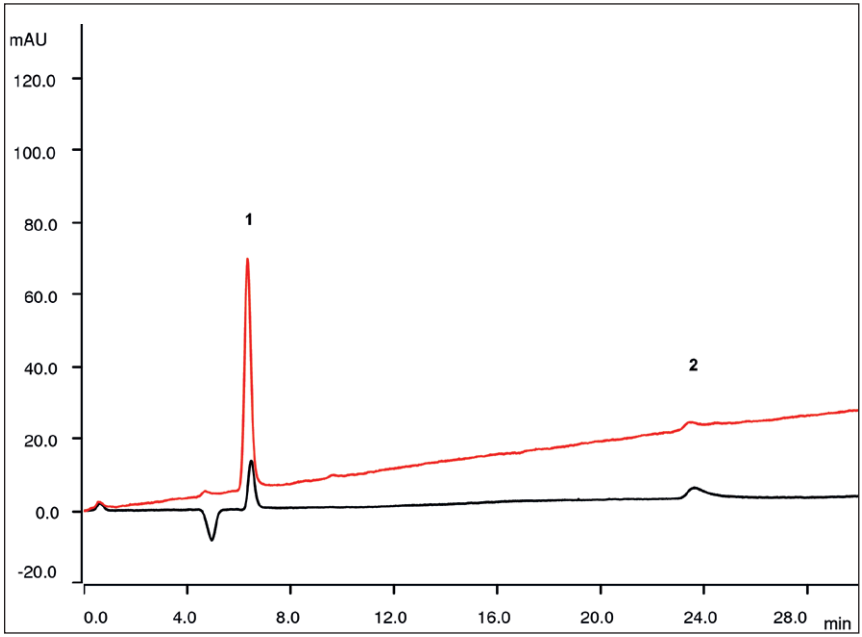



*Figure 39: Silicate determination in reverse osmosis effluent. Overlay of sample (red) and standard (black) chromatogram.*

| Peak no. | Component | $t_R$ [min] | Sample conc. | Standard conc. |
|---|---|---|---|---|
| 1 | Silicate | 4.1 | 23.0 | 0.25 |
| 2 | Phosphate | 22.9 | 3.3* | 0.25* |

** Phosphate quantified by suppressed conductivity detection*

| | |
|---|---|
| Instrument | Compact or Professional with a UV/VIS detector |
| Column | 6.1006.530 Metrosep A Supp 5 - 250/4.0 |
| Eluent | $c(Na_2CO_3)$ = 3.2 mmol/L (CAS 497-19-8)<br>$c(NaHCO_3)$ = 1.0 mmol/L (CAS 144-55-8) |
| PCR reagent | $c(Na_2MoO_4)$ = 20 mmol/L (CAS 231-551-7 )<br>$c(HNO_3)$ = 200 mmol/L (CAS 7697-37-2) |
| Flow | 0.7 mL/min |
| Flow (PCR) | 0.3 mL/min |
| Injection volume | 10 µL |
| Column temperature | 45 °C |
| PCR temperature | 45 °C |
| Wavelength | 360 nm |

## Metrohm literature

IC Application Note AN-N-054: «Borate and silicate in ultrapure water»

IC Application Note AN-N-056: «Silicate besides fluoride in tap water»

IC Application Note AN-N-060: and AN-Q-001 «Online monitoring of trace levels of silicate in boiler feed water»

IC Application Work AN-U-048: «Silicate and hexafluorosilicate»

IC Application Work AN-U-050: «Hexafluorosilicate in etching baths»

# 4.19 Sulfite, sulfate, and thiosulfate with IC



## General remarks

With ion chromatography the determination of the sulfur species sulfite, sulfate, thiocyanate, and thiosulfate can be carried out in one run. This determination is of high interest in the analysis of wastewaters, especially in the paper industry, where sulfate and sulfite-containing solutions are used for paper production to meet the industry requirements.

## Sample preparation

All water samples should be filtered through a filter with 0.2 µm pore size. As wastewaters can contain considerable amounts of organic substances, an additional sample preparation using an IC-$C_{18}$ sample preparation cartridge – 0.5 mL (6.1012.050) is recommended.

## Analysis

Quantitation is carried out by means of an external multipoint calibration covering the range concerned. To obtain the required concentrations, the above-mentioned standards are diluted with ultrapure water. To stabilize the diluted sulfite standards, formaldehyde (0.0037%) or 2-propanol (1%) must be added.
These four sulfur species are analyzed easily by conductivity detection after suppression. If sulfate is not of interest or higher selectivity is required, UV/VIS detection is an option.

### a) Sulfite, sulfate, thiocyanate, and thiosulfate in scrubber solution with conductivity detection after sequential suppression

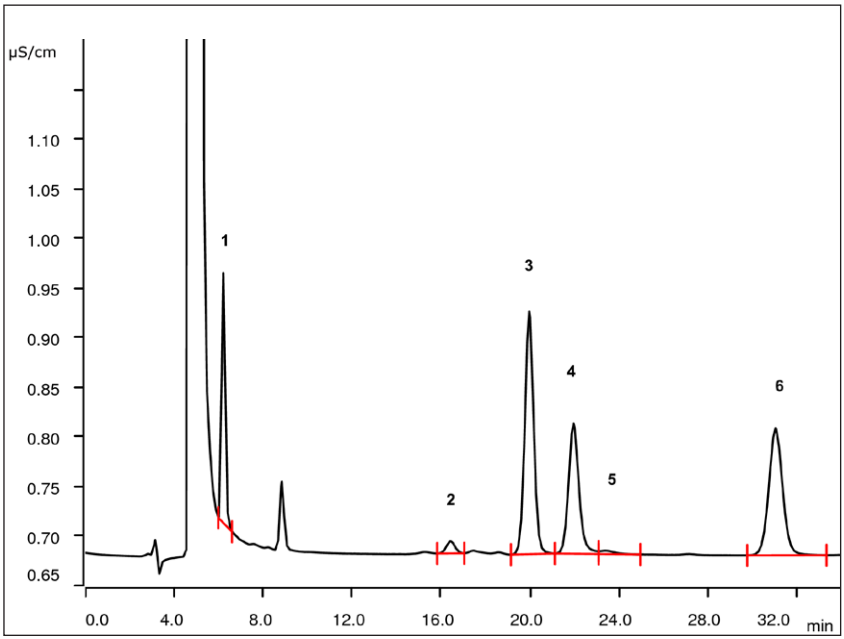



*Figure 40: Sulfur species in a scrubber solution from a gas sweetening process.*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/L] |
|---|---|---|---|
| 1 | Chloride | 6.2 | 22.4 |
| 2 | Sulfite | 16.4 | 38.4 |
| 3 | Sulfate | 20.0 | 65.8 |
| 4 | Oxalate | 21.9 | 40.8 |
| 5 | Thiocyanate | 23.4 | 17.6 |
| 6 | Thiosulfate | 31.0 | 69.8 |

| | |
|---|---|
| Instrument | Compact or Professional IC instruments |
| Column | 6.1006.520 Metrosep A Supp 5 - 150/4.0 |
| Eluent | c($Na_2CO_3$) = 2.5 mmol/L (CAS 497-19-8)<br>c($NaHCO_3$) = 0.8 mmol/L (CAS 144-55-8)<br>c(acetone) = 13% v/v (CAS 67-64-1) |
| Suppressor regenerant | c($H_2SO_4$) = 100 mmol/L (CAS 7664-93-9) |
| Suppressor rinsing | STREAM |
| Flow | 0.7 mL/min |
| Injection volume | 10 µL |
| Column temperature | 30 °C |

**b) Sulfite, thiocyanate, and thiosulfate in a mining leachate with UV/VIS detection**

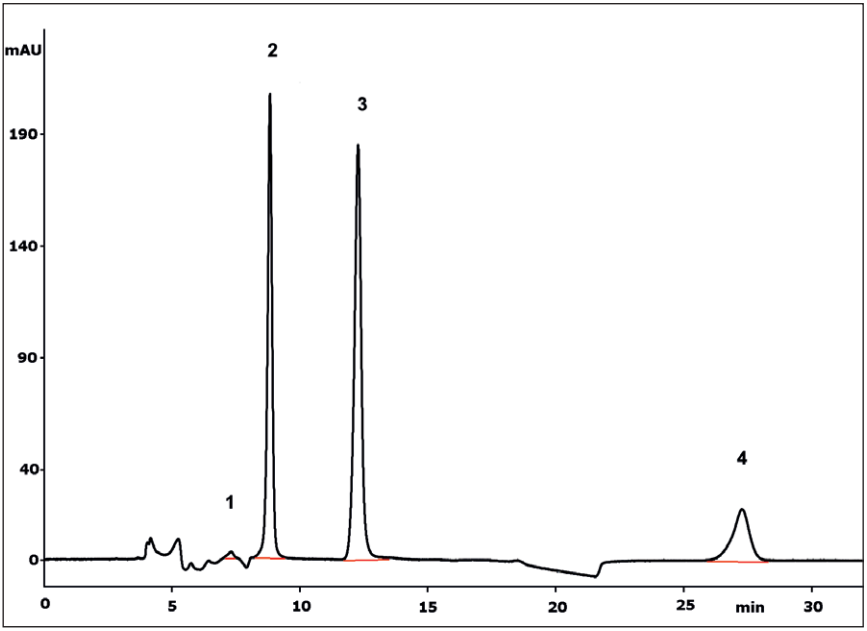



*Figure 41: Sulfite, thiocyanate, and thiosulfate in a mining leachate.*

| Peak no. | Component | $t_R$ [min] | Conc. [g/L] |
|---|---|---|---|
| 1 | Sulfite | 5.1 | 0.994 |
| 2 | Thiosulfate | 6.0 | 2.314 |
| 3 | Thiocyanate | 9.0 | 2.000 |
| 4 | Tetrathionate | 14.3 | 8.066 |

| | |
|---|---|
| Instrument | Compact or Professional IC instruments with a UV/VIS detector |
| Column | 6.1006.530 Metrosep A Supp 5 - 250/4.0 |
| Eluent | c(NaCl) = 10 mmol/L (CAS 7601-89-0)<br>c($NaHCO_3$) = 1.0 mmol/L (CAS 144-55-8) |
| Flow | 0.7 mL/min |
| Injection volume | 20 µL |
| Column temperature | 35 °C |
| Wavelength | 215 nm |

## Metrohm literature

IC Application Note AN-S-144: «Heat stable salts in scrubber solutions»

IC Application Note AN-S-155: «Sulfite, oxalate and thiosulfate besides standard anions in process water of paper industry»

IC Application Note AN-S-248: «Sulfur species in process water of the paper industry by simultaneous conductivity and UV detection»

IC Application Note AN-U-073: «Sulfur speciation in mining leachate by ion chromatography appling a perchlorate eluent and UV/VIS detection»

# 4.20 Organic and weak acids with IC



## General remarks

The determination of weak organic acids such as acetic acid or propionic acid is carried out using ion exclusion chromatography. The completely dissociated acids are not retained on the stationary phase by Donnan exclusion and therefore elute within the dead time.

The determination of short-chain organic acids is applied for example in wastewater analysis. Compared to gas chromatography, which is also used for such analyses but requiring a sample derivatization step, ion-exclusion chromatography has the advantage of requiring significantly less sample preparation effort. Besides organic acids also anions of medium weak to weak inorganic acids (fluoride, borate, silicate, carbonic acid, etc.) may be separated and determined.

The determination of the organic acids after their separation on an ion-exclusion column can be done with direct conductivity measurement or after inverse suppression with e.g., lithium.

## Sample preparation

All water samples should be filtered through a filter with 0.2 µm pore size. It is recommended to pass the samples through a $H^+$ cartridge (6.1012.010) to neutralize them and to eliminate the divalent cations.

## Analysis

The determination is carried out by means of an external multipoint calibration covering the concentration range concerned. To obtain the required concentrations, the above-mentioned standards are diluted with ultrapure water. Also intelligent Partial Loop Injection Technique as well as intelligent Pick-up Technique may be applied.

## a) Organic acids in process water with inverse suppression

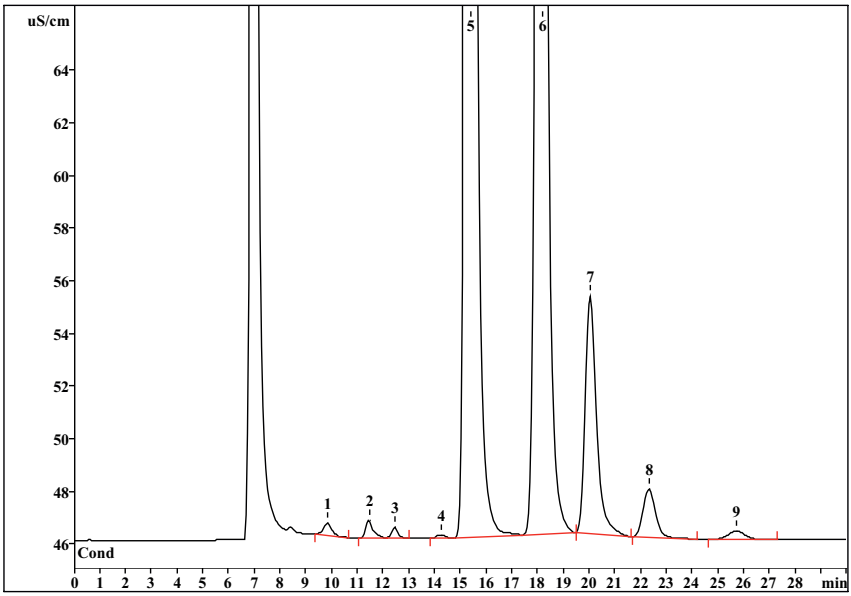



*Figure 42: Organic acids in process water*

| Peak no. | Component | $t_R$ [min] | Conc. [g/L] |
|---|---|---|---|
| 1 | not identified | 9.85 | – |
| 2 | Glycolic acid | 11.44 | 3.30 |
| 3 | Formic acid | 12.45 | 0.97 |
| 4 | Glutaric acid | 14.23 | 0.93 |
| 5 | Acetic acid | 15.41 | 724 |
| 6 | Propionic acid | 18.14 | 530 |
| 7 | Carbonate | 20.04 | n.q. |
| 8 | Butyric acid | 22.32 | 24.2 |
| 9 | Sulfide | 25.73 | n.q. |

n.q. = not quantified

| | |
|---|---|
| Instrument | Compact or Professional IC instruments |
| Column | 6.1006.520 Metrosep Organic Acids - 250/7.8 |
| Eluent | c($H_2SO_4$) = 0.5 mmol/L (CAS 7664-93-9) |
| Suppressor regenerant | c(LiCl) = 10 mmol/L (CAS 7447-41-8) |
| Suppressor rinsing | Ultrapure water |
| Flow | 0.5 mL/min |
| Injection volume | 20 µL |
| Column temperature | ambient |

## b) Inorganic acid anions in fluorinated drinking water

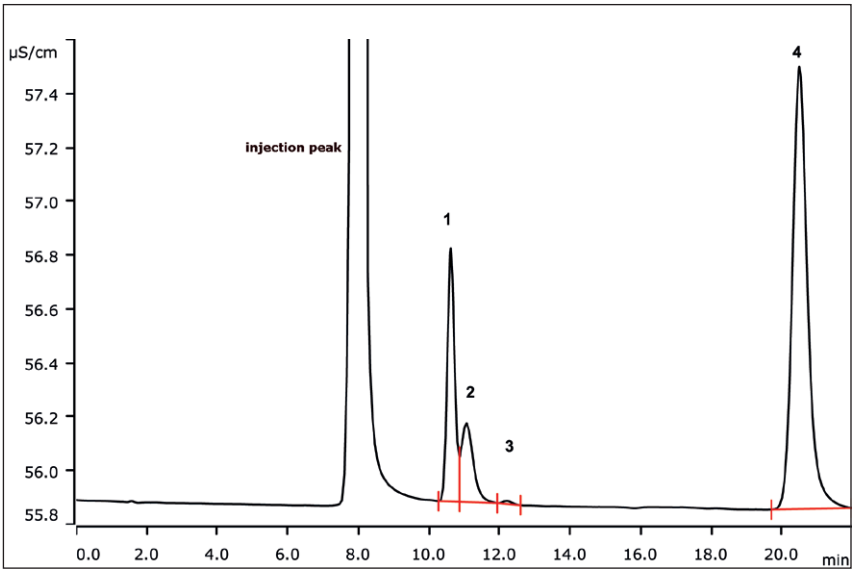



*Figure 43: Hydrofluoric acid, boric acid, and silicic acid in water*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/L] |
|---|---|---|---|
| 1 | Fluoride | 10.6 | n.q. |
| 2 | unknown | 11.1 | – |
| 3 | Borate | 12.2 | 0.012 |
| 4 | Silicate | 20.5 | n.q. |

n.q. = not quantified

| | |
|---|---|
| Instrument | Compact or Professional IC instruments |
| Column | 6.1006.520 Metrosep Organic Acids - 250/7.8 |
| Eluent | $c(H_2SO_4)$ = 0.3 mmol/L (CAS 7664-93-9)<br>c(mannnitol) = 100 mmol/L (CAS 69-65-8) |
| Suppressor regenerant | c(LiCl) = 10 mmol/L (CAS 7447-41-8) |
| Suppressor rinsing | Ultrapure water |
| Flow | 0.5 mL/min |
| Injection volume | 20 µL |
| Column temperature | 30 °C |

## Metrohm literature

IC Application Note AN-O-02: «Six organic acids in a process water of the paper industry»

IC Application Note AN-O-034: «Aliphatic monocarboxylic acids in produced water using IC/MS coupling»

IC Application Note AN-O-039: «Organic acids in samples from biogas production by ion-exclusion chromatography after dialysis»

IC Application Note AN-O-042: «Organic acids in organic compounds using conductivity detection after inverse suppression»

IC Application Note AN-O-043: «Carbonate in caustic soda with conductivity detection following inverse suppression»

IC Application Note AN-O-044: «Boron in fluorinated drinking water by ion-exclusion chromatography with inverse suppression»

IC Application Note AN-O-046: «Organic acids in gas sweetening solvent by ion-exclusion chromatography with inverse suppression»

# 4.21 VA methods: Introduction



Metrohm has been dealing with voltammetric water analysis for many years. Progress has been remarkable since the introduction of the Polarecord E 261 in 1957. This is true for instrument technology as well as for keeping pace with general trends: lower detection limits, higher precision, validation, etc. Today, metal traces down to the ng/L level can be determined using voltammetric methods. Further advantages of voltammetric methods are species analyses and – last not least – the relatively modest acquisition and running costs. Traditionally voltammetric determinations were usually carried out on the mercury drop electrode as working electrode. In recent years new reliable combined, mercury-free sensors like the scTRACE Gold were developed that made voltammetric determinations easier and safer.

The important parameters are the type of metal ions, their concentration, and the type of water to be analyzed (wastewater, groundwater, drinking water, lake water, river water, seawater, or rainwater). Concentrations ranging from ng/L to mg/L can be determined. When analyzing surface waters, species analyses are very important to answer the question: «Are the metals present as free ions or as metal complexes?» Voltammetry is an elegant, specific, economic, and quite modern tool that allows to answer this question. The examples given here cannot show the whole spectrum of voltammetric applications but restrict themselves to analysis methods for determining the total metal content at the trace level.

Voltammetric methods also allow to determine other species that occur in water at trace levels such as nitrophenols, TNT, iodide/iodate, thiosulfate, organo-tin compounds, etc.

## Metrohm Application Bulletins

This following overview shows a selection of the currently existing Metrohm Application Bulletins that describe VA methods for water analysis. The documents can be downloaded free of charge from the Metrohm website:

Application Bulletin AB-036: «Half wave potentials of metal ions for the determination by polarography»

Application Bulletin AB-074: «Determination of antimony, bismuth, and copper by anodic stripping voltammetry»

Application Bulletin AB-110: «Determination of free cyanide by polarography»

Application Bulletin AB-113: «Determination of cadmium, lead and copper in foodstuffs, waste water and sewage sludge by anodic stripping voltammetry after digestion»

Application Bulletin AB-114: «Determination of copper, nickel, cobalt, zinc, and iron in a single operation by polarography»

Application Bulletin AB-116: «Determination of chromium in small quantities by polarography and adsorptive stripping voltammetry after digestion»

Application Bulletin AB-117: «Determination of selenium by cathodic stripping voltammetry»

Application Bulletin AB-123: «Determination of manganese in water samples by anodic stripping voltammetry»

Application Bulletin AB-146: «Determination of trace amounts of molybdenum (or tungsten) in water by polarography»

Application Bulletin AB-176: «Determination of lead and tin by anodic stripping voltammetry»

Application Bulletin AB-199: «Determination of sulfide and sulfite by polarography»

Application Bulletin AB-207: «Determination of silver by anodic stripping voltammetry at the carbon RDE»

Application Bulletin AB-220: «Determination of platinum and rhodium in the ultratrace range by adsorptive stripping voltammetry»

Application Bulletin AB-231: «Determination of zinc, cadmium, lead, copper, thallium, nickel and cobalt in watersamples by anodic and adsorptive stripping voltammetry according to DIN 38406-16»

Application Bulletin AB-241: «Determination of cadmium and lead by anodic stripping voltammetry at a mercury film electrode»

Application Bulletin AB-254: «Determination of zinc, cadmium and lead by anodic stripping voltammetry at a mercury film electrode»

Application Bulletin AB-266: «Determination of titanium by adsorptive stripping voltammetry»

Application Bulletin AB-317: «Determination of iron in the µg/L-range by polarography»

Application Bulletin AB-416: «Determination of arsenic in water with the scTRACE Gold»

Application Bulletin AB-422: «Determination of mercury in water with the scTRACE Gold»

Application Bulletin AB-429: «Determination of copper in water with the scTRACE Gold»

Application Bulletin AB-430: «Determination of uranium by adsorptive stripping voltammetry according to DIN 38406-17»

Application Bulletin AB-431:«Determination of iron, copper and vanadium by adsorptive stripping voltammetry»

Application Bulletin AB-433: «Determination of lead in water with the scTRACE Gold modified with a silver film»

# 4.22 Chromate/dichromate – Cr(VI) with VA using the Multi-Mode Electrode pro



## General remarks

Chromium is considered as an essential trace element. Only the compounds of hexavalent chromium are toxic because of their oxidative effect on cell constituents. Cr(VI) has mutagenic and carcinogenic properties and can cause skin allergies. It is therefore important to know the chromium content of the different types of water.

The chromium content of surface waters ranges from 0.2 to 20 µg/L. The requirements for drinking water depend on local legislation, the limiting values ranging from <1 µg/L Cr(VI) to 50 µg/L total chromium.

Two methods will be described:

- Polarography for chromium concentrations >10 µg/L
- Adsorptive stripping voltammetry for chromium concentrations from 0.02 to 1.5 µg/L

Using the described VA methods only Cr(VI) gives reproducible signals. The direct determination of Cr(VI) is possible in sample with low organic contamination without sample preparation. For the determination of total chromium all samples have to be oxidized.

## Instruments

VA instrument with Multi-Mode Electrode pro

UV Digester

## Sample preparation

### Digestion of waters with low to moderate load of organic substances with the UV Digester

Add 10 µL hydrochloric acid (w(HCl) = 30%) and 50 µL $H_2O_2$ solution (w($H_2O_2$) = 30%) to 10 mL of the sample solution and treat in the 909 UV Digester during 90 min at 90 °C.

### Oxidation of Cr(III) to Cr(VI) in the UV Digester

To oxidize Cr(III) to Cr(VI) adjust the sample to a pH value of 4–6. Add another 50 µL $H_2O_2$ and treat the sample for another 30 min at 90 °C in the UV Digester.



### Digestion of wastewater with high content of organic substances

This type of wastewater requires wet acid digestion (e.g., with $H_2SO_4$ / $H_2O_2$).

### Oxidation of Cr(III) to Cr(VI) with chemical oxidation

Oxidation of Cr(III) to Cr(VI): After the digested solution has cooled down, add 10 mL ultrapure water and 2 drops of c($KMnO_4$) = 0.02 mol/L and heat to boiling. Dropwise add permanganate solution until the pink color remains. Keep the solution boiling for approx. 5 min while maintaining the total volume constant by adding small amounts of ultrapure water. Before it has cooled down, adjust the solution to pH = 5–9 with KOH solution. Rinse the solution into the polarographic vessel with ultrapure water.

## Polarographic method

## Reagents

Use only reagents for trace analysis (e. g., Merck Suprapur, Honeywell Fluka TraceSelect) and ultrapure water (resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)).

- Potassium hydroxide solution, for trace analysis, w(KOH) = 30%, CAS 1310-58-3
- Ammonia solution, for trace analysis, w($NH_3$) = 25%, CAS 1336-21-6
- Acetic acid, for trace analysis, w($CH_3COOH$) = 96–100%, CAS 64-19-7
- Ethylene diamine, for analysis, CAS 107-15-3
- Cr(VI) standard stock solution: β(Cr(VI)) = 1 g/L. The solution is commercially available
- Cr(VI) standard solution: β(Cr(VI)) = 10 mg/L in ultrapure water

## Analysis

Add 10 mL sample or digested solution into the polarographic vessel. Add 10 µL ethylene diamine, 150 µL acetic acid and 200 µL ammonia solution. If necessary adjust the pH value to approx. 6.8 ± 0.1 by adding KOH solution or acetic acid. Deaerate with nitrogen and record the polarogram applying the following conditions:

| | |
|---|---|
| Working electrode | SMDE |
| Mode | DP – Differential Pulse |
| Start potential | 0.1 V |
| End potential | –0.17 V |
| Potential step | 4 mV |
| Potential step time | 0.6 s |
| Sweep rate | 0.0067 V/s |
| Peak potential Cr(VI) | approx. –0.04 V |

The Cr(VI) concentration in the sample is determined by means of the standard addition method: three additions of 100 µL Cr(VI) standard solution, β(Cr(VI)) = 10 mg/L.

## Example

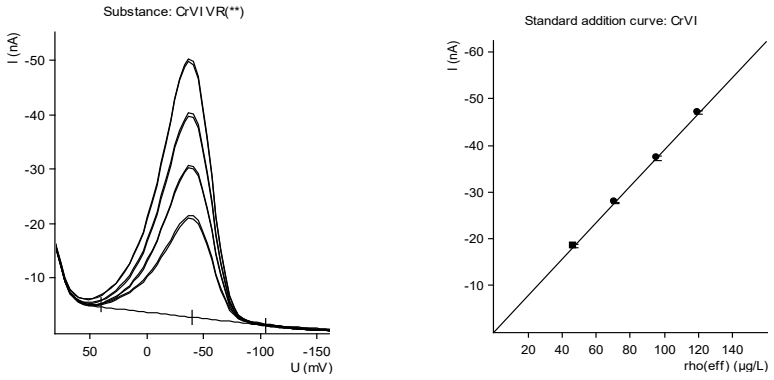



*Figure 44: Chromium in wastewater: Voltammograms and standard addition curve*

The concentration of chromium in the wastewater sample is 47.7 µg/L.

## Adsorptive stripping voltammetric method

## Reagents

Use only reagents for trace analysis (e.g., Merck Suprapur, Honeywell Fluka TraceSelect) and ultrapure water (resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)).

- Sodium hydroxide solution, for trace analysis, w(NaOH) = 30%, CAS 1310-73-2
- Supporting electrolyte: c(sodium acetate) = 0.2 mol/L + c(diethylenetriamine pentaacetic acid (DTPA)) = 0.05 mol/L + c($NaNO_3$) = 2.5 mol/L in ultrapure water.
- Cr(VI) standard stock solution: β(Cr(VI)) = 1 g/L. The solution is commercially available.
- Cr(VI) standard solution: β(Cr(VI)) = 100 mg/L in ultrapure water. Prepare the soltion fresh daily.
- Cr(VI) standard solution: β(Cr(VI)) = 0.02 mg/L in ultrapure water. Prepare the solution fresh daily.

## Analysis

Transfer 10 mL sample or digested solution (or an aliquot) into the polarographic vessel and add 5 mL supporting electrolyte. Adjust the pH value of the mixture to 6.2 ± 0.1 with NaOH solution and record the stripping voltammogram applying the following conditions:

| | |
|---|---|
| Working electrode | HMDE |
| Mode | DP – Differential Pulse |
| Deposition potential | –1.0 V |
| Deposition time | 60 s |
| Start potential | –1.0 V |
| End potential | –1.45 V |
| Peak potential Cr(VI) | approx. –1.25 V |

The Cr(VI) concentration in the sample is determined by means of the standard addition method: two additions of 100 µL Cr(VI) standard solution, β(Cr(VI)) = 0.02 mg/L. A blank value is also determined separately.

## Example

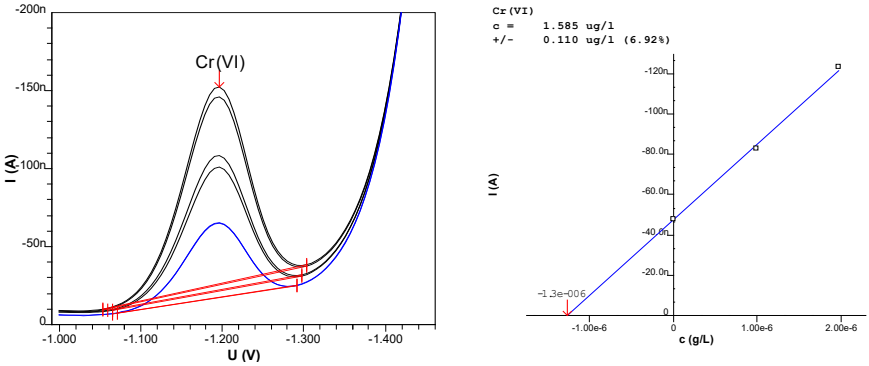



*Figure 45: Chromium in seawater: Voltammograms and standard addition curve*

The concentration of chromium in the seawater sample is 1.6 µg/L.

### Metrohm literature

Application Bulletin AB-116: «Determination of chromium in small quantities by polarography and adsorptive stripping voltammetry after digestion»

# 4.23 Cyanide with VA using the Multi-Mode Electrode pro

## General remarks

The determination of cyanides in waters (e.g., landfill leachate, electroplating wastewater before and after detoxification) is highly important. Cyanide concentrations as low as 50 µg/L can be lethal for fish. Depending on the legislation for drinking water, the maximum allowable cyanide concentrations vary between 50 and 100 µg/L. The described polarographic method is suitable for samples with cyanide concentrations between 0.01–10 mg/L.

## Instruments

VA instrument with Multi-Mode Electrode pro



## Reagents

Use only reagents for trace analysis (e.g. Merck Suprapur, Honeywell Fluka TraceSelect) and ultrapure water (resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)).

- Supporting electrolyte: $c(H_3BO_3)$ = 0.2 mol/L + c(KOH) = 0.17 mol/L in ultrapure water, adjusted to pH 10.2.
- Cyanide standard stock solution: $\beta(CN^-)$ = 1 g/L in c(KOH) = 0.01 mol/L.
- Cyanide standard solution: $\beta(CN^-)$ = 100 mg/L in c(KOH) = 0.01 mol/L. The solution has to be prepared daily.

## Sample preparation

Only free cyanide can be determined in the samples directly without sample preparation. For the determination of the total cyanide content the cyanide has to be separated by distillation, e.g. according to DIN 38405-13. For voltammetric determinations it is recommended to use the supporting electrolyte as absorption solution instead of NaOH.

## Analysis

Add 10 mL (diluted) sample solution and 10 mL supporting electrolyte into the polarographic vessel. Deaerate with nitrogen and record the polarogram applying the following conditions:

| | |
|---|---|
| Working electrode | DME |
| Mode | DP – Differential Pulse |
| Start potential | –0.05 V |
| End potential | –0.4 V |
| Peak potential $CN^-$ | approx. –0.22 V |

The cyanide concentration in the sample is determined by means of the standard addition method: 2 additions of 50 µL cyanide standard solution, $\beta(CN^-)$ = 100 mg/L.

## Example



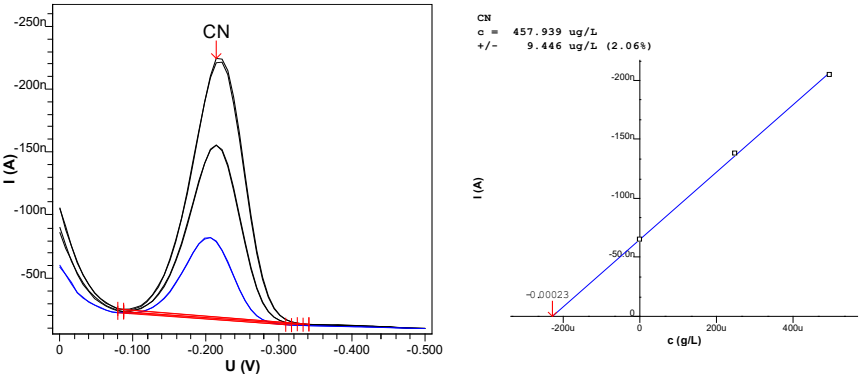



*Figure 46: Cyanide in wastewater: Voltammograms and standard addition curve*

The concentration of cyanide in the wastewater sample is 0.46 mg/L.

### Metrohm literature

Application Bulletin AB-110: «Determination of free cyanide by polarography»

# 4.24 Sulfide and hydrogen sulfide with VA using the Multi-Mode Electrode pro

## General remarks

Sulfides and/or $H_2S$ can be present in reductive groundwater, in landfill leachates and, under anaerobic conditions, at the bottom of surface waters. Sulfides are volatile and easily oxidized by atmospheric oxygen. Care has therefore to be taken during sampling: the samples must be made alkaline with NaOH and be well sealed for transport.

Sulfides can be easily determined with polarography. The method is suitable for contents ranging from 0.02 to 1.5 mg/L.

## Instruments

VA instrument with Multi-Mode Electrode pro



## Reagents

Use only reagents for trace analysis (e.g., Merck Suprapur, Honeywell Fluka TraceSelect) and ultrapure water (resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)).

- Sodium hydroxide solution: c(NaOH) = 0.1 mol/L in ultrapure water
- Sulfide standard stock solution: $\beta(S^{2-})$ = 1 g/L in oxygen-free sodium hydroxide solution c(NaOH) = 0.1 mol/L. Store the resulting solution in a sealed dark bottle in the refrigerator. The solution has a storage life of approx. 1 week.
- Sulfide standard solution: $\beta(S^{2-})$ = 5 mg/L in oxygen-free sodium hydroxide solution c(NaOH) = 0.1 mol/L. Prepare the solution fresh daily.

## Analysis

Deaerate 10 mL sodium hydroxide solution (c(NaOH) = 0.1 mol/L) for 5 min with nitrogen in the measuring vessel. Add 10 mL (diluted) sample and mix by purging with nitrogen. Then record the polarogram applying the following conditions:

| | |
|---|---|
| Working electrode | SMDE |
| Mode | DP – Differential Pulse |
| Start potential | –0.5 V |
| Stop potential | –0.9 V |
| Peak potential sulfide | approx. –0.75 V |

The sulfide concentration in the sample is determined by means of the standard addition method: 2 additions of 100 µL sulfide standard solution, $\beta(S^{2-})$ = 5 mg/L.

## Example



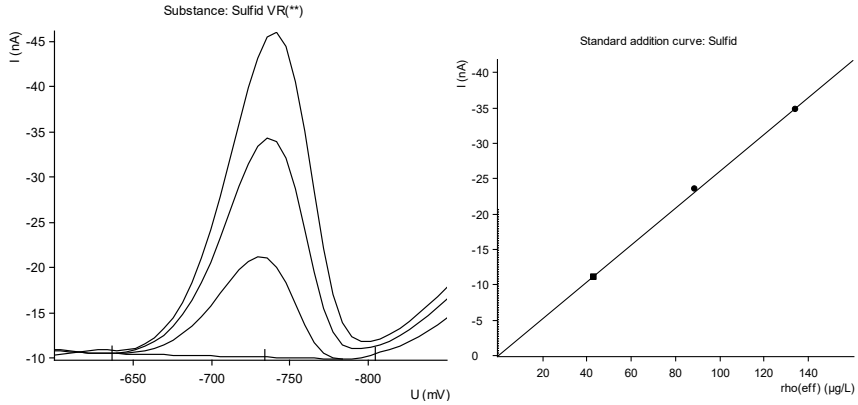



*Figure 47: Sulfide in spiked groundwater: Voltammograms and standard addition curve*

The concentration of sulfide in the spiked groundwater sample is 475 µg/L.

### Literature

Metrohm Application Bulletin AB-199: «Determination of sulfide and sulfite by polarography»

He, Y., Zheng, Y., Locke, D.C. Differential pulse cathodic stripping voltammetric determination of nanomolar levels of dissolved sulfide applicable to field analysis of groundwater. Anal.Chim. Acta 459, (2002) 209-217

# 4.25 Sulfite with VA using the Multi-Mode Electrode pro

## General remarks

Sulfite only occurs in wastewaters, for example of the photo and the paper industries – it is not found in industrial water, groundwater, and surface water. Ambient oxygen rapidly oxidizes sulfite to sulfate, especially in alkaline solution. This has to be taken into account during sampling and sample treatment.

The method described here allows to determine, in a simple manner, sulfite concentrations ranging from 1 mg/L to approx. 10 mg/L by means of polarography.

## Instruments

VA instrument with Multi-Mode Electrode pro



## Reagents

Use only reagents for trace analysis (e.g., Merck Suprapur, Honeywell Fluka TraceSelect) and ultrapure water (resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)).

- Acetate buffer: c(NaOH) = 0.2 mol/L + $c(CH_3COOH)$ = 0.4 mol/L in ultrapure water
- Sulfite standard stock solution: $\beta(SO_3^{2-})$ = 1 g/L in oxygen-free ultrapure water. The solution has a shelf life of approx. 1 week.
- Sulfite standard solution: $\beta(SO_3^{2-})$ = 100 mg/L in oxygen-free ultrapure water and mix. Prepare the solution fresh daily.

## Analysis

Deaerate 10 mL acetate buffer for 5 min with nitrogen in the measuring vessel. Add 10 mL (diluted) sample and mix manually (do not purge with nitrogen). Record the polarogram applying the following conditions:

| | |
|---|---|
| Working electrode | SMDE |
| Mode | DP – Differential Pulse |
| Start potential | –0.4 V |
| End potential | –0.85 V |
| Peak potential sulfite | approx. –0.61 V |

The sulfite concentration in the sample is determined by means of the standard addition method: 2 additions of 20 µL sulfite standard solution, $\beta(SO_3^{2-})$ = 100 mg/L.

## Remarks

In the presence of sulfide a peak at approx. –0.45 V can be observed.
In the presence of thiosulfate two overlapping peaks between –0.14 V and –0.28 V can be observed.

## Example

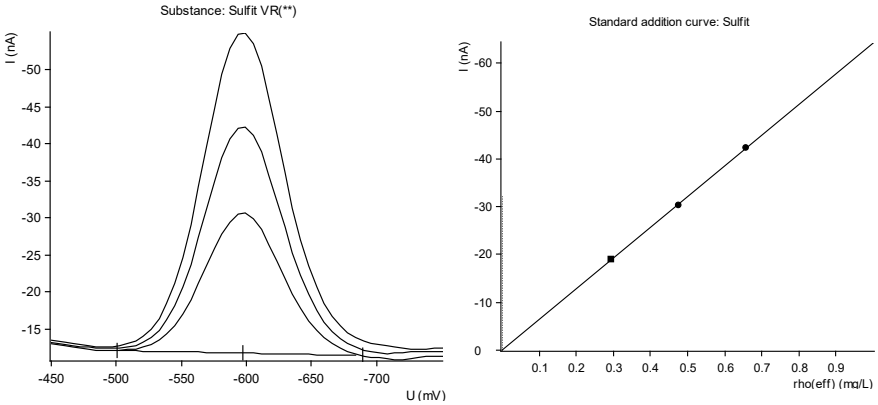



*Figure 48: Sulfite in wastewater: Voltammograms and standard addition curve*

The concentration of sulfite in the wastewater sample is 3.2 mg/L.

### Metrohm literature

Metrohm Application Bulletin AB-199: «Determination of sulfide and sulfite by polarography»

# 5 Cations



## 5.1 Calcium and magnesium by titration

Please find the detailed procedures for these determinations in the chapter «Water hardness» on page 27.

## 5.2 Ammonia by ion measurement

### General remarks

Nitrogen is an important nutrient for most organisms. Ammonia is one of the forms in which nitrogen can be present. Ammonia is highly soluble in water, where it form ammonium ions. Ammonia in water may occur from waste streams or anaerobic decomposition of nitrogen containing substances.

Although the known photometric methods for the determination of ammonia/ammonium are accurate, they require a considerable amount of time (Nessler method 30 min, indophenol method 90 min reaction time). A further disadvantage of these methods is that only clear solutions can be measured. Opaque solutions must first be clarified by time-consuming procedures.

These problems do not exist with the ion-selective ammonia electrode. Measurements can be easily performed in wastewater, liquid fertilizer, and urine as well as in soil extracts.
Especially for fresh water and waste water samples several standards, such as ISO 6778, US EPA 350.2, US EPA 350.3, and ASTM D1426, describe the analysis of ammonium by ion measurement.

This section describes the determination according to US EPA 350.3 and ASTM D1426 for an ammonia content in the range of 0.03 to 1400 mg/L ammonia in drinking, surface, and saline water as well as domestic and industrial wastes. Additionally the determination according to ISO 6778 for an ammonia content of 0.2 to 50 mg/L for raw water, wastewater, and sewage is described.

## Instrument and relevant accessories

- Ion meter or instrument with ion measurement mode
- Stirrer
- 6.0506.100 $NH_3$-selective electrode for low concentration (concentrations lower than $10^{-2}$ mol/L)
- 6.0506.150 $NH_3$-selective electrode for high concentration (concentrations higher than $10^{-4}$ mol/L)



## Reagents

- Ionic strength adjuster (ISA) for low ammonia concentrations: c(NaOH) = 10 mol/L (CAS 1310-73-2)
- ISA for high ammonia concentrations: c(NaOH) = 1 mol/L (CAS 1310-73-2) and c(EDTA) = 0.1 mol/L (CAS 6381-92-6)
- Diluted electrolyte for low ammonia concentrations: The Metrohm measuring electrolyte 6.2316.030 is diluted 1:9 with deionized water.
- Hydrochloric acid, c(HCl) = 1 mol/L (CAS 7647-01-0)

## Sample preparation

For purpose of storage, acidulate the sample with hydrochloric acid to approx. pH 6 (approx. 0.5 mL c(HCl) = 1 mol/L per liter of sample) and store it in well-sealed vessels.

## Calibration

Carry out a calibration with at least 3 different standard concentrations. Use the same ratio of calibration standard to ISA as for the sample measurement. In between each measurement, condition the electrode in deionized water for 10 min.

## Analysis

### Wastewater with high ammonia concentration according to ISO 6778

Transfer 50 mL wastewater into a plastic beaker, add 5 mL ISA solution for high ammonia concentrations, and immediately start the measurement. Between measurements, rinse the sensor with deionized water and then condition it in deionized water for exactly 10 min.

### Water with low ammonia concentration according to US EPA 350.3 and ASTM D1426

Transfer 20 mL water into a plastic beaker, add 1 mL ISA solution for low ammonia concentrations, and immediately start the measurement. Between measurements, rinse the sensor with deionized water and then condition it in deionized water for exactly 10 min.

## Parameters

| | |
|---|---|
| Mode | MEAS CONC |
| Stirring rate | 8 |
| Signal drift | 0.5 mV/min |
| Min. waiting time | 10 s |
| Max. waiting time | 600 s |
| Measuring interval | 2 s |

## Remarks

- If low concentrations of ammonia are measured, the electrolyte of the outer compartment is diluted 1:9 with deionized water.
- Condition the electrode prior to measurement in an ammonia-free pH 4 buffer solution.
- The standards US EPA 350.2, US EPA 350.3, and ASTM D1426 differ from the here described procedure in such a way that 100 mL sample are used instead of the 20 mL.

- For low concentrations, it is important to prepare the standards as shortly as possible before measurement. Otherwise the calibration curve will not be linear and the measurement becomes faulty.
- After the addition of NaOH, the pH value must be at least 12. Acidic samples must be neutralized before the addition of NaOH. After addition of NaOH, the measurement must take place immediately. Otherwise, the ammonia evaporates leading to too low results.
- For more tips and tricks on ammonia determination by ion measurement please refer to Metrohm Application Bulletin AB-133.



## Example

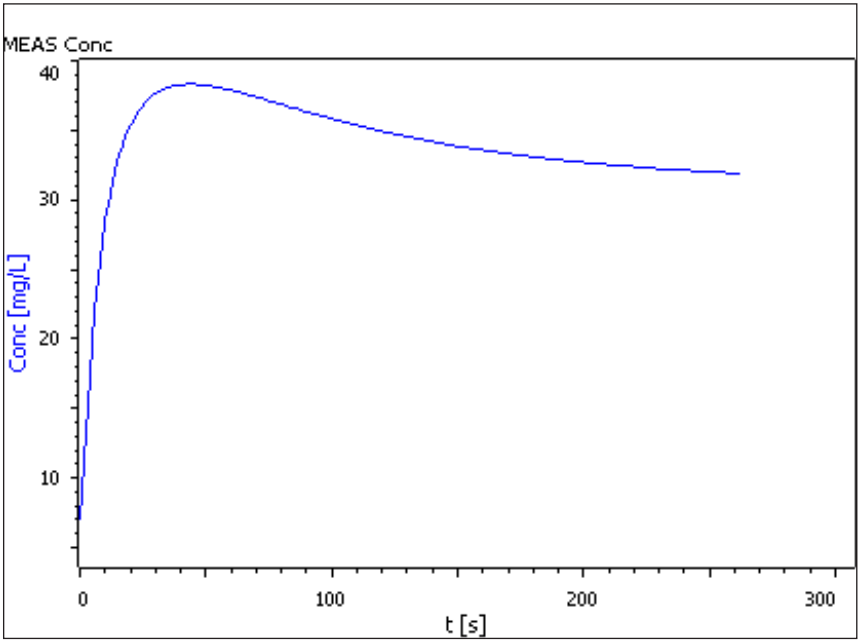



*Figure 49:Measuring curve for the ammonia determination in wastewater.*

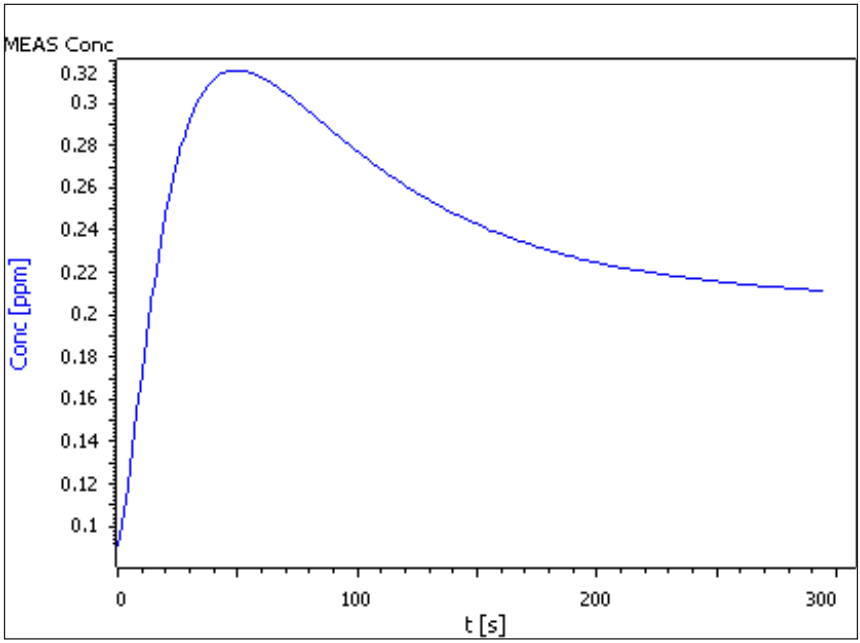



*Figure 50: Measuring curve for the ammonia determination in water with a mass concentration of β($NH_4$) = 0.25 mg/L.*

### Metrohm literature

Application Bulletin AB-133: «Determination of ammonia with the ion-selective electrode – Tips and tricks for a reliable determination according to common standards»

Application Note AN-I-012: «Automated calibration of the NH3 ISE for low ammonia concentrations»

# 5.3 Cation determination with IC

## General remarks

The determination of lithium, sodium, ammonium, potassium, calcium, magnesium, barium, and strontium in different water types (drinking water, mineral water, etc.) is of paramount importance for the assessment of the water quality. The determination of these cations by means of ion chromatography is therefore the subject of various standards.

## Sample preparation

The samples have to be filtered, for example using Minisart (Sartorius) or disposable filter supports (Whatman, formerly Schleicher & Schuell) with a pore size of 0.2 µm. Even seemingly clear solutions can contain very fine particles that damage the column. The samples can be filtered automatically applying Inline Ultrafiltration. At higher concentrations it may be necessary to dilute the samples. For water samples containing a high proportion of organic substances we recommend to apply Inline dialysis as a sample preparation step that can be completely automated. The pH value of the samples should be adjusted to pH 2.5 by means of nitric acid. Metrohm offers fully automated IC systems that carry out Inline Ultrafiltration, Inline Dialysis, as well as Inline Dilution. The MISP systems (Metrohm Inline Sample Preparation) simplify and improve sample preparation significantly.



## Analysis

When working in the concentration range 10 ppb to 100 ppm, one normally injects 10–100 µL sample, which is separated on the cation exchanger column followed by conductometric detection. If lower detection limits need to be achieved, the sample volume can be increased or apply sequential cation suppression can be applied prior to the conductivity detection.

Sample preconcentration is a simple method for lowering the detection limit by several orders of magnitude. The sample loop is replaced by a preconcentration column. An increased sample volume, e.g., 10 mL, is passed over the preconcentration column, which contains essentially the same material as the separation column. This ensures that all cations contained in the sample solution to be analyzed (e.g., ultrapure water) are kept back on the column and are preconcentrated. The preconcentrated analyte ions are then brought to the separation column by the eluent flowing counter-current.

The determination is performed by means of an external calibration in the concentration range concerned. A three-point calibration is recommended for the determination of cations.

# Examples

## a) Cations in wastewater

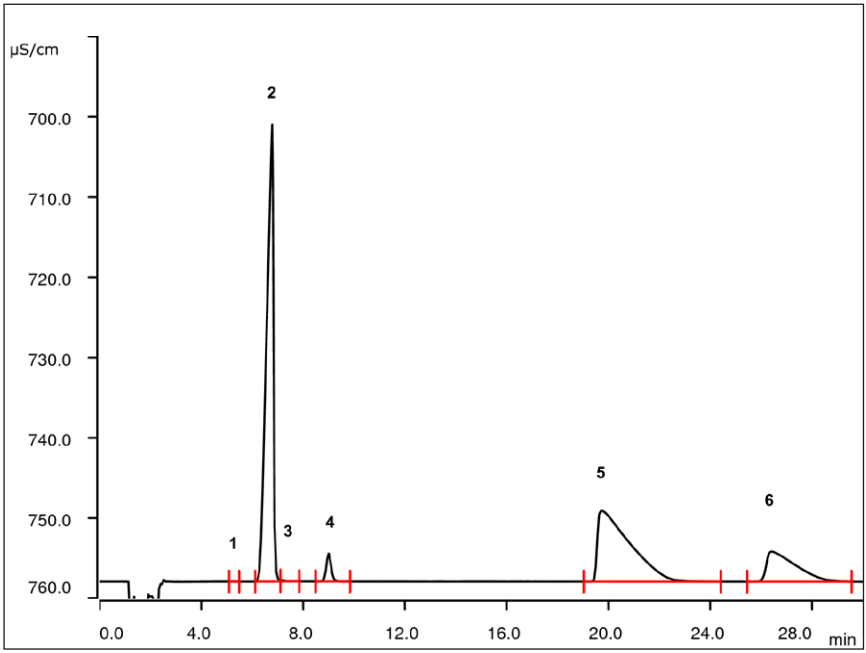



*Figure 51: Cations in wastewater applying direct conductivity detection*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/L] |
|---|---|---|---|
| 1 | Lithium | 5.3 | < 0.01 |
| 2 | Sodium | 6.8 | 70.1 |
| 3 | Ammonium | 7.2 | n.q. |
| 4 | Potassium | 9.0 | 6.03 |
| 5 | Calcium | 19.7 | 61.7 |
| 6 | Magnesium | 26.4 | 11.1 |

n.q. = not quantified

| | |
|---|---|
| Instrument | Compact or Professional IC instruments |
| Column | 6.1050.230 Metrosep C 4 - 250/4.0 |
| Eluent | c($HNO_3$) = 1.7 mmol/L (CAS 7697-37-2)<br>c(dipicolinic acid) = 0.7 mmol/L (CAS 499-83-2) |
| Flow | 0.9 mL/min |
| Injection volume | 20 µL |
| Column temperature | 45 °C |

Remark: Ammonium is only partially separated from sodium. This does not allow the quantification of ammonium. The application of the high capacity Metrosep C 6 - 250/4.0 could improve the separation and quantification of ammonium.

## b) Cations in wastewater (including manganese)

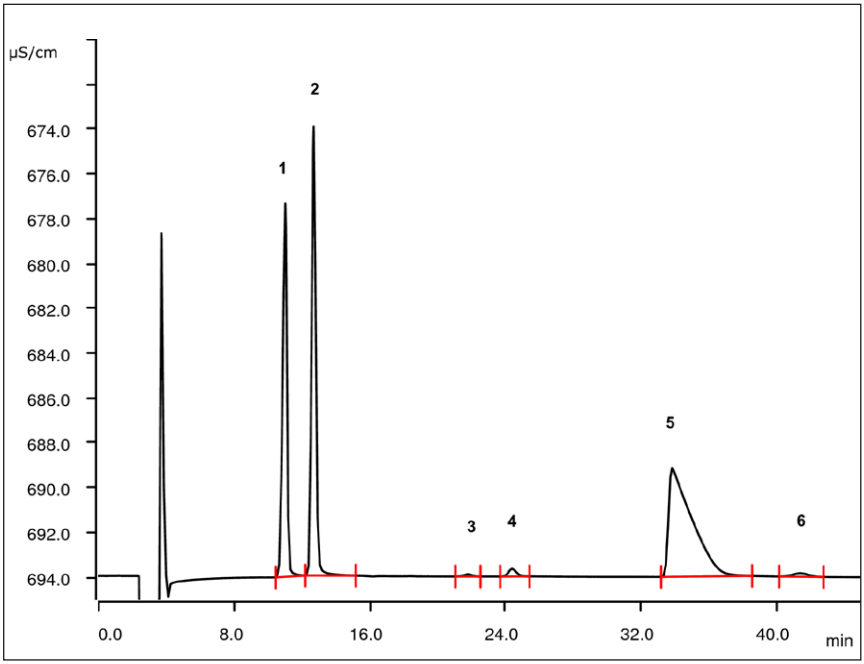



*Figure 52: Cations in wastewater including manganese*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/L] |
|---|---|---|---|
| 1 | Sodium | 11.3 | 448.4 |
| 2 | Ammonium | 12.7 | 456.1 |
| 3 | Manganese | 21.8 | 8.47 |
| 4 | Potassium | 24.4 | 33.81 |
| 5 | Calcium | 33.8 | 800.5 |
| 6 | Magnesium | 41.4 | 8.70 |

| | |
|---|---|
| Instrument | Compact or Professional IC instruments |
| Column | 6.1050.230 Metrosep C 4 - 250/2.0 |
| Eluent | c($HNO_3$) = 1.7 mmol/L (CAS 7697-37-2)<br>c(dipicolinic acid) = 0.7 mmol/L (CAS 499-83-2)<br>c(18-crown-6) = 0.5 mmol/L (CAS 17455-13-9) |
| Flow | 0.2 mL/min |
| Injection volume | 10 µL |
| Column temperature | 35 °C |
| Dilution | 1:50 |

Remark: Dipicolinic acid in the eluent complexes calcium and manganese partially. The complex is neutral and therefore shortens the retention times of divalent cations. As magnesium is almost not complexed, the other divalent cations can be eluted ahead of magnesium. 18-crown-6 builds a complex with potassium in which the positive charge is maintained. This enlarges the retention time.

## c) Cations in drinking water

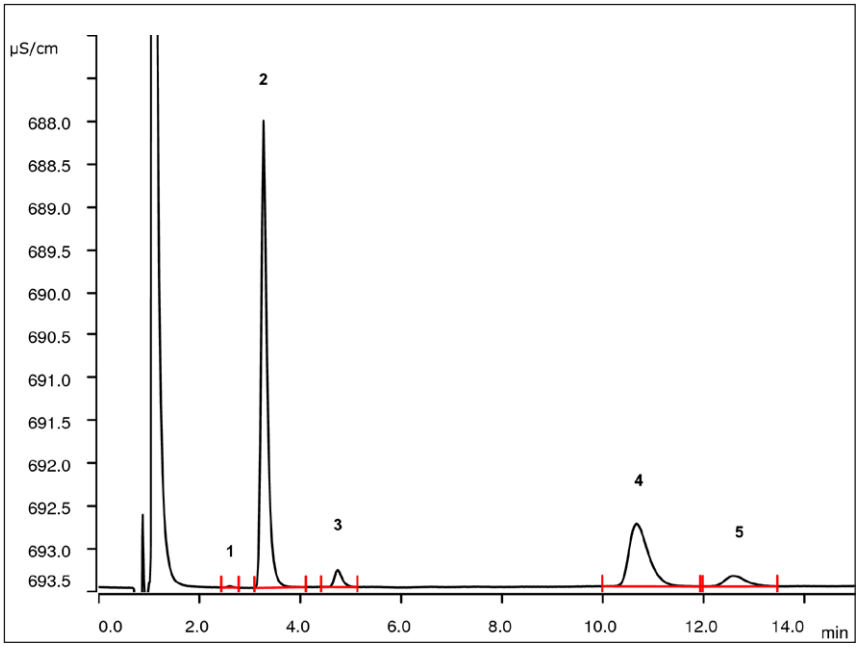



*Figure 51: Cations in drinking water*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/L] |
|---|---|---|---|
| 1 | Lithium | 2.6 | < 0.1 |
| 2 | Sodium | 3.3 | 7.47 |
| 3 | Potassium | 4.7 | 0.67 |
| 4 | Calcium | 10.7 | 3.40 |
| 5 | Magnesium | 12.6 | 0.62 |

| | |
|---|---|
| Instrument | Compact or Professional IC instruments |
| Column | 6.1050.100 Metrosep C 4 - 100/4.0 |
| Eluent | c($HNO_3$) = 1.7 mmol/L (CAS 7697-37-2)<br>c(dipicolinic acid) = 0.7 mmol/L (CAS 499-83-2) |
| Flow | 1.0 mL/min |
| Injection volume | 20 µL |
| Column temperature | 35 °C |

## d) Cations in mineral water

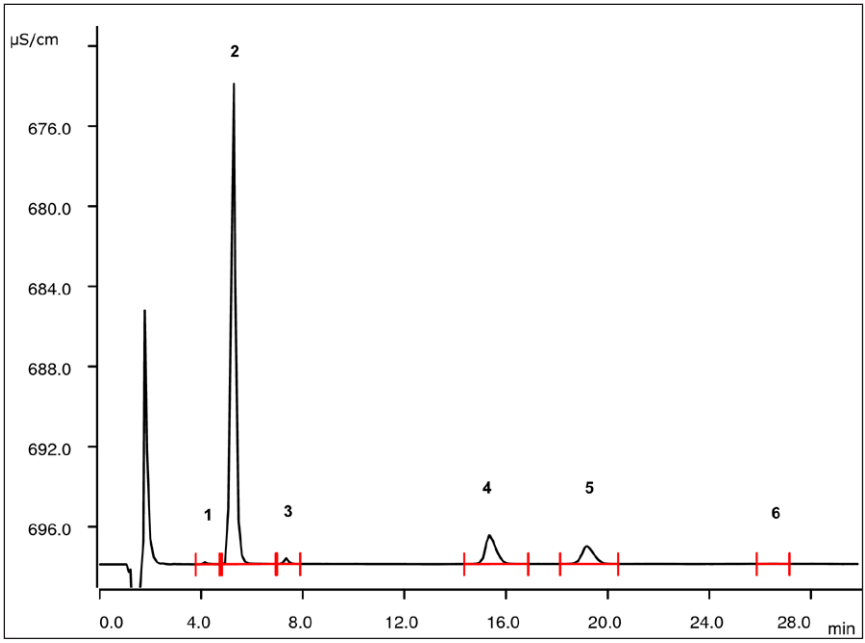



*Figure 52: Cations in mineral water*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/L] |
|---|---|---|---|
| 1 | Lithium | 4.2 | 0.36 |
| 2 | Sodium | 5.3 | 310.3 |
| 3 | Potassium | 7.3 | 15.4 |
| 4 | Calcium | 15.3 | 98.6 |
| 5 | Magnesium | 19.1 | 37.2 |
| 6 | Strontium | 26.4 | 1.51 |

| | |
|---|---|
| Instrument | Compact or Professional IC instruments |
| Column | 6.1050.420 Metrosep C 4 - 150/4.0 |
| Eluent | c($HNO_3$) = 1.7 mmol/L (CAS 7697-37-2)<br>c(dipicolinic acid) = 0.7 mmol/L (CAS 499-83-2) |
| Flow | 0.9 mL/min |
| Injection volume | 10 µL |
| Column temperature | 45 °C |
| Dilution | 1:15 |

## e) Cations in produced water (oil production)

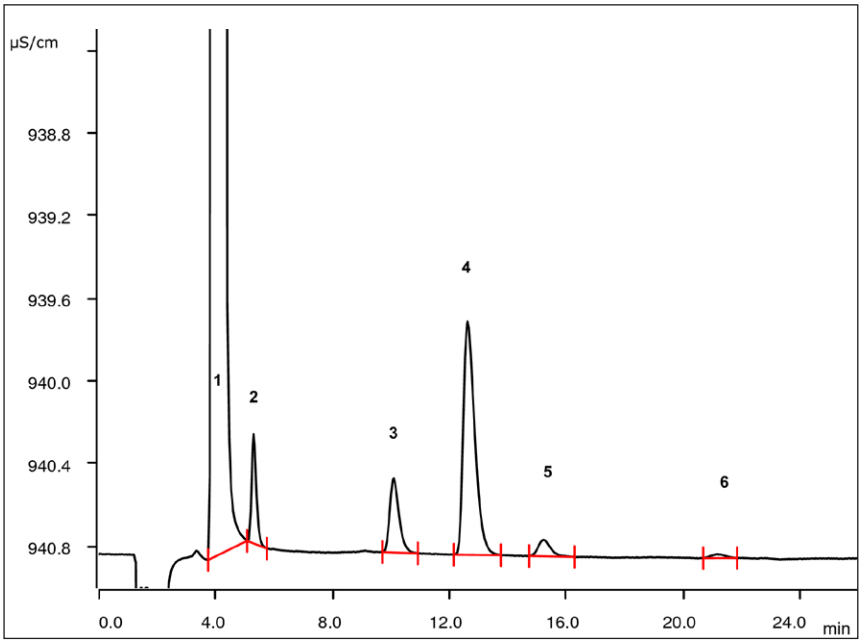



*Figure 53: Cations in produced water*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/L] |
|---|---|---|---|
| 1 | Sodium | 4.2 | 6910 |
| 2 | Potassium | 5.3 | 72.8 |
| 3 | Magnesium | 10.1 | 26.2 |
| 4 | Calcium | 12.6 | 179.1 |
| 6 | Strontium | 15.2 | 30.5 |
| 7 | Barium | 21.2 | 10.1 |

| | |
|---|---|
| Instrument | Compact or Professional IC instruments |
| Column | 6.1050.420 Metrosep C 4 - 150/4.0 |
| Eluent | c(oxalic acid) = 3.0 mmol/L (CAS 144-62-7)<br>c(acetonitrile) = 3% v/v (CAS 75-05-8) |
| Flow | 0.7 mL/min |
| Injection volume | 20 µL |
| Column temperature | 30 °C |

### f) Cations in deionized water applying sequential cation suppression (ng/L analysis)

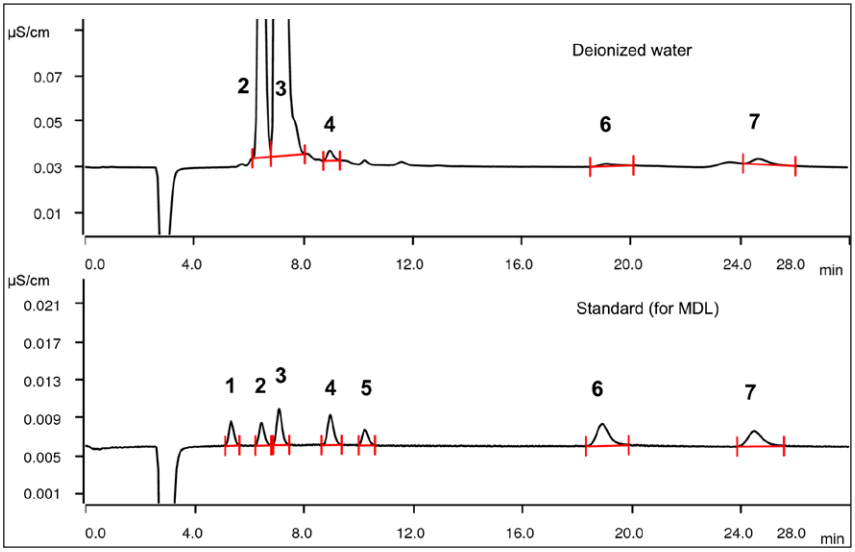



*Figure 54: Cation determination applying sequentially suppressed conductivity detection*

| Peak no. | Component | $t_R$ [min] | Sample conc. | Standard conc. | MLD [ng/L] |
|---|---|---|---|---|---|
| 1 | Lithium | 4.2 | n.d. | 10.9 | 1.1 |
| 2 | Sodium | 5.3 | 1.82 | 31.7 | 1.9 |
| 3 | Ammonium | 7.3 | 13.7 | 34.4 | 2.6 |
| 4 | Potassium | 15.3 | 0.08 | 66.3 | 7.3 |
| 6 | Magnesium | 19.1 | 0.05 | 64.0 | 6.3 |
| 7 | Calcium | 26.4 | 0.14 | 100.7 | 10.5 |

MDL = method detection limit, n.d. = not detected

| | |
|---|---|
| Instrument | Professional IC instruments |
| Column | 6.1052.430 Metrosep C Supp 1 - 250/4.0 |
| Eluent | c($HNO_3$) = 4.0 mmol/L (CAS 7697-37-2)<br>c($Rb^+$) = 100 µg/L (as $RbNO_3$, CAS 13126-12-0) |
| Suppressor regenerant | c($Na_2CO_3$) = 70 mmol/L (CAS 497-19-8)<br>c($NaHCO_3$) = 70 mmol/L (CAS 144-55-8) |
| Suppressor rinsing | STREAM |
| Flow | 1.0 mL/min |
| Injection volume (preconcentration) | 300 µL (ultrapure water) 6000 µL (standard) |
| Column temperature | 40 °C |

## Metrohm literature

Application Note AN-C-060: «Magnesium, strontium and barium in produced water»

Application Note AN-C-083: «Online monitoring of trace levels of cations in boiler feed water»

Application Note AN-C-135: «Cations in drinking water using Metrosep C 4 - 150/4.0 column according to ISO 14911»

Application Note AN-C-138: «Zinc, nickel, calcium, and magnesium in borated water of a pressurized water reactor (PWR)»

Application Note AN-C-141: «Cations in small sample volumes by using the intelligent Pick-up Injection Technique (MiPuT)»

Application Note AN-C-147: «Fast analysis of cations in tap water using Metrosep C 4-100/2.0»

Application Note AN-C-154: «Fast IC: Cations in drinking water on a high-capacity column in eleven minutes»

Application Note AN-CS-007: «Lithium in addition to other cations in seepage water from minerals through sequential suppression»

Application Note AN-CS-009: «Leaching tests for sample vials in cation trace analysis with sequential suppression»

Application Note AN-CS-018: «Metrosep C Supp 2 - 250/4.0: Cations in wastewater applying a Dose-in gradient»

Application Note AN-CS-020: «Fast IC with Metrosep C Supp 2 - 100/4.0: Four cations in five minutes»

Monograph «Practical ion chromatography»

## Additional literature

EN ISO 14911: «Determination of dissolved $Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Mn^{2+}$, $Ca^{2+}$, $Mg^{2+}$, $Sr^{2+}$ and $Ba^{2+}$ using ion chromatography»

ASTM D6919: «Standard Test Method of Dissolved Alkali and Alkaline Earth Cations and Ammonium in Water and Wastewater by Ion Chromatography»

# 5.4 Amines, for example methylamine, ethanolamine with IC



## General remarks

The determination of amines such as ethanolamine, diethanolamine, methylamine, dimethylamine, guanidine, etc., can be carried out by means of ion chromatography. The amines are separated on a cation exchange column and determined using indirect conductivity detection.

## Sample preparation

All water samples should be filtered through a filter with 0.2 µm pore size.
At higher concentrations it may be necessary to dilute the samples.
Inline Dialysis or $C_{18}$ sample preparation cartridges (6.1012.050) can be used for the preparation of samples with high organic loads.

## Analysis

The determination is performed by means of an external calibration in the concentration range concerned. A three-point calibration is recommended for the determination of cations.

## Examples

### a) Amines and standard cations applying direct conductivity detection

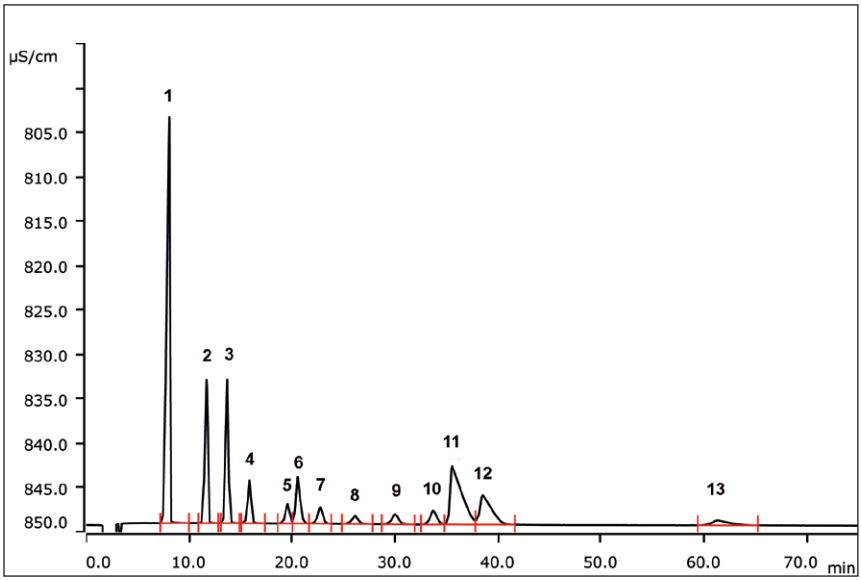



*Figure 55: Cations and amines in a standard solution*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/L] |
|---|---|---|---|
| 1 | Lithium | 8.1 | 49.3 |
| 2 | Sodium | 11.7 | 49.3 |
| 3 | Ammonium | 13.7 | 49.3 |
| 4 | Monoethanolamine | 15.9 | 50.1 |
| 5 | Diethanolamine | 19.6 | 50.0 |
| 6 | Potassium | 20.5 | 49.3 |
| 7 | Diglycolamine | 22.8 | 50.0 |
| 8 | Triethanolamine | 26.1 | 49.9 |
| 9 | Methyldiethanolamine | 30.0 | 49.9 |
| 10 | 3-methoxypropylamine | 33.7 | 50.1 |
| 11 | Magnesium | 35.5 | 49.3 |
| 12 | Calcium | 38.5 | 49.3 |
| 13 | Cyclohexylamine | 61.3 | 49.7 |

| | |
|---|---|
| Instrument | Compact or Professional IC instruments |
| Column | 6.1051.430 Metrosep C 6 - 250/4.0 |
| Eluent | c($HNO_3$) = 1.0 mmol/L (CAS 7697-37-2)<br>c(oxalic acid) = 1.5 mmol/L (CAS 144-62-7)<br>c(dipicolinic acid) = 0.75 mmol/L (CAS 499-83-2)<br>c(acetone) = 3% v/v (CAS 67-64-1) |
| Flow | 0.9 mL/min |
| Injection volume | 10 µL |
| Column temperature | 40 °C |

**b) Cations and amines in the water-steam circuit (standard solution)**

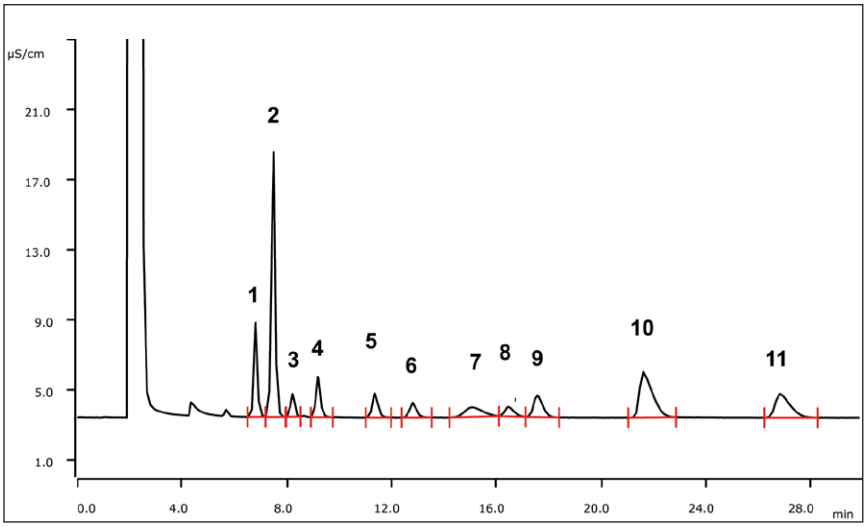



*Figure 56: Standard solution for a water-steam circuit cation analysis*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/L] |
|---|---|---|---|
| 1 | Sodium | 6.8 | 1.0 |
| 2 | Ammonium | 7.5 | 1.0 |
| 3 | Ethanolamine | 8.2 | 1.0 |
| 4 | Potassium | 9.2 | 1.0 |
| 5 | Dimethylamine | 11.4 | 1.0 |
| 6 | Morpholine | 12.8 | 1.0 |
| 7 | Nickel | 15.0 | 1.0 |
| 8 | 3-methoxypropylamine | 16.5 | 1.0 |
| 9 | Zinc | 17.6 | 1.0 |
| 10 | Magnesium | 21.6 | 1.0 |
| 11 | Calcium | 26.8 | 1.0 |

| | |
|---|---|
| Instrument | Professional IC instruments |
| Column | 6.1050.410 Metrosep C 4 - 100/4.0 |
| Eluent | $c(HNO_3)$ = 2.0 mmol/L (CAS 7697-37-2)<br>c(acetone) = 10% v/v (CAS 67-64-1) |
| Flow | 0.9 mL/min |
| Injection volume | 100 µL (MiPCT-ME) |
| Column temperature | 30 °C |

MiPCT-ME: Metrohm intelligent Preconcentration Technique with Matrix Elimination

## c) Trace ammonium and trimethylamine in 30% $H_2O_2$ applying sequential suppression

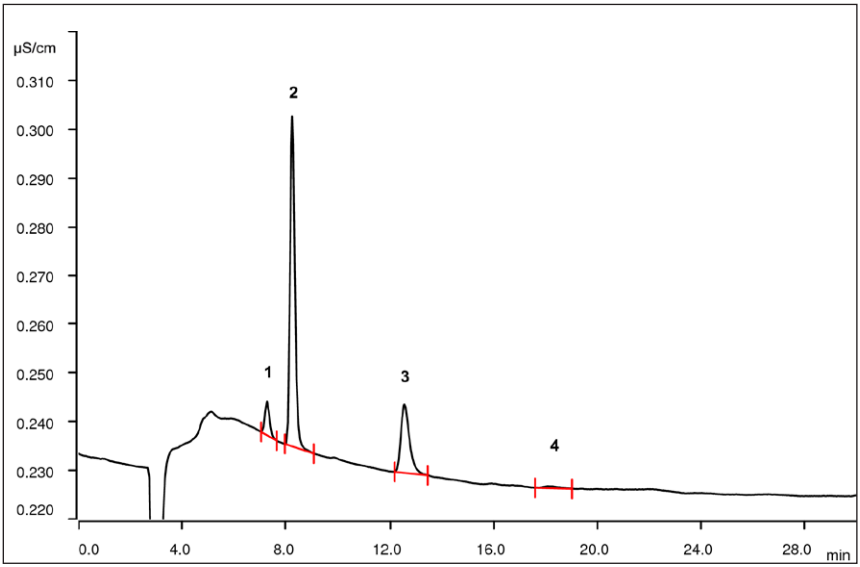



*Figure 57: Ammonium and trimethylamine in hydrogen peroxide applying sequential cation suppression*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/kg] |
|---|---|---|---|
| 1 | Sodium | 2.8 | n.q. |
| 2 | Ammonium | 3.3 | 1.72 |
| 3 | Potassium | 3.6 | n.q. |
| 4 | Trimethylamine | 3.9 | 0.17 |

n.q. = not quantified

| | |
|---|---|
| Instrument | Professional IC instruments |
| Column | 6.01053.430 Metrosep C Supp 2 - 250/4.0 |
| Eluent | c($HNO_3$) = 5.0 mmol/L (CAS 7697-37-2)<br>c($Rb^+$) = 50 µg/L (as $RbNO_3$, CAS 13126-12-0)<br>c(acetonitrile) = 2% v/v (CAS 75-05-8) |
| Suppressor | c($Na_2CO_3$) = 70 mmol/L (CAS 497-19-8)<br>c($NaHCO_3$) = 70 mmol/L (CAS 144-55-8) |
| Flow | 1.0 mL/min |
| Injection volume | 1000 µL (MiPCT-ME) |
| Column temperature | 50 °C |

MiPCT-ME: Metrohm intelligent Preconcentration Technique with Matrix Elimination

## Metrohm literature

Application Note AN-C-152: «Fast IC: Separation of ethanolamines in 2.5 minutes»

Application Note AN-C-153: «Fast IC: Separation of methylamines in four minutes»

Application Note AN-C-164: «Amine analysis in gas scrubber solutions from refineries with direct conductivity detection»

Application Note AN-C-177: «Dicyclohexylamine (DCHA) and methyldicyclohexylamine (MDCHA) in cooling lubricant applying Inline Dialysis»

# 5.5 Transition metals – zinc, manganese etc. with IC



## General remarks

The determination of transition metals such as zinc, manganese, nickel, etc., can be carried out by separation on a cation exchange column followed by indirect conductivity detection. This method has the advantage that alkali and alkaline earth metals can be determined simultaneously.

There is also the possibility of determining the transition metals by means of UV/VIS detection after post-column derivatization with PAR (4-(2-pyridylazo)resorcinol). The metals form colored complexes with the PAR reagent, which can be detected at 520 nm. As this method is very selective for the transition metals, which can be determined without interferences also in samples with very high alkali metal concentrations. Both methods will be described briefly.

## Sample preparation

The samples have to be filtered, for example using Minisart (Sartorius) or disposable filter supports (Whatman, formerly Schleicher & Schuell) with a pore size of 0.2 µm or less. Even seemingly clear solutions can contain very fine particles that damage the column.
The samples can be filtered automatically applying Inline Ultrafiltration. At higher concentrations it may be necessary to dilute the samples.
For water samples containing a high proportion of organic substances we recommend to apply Inline Dialysis as a sample preparation step that can be completely automated.
In addition, the pH value of the samples should be adjusted to pH 2.5 with nitric acid.
Metrohm offers fully automated IC systems that carry out Inline Ultrafiltration, Inline Dialysis, and also Inline Dilution. The MISP systems (Metrohm Inline Sample Preparation) simplify and improve sample preparation significantly.

## Analysis

Depending on the concentration range, 10–1000 µL sample are introduced.

Quantification is performed by means of an external calibration in the concentration range concerned. A three-point calibration is recommended for the determination of cations.

## Examples

### a) Transition metals with direct conductivity detection

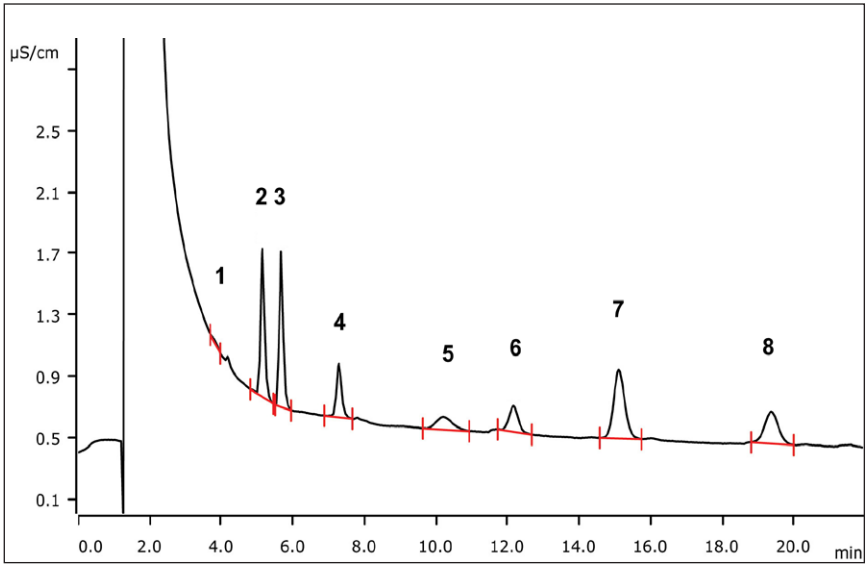



*Figure 58: Copper, nickel, zinc, and common cations in the water-steam circuit (standard solution)*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/kg] |
|---|---|---|---|
| 1 | Copper | 3.8 | 0.5 |
| 2 | Sodium | 5.2 | 0.5 |
| 3 | Ammonium | 5.7 | 0.5 |
| 4 | Potassium | 7.3 | 0.5 |
| 5 | Nickel | 10.2 | 0.5 |
| 6 | Zinc | 12.2 | 0.5 |
| 7 | Magnesium | 15.1 | 0.5 |
| 8 | Calcium | 19.4 | 0.5 |

| | |
|---|---|
| Instrument | Professional IC instruments |
| Column | 6.1050.230 Metrosep C 4 - 250/2.0 |
| Eluent | c($HNO_3$) = 2.5 mmol/L (CAS 7697-37-2)<br>c(oxalic acid) = 0.5 mmol/L (CAS 144-62-7) |
| Flow | 0.4 mL/min |
| Injection volume | 9.8 mL (MiPCT-ME) |
| Column temperature | 32 °C |

*MiPCT-ME: Metrohm intelligent Preconcentration Technique with Matrix Elimination*

## b) Transition metals in boiler feed water, spiked

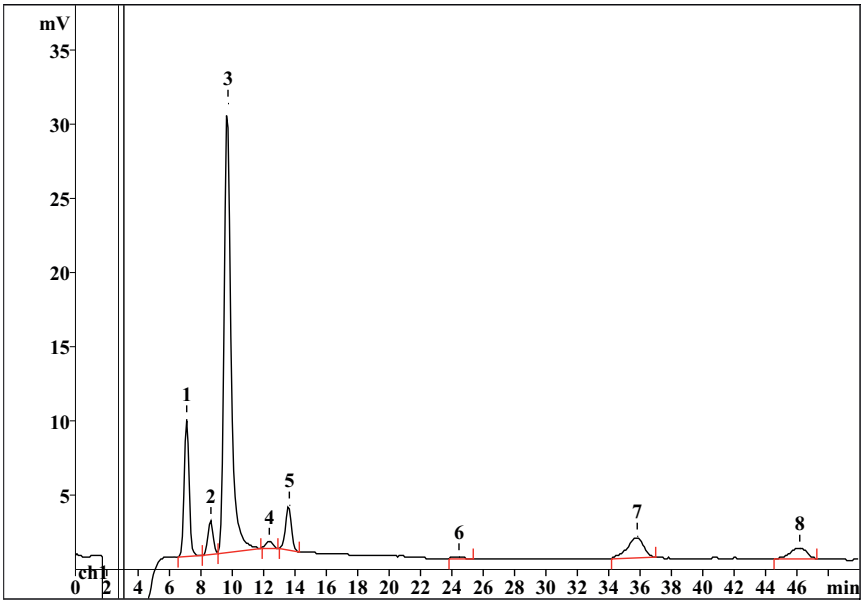



*Figure 59: Transition metals in boiler feed water (spiked)*

| Peak no. | Component | $t_R$ [min] | Conc. [µg/kg] |
|---|---|---|---|
| 1 | Lithium | 7.13 | 24.4 |
| 2 | Sodium | 8.65 | 19.3 |
| 3 | Ammonium | 9.72 | 31.0 |
| 4 | Potassium | 12.36 | 24.8 |
| 5 | Zinc | 13.64 | 2.53 |
| 6 | Iron(II) | 24.49 | 14.6 |
| 7 | Magnesium | 35.81 | 10.3 |
| 8 | Calcium | 46.21 | 6.08 |

| | |
|---|---|
| Instrument | Compact or Professional IC instruments |
| Column | 6.1010.230 Metrosep C 2 - 250/4.0* |
| Eluent | c(oxalic acid) = 1.75 mmol/L (CAS 144-62-7)<br>c(ascorbic acid) = 1.75 mmol/L (CAS 50-81-7) |
| Flow | 1.0 mL/min |
| Injection volume | 200 µL |
| Column temperature | ambient |

** replaced by 6.1050.430 Metrosep C 4 - 250/4.0*

**c) Transition metals by means of post-column derivatization with PAR and UV/VIS detection:**

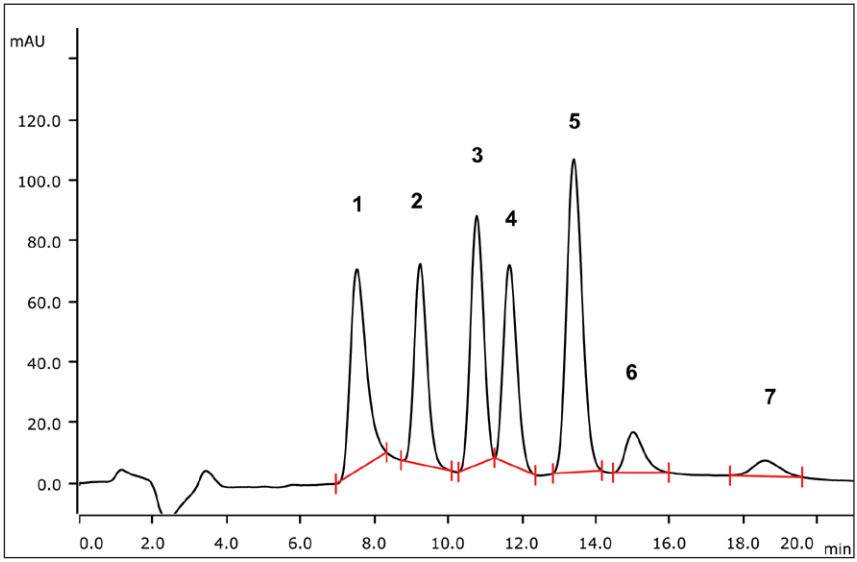



*Figure 60: Trace determination of transition metals with preconcentration (MiPCT), post-column reaction, and UV/VIS detection*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/kg] |
|---|---|---|---|
| 1 | Iron (III) | 7.5 | 7.5 |
| 2 | Copper | 9.3 | 10.0 |
| 3 | Nickel | 10.8 | 10.0 |
| 4 | Zinc | 11.7 | 10.0 |
| 5 | Cobalt | 13.4 | 10.0 |
| 6 | Cadmium | 15.0 | 10.0 |
| 7 | Iron (II) | 18.6 | 12.4 |

| | |
|---|---|
| Instrument | Professional IC instruments with UV/VIS Detector |
| Column | 6.1020.220 Metrosep A Supp 10 - 150/2.0 |
| Eluent | c(dipicolinic acid) = 3.0 mmol/L (CAS 499-83-2)<br>c($Na_2SO_4$) = 10 mmol/L (CAS 7757-82-6 )<br>c(NaOH) = 66 mmol/L (CAS 1310-73-2)<br>c(formic acid) = 80 mmol/L (CAS 64-18-6) |
| PCR reagent | c(PAR) = 0.15 mmol/L (CAS 1141-59-9)<br>c($HNO_3$) = 80 mmol/L (CAS 7697-37-2)<br>c($NH_4OH$) = 0.4 mol/L (CAS 1336-21-6) |
| Flow | 0.3 mL/min |
| Flow PCR | 0.2 mL/min |
| Injection volume | 3000 µL (MiPCT) |
| Column temperature | 55 °C |
| PCR temperature | 55 °C |

*MiPCT: Metrohm intelligent Preconcentration Technique*

## Metrohm literature

Application Note AN-C-137: «Copper, nickel, zinc, and common cations in the watersteam cycle of a boiling water reactor (BWR)»

Application Note AN-C-138: «Zinc, nickel, calcium, and magnesium in borated water of a pressurized water reactor (PWR)»

Application Note AN-C-139: «Cations and amines in the water-steam cycle»

Application Note AN-U-067: «Trace determination of transition metals with preconcentration (MiPCT), post-column reaction, and UV/VIS detection»

# 5.6 Determination of Zn, Cd, Pb, Cu with VA using the Multi-Mode Electrode pro



## Instruments

VA instrument with Multi-Mode Electrode pro

## Reagents

Use only reagents for trace analysis (e.g., Merck Suprapur, Honeywell Fluka TraceSelect) and ultrapure water (resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)).

- Supporting electrolyte 1: Ammonium acetate buffer: $c(CH_3COOH)$ = 2 mol/L + $c(NH_3)$ = 1 mol/L in ultrapure water. This electrolyte is to be used for samples with a very low chloride content.
- Supporting electrolyte 2: Sodium acetate buffer / KCl: c(KCl) = 1.5 mol/L + $c(CH_3COO\text{-}Na)$ = 0.5 mol/L in ultrapure water. This solution is only used for acidified samples (acidified by adding 1 mL $w(HNO_3)$ = 65% per 1 L sample) with higher chloride contents.
- Standard stock solutions:
  $\beta(Zn^{2+})$ = 1 g/L, $\beta(Cd^{2+})$ = 1 g/L, $\beta(Pb^{2+})$ = 1 g/L, $\beta(Cu^{2+})$ = 1 g/L are commercially available.
- Standard solutions $Zn^{2+}$, $Cd^{2+}$, $Pb^{2+}$, and $Cu^{2+}$ with concentrations of 10 mg/L or 1 mg/L in $c(HNO_3)$ = 0.015 mol/L.

## Sample preparation

After sampling, immediately filter the water samples through a microfilter (0.45 µm) and acidify by adding 1 mL $w(HNO_3)$ = 65% per 1 L.

Add 50–100 µL hydrogen peroxide $w(H_2O_2)$ = 30% to 10 mL acidified sample. The quartz tubes are irradiated for 90 min at 90 °C in the UV Digester. After cooling to room temperature, the digested samples can be transferred directly to the polarographic vessel.

## Analysis

Add 10 mL digested sample and 1 mL supporting electrolyte in the measuring vessel. Deaerate for 5 min and record the voltammogram applying the following conditions:



| | |
|---|---|
| Working electrode | HMDE |
| Mode | DP – Differential Pulse |
| Deposition time | 90 s |
| Deposition potential | –1.15 V |
| Start potential | –1.15 V |
| End potential | +0.05 V |
| Peak potential Zn | approx. –0.98 V |
| Peak potential Cd | approx. –0.56 V |
| Peak potential Pb | approx. –0.38 V |
| Peak potential Cu | approx. –0.1 V |

The concentration in the sample is determined by means of two standard additions.

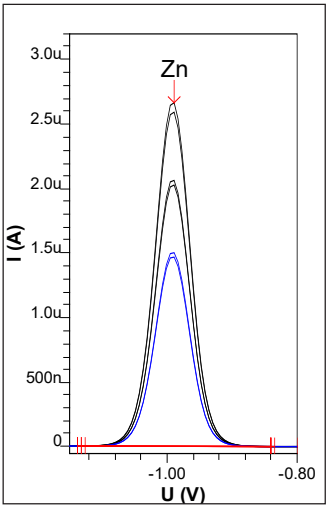
## Remarks

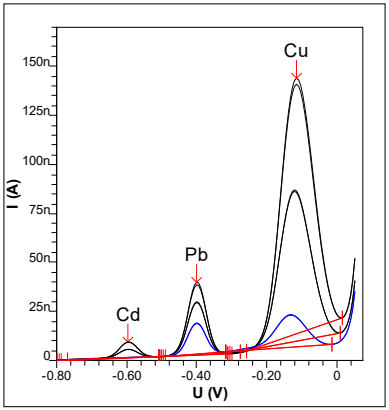
The blank values of the reagents used (including those used for digestion) have to be determined and taken into account when calculating the final concentrations.

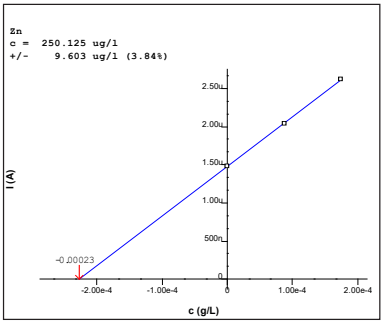
## Example

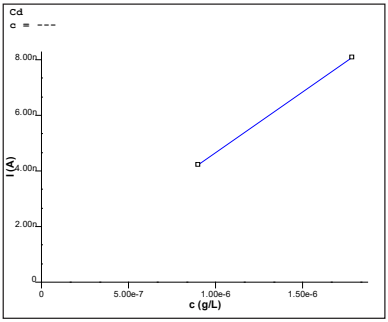
The concentration of the metal ions in the drinking water sample are as follows:

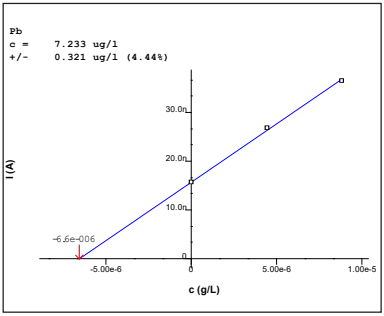
- Zinc: 250 µg/L
- Cadmium: < LOD
- Lead: 7.2 µg/L
- Copper: 7.0 µg/L



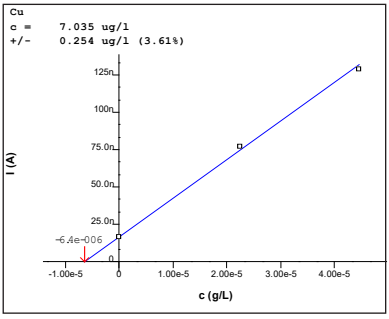




*Figure 61: Zinc, cadmium, lead, and copper in drinking water: Voltammograms and standard addition curves*

**Metrohm literature**

Application Bulletin AB-231: «Determination of zinc, cadmium, lead, copper, thallium, nickel and cobalt in water samples by anodic and adsorptive stripping voltammetry according to DIN 38406-16»

# 5.7 Determination of lead with VA using the scTRACE Gold

## General remarks

Lead is known to be highly toxic and lead salts are easily taken up by humans, animals, or plants. By interfering with enzyme reactions, lead can affect all parts of the human body. It can cause severe damage to brain and kidneys and can cross the blood-brain barrier. Cases of chronic lead poisoning caused by lead metal used in the water piping system are well known. Therefore, the control of drinking water for lead content is of utmost importance. In many countries (e.g., EU, USA), the limit for lead in drinking water is between 10 and 15 µg/L.

This method describes the determination of lead by anodic stripping voltammetry on a silver film on the scTRACE Gold electrode. With a deposition time of 30 s, the limit of detection is in the range of 0.4 to 0.6 µg/L.

## Instruments

VA instrument with scTRACE Gold

## Reagents

Use only reagents for trace analysis (e.g., Merck Suprapur, Honeywell Fluka TraceSelect) and ultrapure water (resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)).

- Supporting electrolyte: c(citric acid) = 0.5 mol/L + c(KCl) = 0.1 mol/L + c(NaOH) = 0.1 mol/L in ultrapure water. The electrolyte has pH 2.2–2.3.
- Standard stock solution: $\beta(Pb^{2+})$ = 1 g/L: This solution is commercially available.
- Standard solution: $\beta(Pb^{2+})$ = 1 mg/L in $c(HNO_3)$ = 0.015 mol/L

## Analysis

Add 10 mL sample and 1 mL supporting electrolyte in the measuring vessel. Deaerate for 5 min and record the voltammogram applying the following conditions:



| | |
|---|---|
| Working electrode | scTRACE Gold |
| Mode | SQW – Square wave |
| Deposition time | 60 s |
| Deposition potential | –0.7 V |
| Start potential | –0.7 V |
| End potential | –0.3 V |
| Peak potential Pb | approx. –0.49 V |

The concentration in the sample was determined by means of two standard additions.

## Example

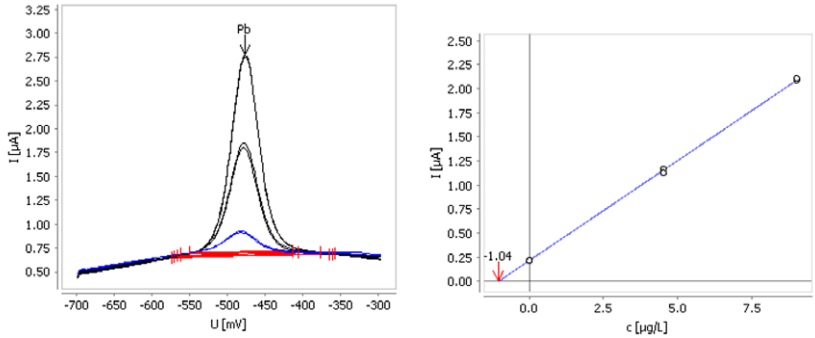



*Figure 62: Lead in drinking water: Voltammograms and standard addition curve*

The concentration of lead in the tap water sample is 1.2 µg/L.

## Remarks



In contrast to other solid electrodes the scTRACE Gold does not need extensive conditioning before it can be used. However, a new sensor needs to be activated once at the beginning of its use. The scTRACE Gold is generally maintenance-free. At the beginning of the working day the silver film is plated on the scTRACE Gold. At the end of the working day it is stripped off using the cleaning method. Dedicated methods and solutions are used for activation, film plating and cleaning. Refer to the Application Bulletin for details.

**Metrohm literature**

Application Bulletin AB-433: «Determination of lead in water with the scTRACE Gold modified with a silver film»

# 5.8 Determination of copper with VA using the scTRACE Gold

## General remarks

The concentration of copper in natural waters is usually very low. However, due to industrial and agricultural emissions, higher concentrations can sometimes be found. Domestic piping installations are the major source of elevated copper concentrations in drinking water.

This method describes describes the determination of copper by anodic stripping voltammetry using the scTRACE Gold electrode. With a deposition time of 30 s, the limit of detection is about 0.5 µg/L.

## Instruments

VA instrument with scTRACE Gold

## Reagents

Use only reagents for trace analysis (e.g., Merck Suprapur, Honeywell Fluka TraceSelect) and ultrapure water (resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)).



- Supporting electrolyte: c(KCl) = 0.3 mol/L + c(HCl) = 0.1 mol/L in ultrapure water
- Standard stock solution: $\beta(Cu^{2+})$ = 1 g/L: This solution is commercially available.
- Standard solution: $\beta(Cu^{2+})$ = 1 mg/L in $c(HNO_3)$ = 0.015 mol/L

## Analysis

Add 10 mL sample and 2 mL supporting electrolyte in the measuring vessel. Mix and record the voltammogram applying the following conditions:

| | |
|---|---|
| Working electrode | scTRACE Gold |
| Mode | DP – Differential Pulse |
| Deposition time | 30 s |
| Deposition potential | –0.3 V |
| Start potential | –0.1 V |
| End potential | 0.6 V |
| Peak potential Cu | approx. 0.25 V |

The concentration in the sample is determined by means of two standard additions.

## Example

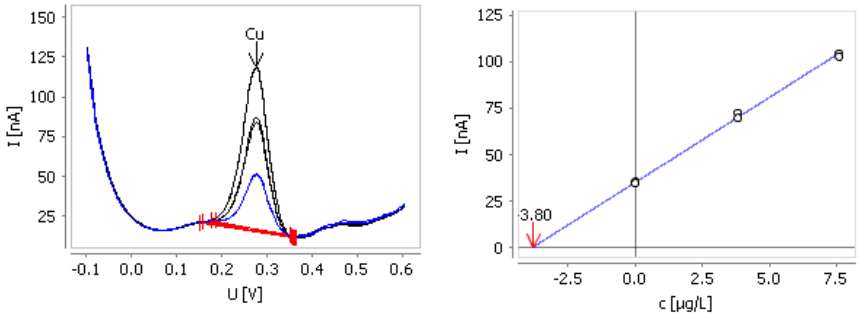



*Figure 63: Cu in drinking water: Voltammograms and standard addition curve*

The concentration of copper in the tap water sample is 49.4 µg/L.

## Remarks



In contrast to other solid electrodes the scTRACE Gold does not need extensive conditioning before it can be used. However, a new sensor needs to be activated once at the beginning of its use. The scTRACE Gold is generally maintenance-free. During its regular use it can be electrochemically cleaned to maintain its electrochemical performance. Dedicated methods and solutions are used for activation and cleaning. Refer to the Application Bulletin for details.

**Metrohm literature**
Application Bulletin AB-429: «Determination of copper in water with the scTRACE Gold»

# 5.9 Determination of nickel and cobalt with VA using the Multi-Mode Electrode pro

## Instruments

VA instrument with Multi-Mode Electrode pro

## Reagents

Use only reagents for trace analysis (e.g., Merck Suprapur, Honeywell Fluka TraceSelect) and ultrapure water (resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)).

- Supporting electrolyte: $NH_3/NH_4Cl$ buffer: $c(NH_4Cl)$ = 1 mol/L + $c(NH_3)$ = 2 mol/L in ultrapure water
- DMG solution (c(DMG) = 0.1 mol/L) in ultrapure water. Prepare the solution fresh every day.
- Standard stock solutions: $\beta(Ni^{2+})$ = 1 g/L, $\beta(Co^{2+})$ = 1 g/L are commercially available.
- Ni standard solution: $\beta(Ni^{2+})$ = 1 mg/L in $c(HNO_3)$ = 0.015 mol/L
- Co standard solution: $\beta(Co^{2+})$ = 1 mg/L in $c(HNO_3)$ = 0.015 mol/L

## Sample preparation

After sampling, immediately filter the water samples through a microfilter (0.45 µm) and acidify by adding 1 mL w($HNO_3$) = 65% per 1 L.



Add 50–100 µL hydrogen peroxide w($H_2O_2$) = 30% to 10 mL acidified sample. The quartz tubes are irradiated for 90 min at 90 °C in the UV Digester. After cooling to room temperature, the digested samples can be transferred directly to the polarographic vessel.

## Analysis

Add 10 mL digested sample, 0.5 mL supporting electrolyte and 100 µL DMG solution in the measuring vessel. The pH value of the measuring solution should be between 8.5 and 9. Deaerate for 5 min and record the voltammogram applying the following conditions:

| | |
|---|---|
| Working electrode | HMDE |
| Mode | DP – Differential Pulse |
| Deposition time | 90 s |
| Deposition potential | –0.7 V |
| Start potential | –0.8 V |
| Stop potential | –1.25 V |
| Peak potential Ni | approx. –0.95 V |
| Peak potential Co | approx. –1.07 V |

The concentration in the sample is determined by means of two standard additions.

## Remarks

The blank values of the chemicals used (including those used for digestion) must be determined and taken into account when calculating the final concentrations.

## Example

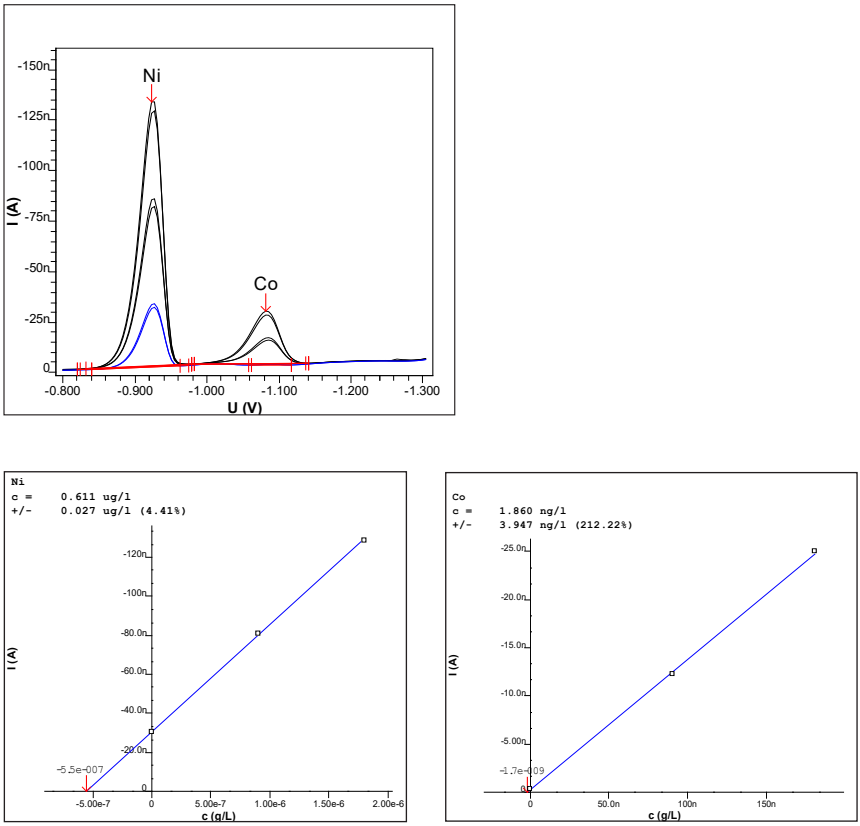



*Figure 64: Nickel and cobalt in seawater: Voltammograms and standard addition curves*

The concentration of the metal ions in the seawater sample are as follows:

- Nickel: 0.61 µg/L
- Cobalt: < LOD

## Metrohm literature

Application Bulletin AB-231: «Determination of zinc, cadmium, lead, copper, thallium, nickel, and cobalt in water samples by anodic and adsorptive stripping voltammetry according to DIN 38406-16»

# 5.10 Determination of iron with VA using the Multi-Mode Electrode pro



## General remarks

The method described is very sensitive for iron. It is especially useful for investigating groundwater, drinking, surface and cooling waters, where iron concentration is important. The method determines the Fe-triethanolamine complex that is formed in the measuring solution. The determination limit is 6 µg/L.

The constituents normally occurring in these water types do not interfere with the determination of iron.

## Instruments

VA instrument with Multi-Mode Electrode pro

## Reagents

Use only reagents for trace analysis (e.g., Merck Suprapur, Honeywell Fluka TraceSelect) and ultrapure water (resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)).

- Supporting electrolyte: c(NaOH) = 0.3 mol/L + c($KBrO_3$) = 0.1 mol/L + c(triethanolamine) = 0.05 mol/L in ultrapure water
- Standard stock solution: β($Fe^{3+}$) = 1 g/L: This solution is commercially available.
- Standard solution: β($Fe^{3+}$) = 10 mg/L in c($HNO_3$) = 0.015 mol/L

## Sample preparation

Add 50–100 µL hydrogen peroxide w($H_2O_2$) = 30% to 10 mL acidified sample. The quartz tubes are irradiated for 90 min at 90 °C in the UV Digester. After cooling to room temperature, the digested samples can be transferred directly to the polarographic vessel.

## Analysis

Add 10 mL sample and 2 mL supporting electrolyte in the measuring vessel. Deaerate for 5 min and record the voltammogram applying the following conditions:



| | |
|---|---|
| Working electrode | HMDE |
| Mode | DP – Differential Pulse |
| Start potential | –0.7 V |
| End potential | –1.25 V |
| Peak potential Fe | approx. –0.96 V |

The concentration in the sample is determined by means of two standard additions.

## Example

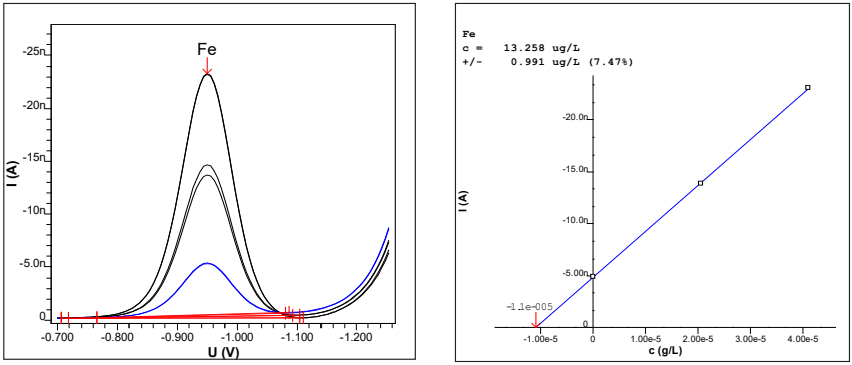



*Figure 65: Iron in drinking water: Voltammograms and standard addition curve*

The concentration of iron in the drinking water sample is 13.3 µg/L.

### Metrohm literature

Application Bulletin AB-317: «Determination of iron in the µg/L-range by polarography»

# 5.11 Determination of arsenic with VA using the scTRACE Gold



## General remarks

The contamination of groundwater with arsenic is to a large extent caused by natural processes. River waters, for example, release arsenic from weathered rock. Arsenic deposits then in the sediments, preferentially in river deltas. If the sediments are in contact with groundwater aquifers, the groundwater becomes contaminated. In addition to this natural origin, also industry and agriculture can contribute to the contamination of water with arsenic as anthropogenic sources. The WHO (World Health Organization) recommends a maximum arsenic content of 10 µg/L for water used as drinking water. This method describes the determination of total arsenic in water samples by anodic stripping voltammetry (ASV) using the scTRACE Gold sensor. With a deposition time of 60 s, the limit of detection for total arsenic is 0.9 µg/L.

## Instruments

VA instrument with scTRACE Gold

## Reagents

Use only reagents for trace analysis (e.g., Merck Suprapur, Honeywell Fluka TraceSelect) and ultrapure water (resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)).

- Supporting electrolyte: c(sulfamic acid) = 1 mol/L + c(citric acid) = 0.5 mol/L + c(KCl) = 0.45 mol/L in ultrapure water
- $KMnO_4$ solution: c($KMnO_4$) = 0.2 mmol/L in ultrapure water
- Standard stock solution: β(As(V)) = 1 g/L: This solution is commercially available.
- Standard solution: β(As(V)) = 0.5 mg/L in c($HNO_3$) = 0.015 mol/L

## Analysis

Add 10 mL sample, 2 mL supporting electrolyte and 0.1 mL $KMnO_4$ solution in the measuring vessel. Mix and record the voltammogram applying the following conditions:



| | |
|---|---|
| Working electrode | scTRACE Gold |
| Mode | SQW – Square wave |
| Deposition time | 60 s |
| Deposition potential | –1.0 V |
| Start potential | –0.3 V |
| End potential | +0.4 V |
| Peak potential As | approx. 0.03 V |

The concentration in the sample is determined by means of two standard additions.

## Example

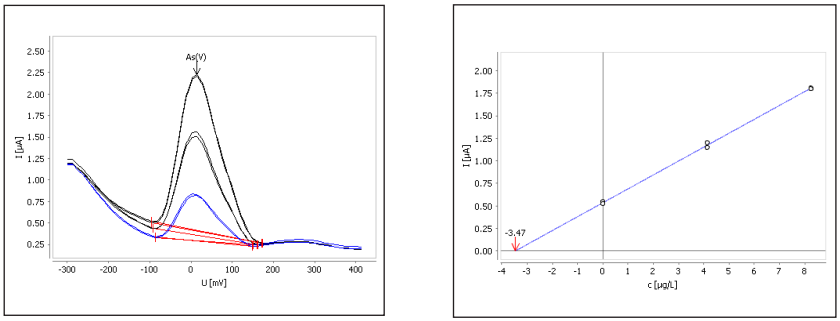



*Figure 66: Total arsenic in bottled mineral water: Voltammograms and standard addition curve*

The concentration of total arsenic in the bottled mineral water sample is 4.2 µg/L.

## Remarks

In contrast to other solid electrodes the scTRACE Gold does not need extensive conditioning before it can be used. However, a new sensor needs to be activated once at the beginning of its use. The scTRACE Gold is generally maintenance-free. During its regular use it can be electrochemically cleaned to maintain its electrochemical performance. Dedicated methods and solutions are used for activation and cleaning. Refer to the Application Bulletin for details.



**Metrohm literature**
Application Bulletin AB-416: «Determination of arsenic in water with the scTRACE Gold»

# 5.12 Determination of mercury with VA using the scTRACE Gold

## General remarks

Mercury and its compounds are toxic. Acute poisoning is rather seldom. More likely is a chronic poisoning with mercury compounds ingested with the food, air, or water. A natural source of mercury in the environment are volcanos. However, a significant part of the mercury present in the environment is human-generated. Considerable anthropogenic sources are coal-fired power plants, steel and nonferrous metal production, waste incineration plants, or the chemical industry, e.g., with the chlor-alkali plants namely the still used mercury-cell process, which is used for the production of important base chemicals such as sodium hydroxide and chlorine. Also not negligible is the contribution of artisanal gold mining where the use of elemental mercury for the extraction of gold from the ore is still common. The WHO (World Health Organization) guideline value for inorganic mercury is 6 µg/L, but the limit value for drinking water in many countries is much lower, e.g., USA 2 µg/L, European Union and Switzerland 1 µg/L.

This method describes the determination of inorganic mercury in water samples by anodic stripping voltammetry using the scTRACE Gold sensor. With a deposition time of 90 s, the limit of detection is 0.5 µg/L; the calibration is linear up to a concentration of 30 µg/L.

## Instruments

VA instrument with scTRACE Gold

## Reagents

Use only reagents for trace analysis (e.g. Merck Suprapur, Honeywell Fluka TraceSelect) and ultrapure water (resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)).



- Supporting electrolyte: c(formic acid) = 0.8 mol/L + c(KCl) = 0.06 mol/L + $\beta(Fe^{3+})$ = 5 mg/L in ultrapure water
- Standard stock solution: $\beta(Hg^{2+})$ = 1 g/L: This solution is commercially available.
- Standard solution: $\beta(Hg^{2+})$ = 1 mg/L in $c(HNO_3)$ = 0.015 mol/L

## Analysis

Add 10 mL sample and 1 mL supporting electrolyte in the measuring vessel. Mix and record the voltammogram applying the following conditions:

| | |
|---|---|
| Working electrode | scTRACE Gold |
| Mode | DP – Differential Pulse |
| Deposition time | 90 s |
| Deposition potential | 0.3 V |
| Start potential | 0.3 V |
| End potential | 0.6 V |
| Peak potential Hg | approx. 0.48 V |

The concentration in the sample is determined by means of two standard additions.

## Example

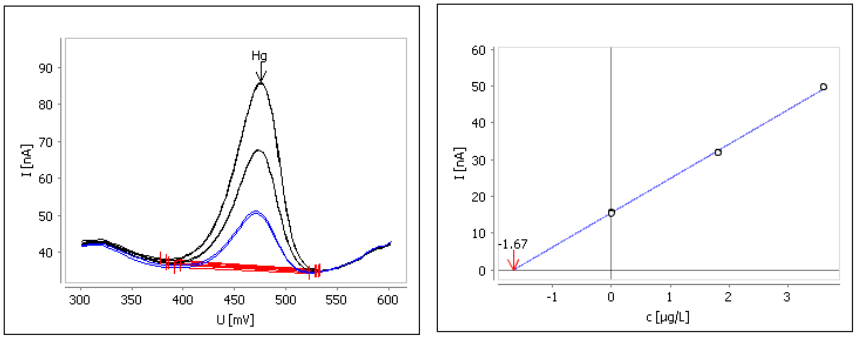



*Figure 67: Mercury in bottled mineral water: Voltammograms and standard addition curve*

The concentration of mercury in the spiked bottled mineral water sample is 1.8 µg/L.

## Remarks

In contrast to other solid electrodes the scTRACE Gold does not need extensive conditioning before it can be used. However, a new sensor needs to be activated once at the beginning of its use. The scTRACE Gold is generally maintenance-free. During its regular use it can be electrochemically cleaned to maintain its electrochemical performance. Dedicated methods and solutions are used for activation and cleaning. Refer to the Application Bulletin for details.

### Metrohm literature

Application Bulletin AB-422: «Determination of mercury in water with the scTRACE Gold»

# 5.13 Determination of molybdenum with VA using the Multi-Mode Electrode pro

## General remarks

Natural waters contain only traces of Mo. The determination limit of the method is 50 ng/L.

The principle of the method is based on the reaction between the molybdate ion $MoO_4^{2-}$ and the complexing agent 8-hydroxy-7-iodo-quinoline-5-sulfonic acid ($H_2L$) to form a $MoO_2L_2^{2-}$ complex, which is adsorbed on the mercury electrode. The adsorbed Mo(VI) is reduced electrochemically to the Mo(V) complex. The hydrogen ions present in the solution oxidize Mo(V) again spontaneously to form the Mo(VI) complex, which is thus newly available for electrochemical reduction. This catalytic reaction is the reason for the high sensitivity of the method.

## Instruments

VA instrument with Multi-Mode Electrode pro

## Reagents

Use only reagents for trace analysis (e.g., Merck Suprapur, Honeywell Fluka TraceSelect) and ultrapure water (resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)).

- Supporting electrolyte: c(8-hydroxy-7-iodo-quinoline-5-sulfonic acid) = $2 \cdot 10^{-4}$ mol/L + c(KCl) = 0.7 mol/L + c($H_2SO_4$) = 0.1 mol/L in ultrapure water
- Standard stock solution: β(Mo(VI)) = 1 g/L: This solution is commercially available.
- Standard solution: β(Mo(VI)) = 1 mg/L in c($H_2SO_4$) = 0.1 mol/L

## Sample preparation

Add 50–100 µL hydrogen peroxide w($H_2O_2$) = 30% to 10 mL acidified sample. The quartz tubes are irradiated for 90 min at 90 °C in the UV Digester. After cooling to room temperature, the digested samples can be transferred directly to the polarographic vessel.

## Analysis

Add 10 mL (diluted) sample and 2 mL supporting electrolyte in the measuring vessel. Deaerate for 5 min and record the polarogram applying the following conditions:



| | |
|---|---|
| Working electrode | SMDE |
| Mode | DP – Differential Pulse |
| Start potential | –0.68 V |
| End potential | –1.18 V |
| Peak potential Mo | approx. –1 V |

The concentration in the sample is determined by means of two standard additions.

## Remark

For accurate concentration determinations, the blank value of the used reagents has to be taken into account. The blank value is obtained by determining the molybdenum concentration of 10 mL ultrapure water plus 2 mL reagent solution.

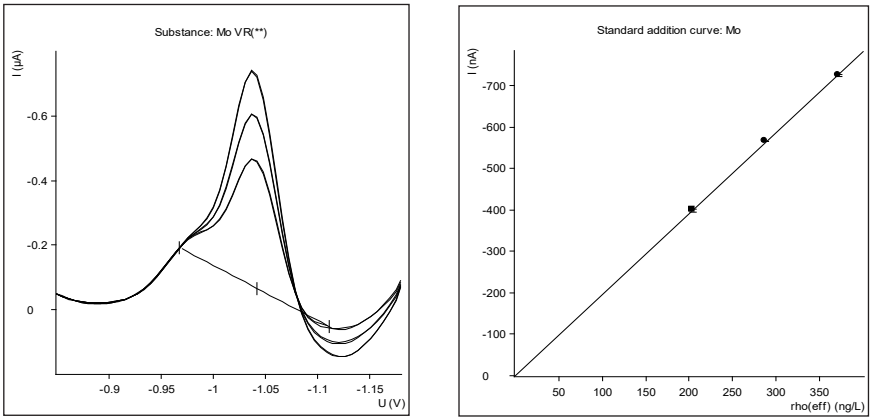



*Figure 68: Molybdenum in drinking water: Voltammograms and standard addition curve*

The concentration of molybdenum in the drinking water sample is 0.25 µg/L.

### Metrohm literature

Application Bulletin AB-146: «Determination of trace amounts of molybdenum (or tungsten) in water by polarography»

# 5.14 Determination of uranium with VA using the Multi-Mode Electrode pro



## General remarks

Generally natural waters only contain very low concentrations of uranium, usually below 1 µg/L. Depending on the degree of contamination or on the geology of the drainage basin, river waters have an uranium content between 30 ng/L and 20 µg/L while seawater and brackish water can contain 2 to 5 µg/L uranium.

The method described is based on the adsorptive stripping voltammetric determination of the uranyl chloranilic acid complex. It is fairly specific and allows the determination of uranium concentrations down to 50 ng/L.

## Instruments

VA instrument with Multi-Mode Electrode pro

## Reagents

Use only reagents for trace analysis (e.g., Merck Suprapur, Honeywell Fluka TraceSelect) and ultrapure water (resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)).

- Chloranilic acid solution c(chloranilic acid) = 0.01 mol/L in ultrapure water
- $KNO_3$ solution: c($KNO_3$) = 1 mol/L in ultrapure water
- Diluted nitric acid. c($HNO_3$) = 1.45 mol/L in ultrapure water
- Diluted KOH solution: c(KOH) = 1.78 mol/L in ultrapure water
- Standard stock solution: β(U(VI)) = 1 g/L: The solution is commercially available
- Standard solution: β(U(VI)) = 1 mg/L in c($HNO_3$) = 0.015 mol/L

## Sample preparation

Add 50–100 µL hydrogen peroxide w($H_2O_2$) = 30% to 10 mL acidified sample. The quartz tubes are irradiated for 90 min at 90 °C in the UV Digester. After cooling to room temperature, the digested samples can be transferred directly to the polarographic vessel.

## Analysis

Add 10 mL digested sample and 100 µL chloranilic acid solution in the measuring vessel. Adjust the pH value to 2.3 ± 0.3 by adding KOH or $HNO_3$. Deaerate for 5 min and record the voltammogram applying the following conditions:



| | |
|---|---|
| Working electrode | HMDE |
| Mode | DP – Differential Pulse |
| Deposition time | 60 s |
| Deposition potential | +0.15 V |
| Start potential | +0.05 V |
| End potential | –0.2 V |
| Peak potential U | approx. –0.05 V |

The concentration in the sample is determined by means of two standard additions.

## Example

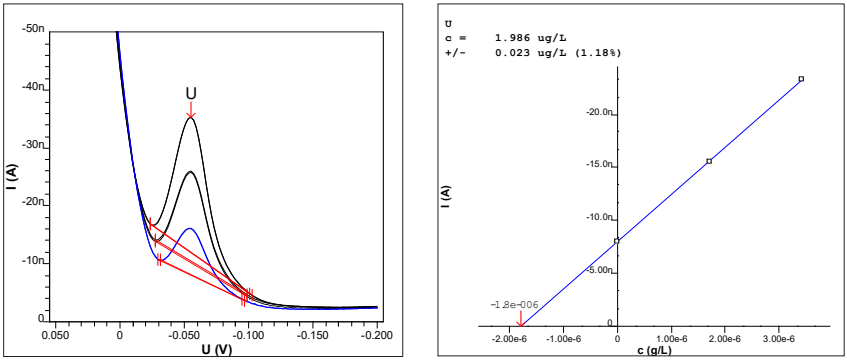



*Figure 69: Uranium in drinking water: Voltammograms and standard addition curve*

The concentration of uranium in the drinking water sample is 2.0 µg/L.

### Metrohm literature

Application Bulletin AB-430: «Determination of uranium by adsorptive stripping voltammetry according to DIN 38406-17»

# 5.15 Determination of titanium with VA using the Multi-Mode Electrode pro



## General remarks

Natural waters contain only traces of titanium. For example 20 to 70 ng/L titanium were found in seawater. Clearly, once again a sensitive analysis method is required to determine such low contents. The method is based on the adsorptive stripping voltammetric determination of the titanium-mandelic acid complex. The limit of detection is approx. 0.5 µg/L.

## Instruments

VA instrument with Multi-Mode Electrode pro

## Reagents

Use only reagents for trace analysis (e.g., Merck Suprapur, Honeywell Fluka TraceSelect) and ultrapure water (resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)).

- Mandelic acid solution: c(mandelic acid) = 0.4 mol/L in ultrapure water
- Diluted ammonia solution: $w(NH_3)$ = 10% in ultrapure water
- Standard stock solution: $\beta(Ti^{4+})$ = 1 g/L: The solution is commercially available.
- Standard solution: $\beta(Ti^{4+})$ = 1 mg/L in c(HCl) = 0.1 mol/L

## Sample preparation

Add 50–100 µL hydrogen peroxide w($H_2O_2$) = 30% to 10 mL acidified sample. The quartz tubes are irradiated for 90 min at 90 °C in the UV Digester. After cooling to room temperature, the digested samples can be transferred directly to the polarographic vessel.



## Analysis

Add 10 mL digested sample and 1 mL mandelic acid solution in the measuring vessel. Adjust the pH value to 3 by adding ammonia solution. Deaerate for 5 min and record the voltammogram applying the following conditions:

| | |
|---|---|
| Working electrode | HMDE |
| Mode | DP – Differential Pulse |
| Deposition time | 30 s |
| Deposition potential | –0.57 V |
| Start potential | –0.57 V |
| End potential | –0.95 V |
| Peak potential Ti | approx. –0.79 V |

The concentration in the sample is determined by means of two standard additions.

## Remarks

The blank value of the used chemicals has to be determined and taken into account. The concentration of the standard solution should be chosen in such a way that approx. 10 µL can be added with each addition. The peak potential of titanium moves to more negative values if the pH value decreases (this effect occurs if the standard solution is too acidic).

## Example

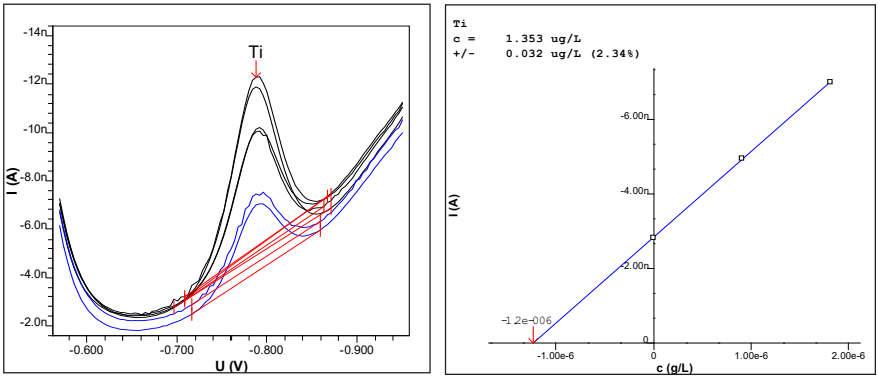



*Figure 70: Titanium in seawater*

The concentration of titanium in the seawater sample is 1.4 µg/L.

### Metrohm literature

Application Bulletin AB-266: «Determination of titanium by adsorptive stripping voltammetry»

# 5.16 Determination of antimony with VA using the Multi-Mode Electrode pro

## General remarks

In natural waters and other environmental water samples such as snow or rainwater, antimony occurs only at trace levels. The ranges of total antimony found are as follows: seawater 3 to 12 µg/L, lake water 0.1 to 0.5 µg/L, rainwater 0.4 to 0.9 µg/L, and molten snow 0.2 to 0.4 µg/L.

The anodic stripping voltammetric method determines the total antimony content. The determination is carried out in strongly acidic solution to prevent interferences by copper, which is present in most cases. If Sb(III) and Sb(V) have to be determined separately, please refer to the Application Bulletin listed in the references below.

## Instruments

VA instrument with Multi-Mode Electrode pro



## Reagents

Use only reagents for trace analysis (e.g., Merck Suprapur, Honeywell Fluka TraceSelect) and ultrapure water (resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)).

- Hydrochloric acid, w(HCl) = 30%, for trace analysis, CAS 7647-01-0
- Standard stock solution: β(Sb(III)) = 1 g/L: This solution is commercially available.
- Standard solution: β(Sb(III)) = 1 mg/L in c(HCl) = 0.1 mol/L

## Sample preparation

Add 50–100 µL hydrogen peroxide w($H_2O_2$) = 30% to 10 mL acidified sample. The quartz tubes are irradiated for 90 min at 90 °C in the UV Digester. After cooling to room temperature, the digested samples can be transferred directly to the polarographic vessel.

## Analysis

Add 10 mL digested sample and 5 mL hydrochloric acid (w(HCl) = 30%) in the measuring vessel. Deaerate for 5 min and record the voltammogram applying the following conditions:

| | |
|---|---|
| Working electrode | HMDE |
| Mode | DP – Differential Pulse |
| Deposition time | 180 s |
| Deposition potential | –0.4 V |
| Start potential | –0.45 V |
| End potential | –0.07 V |
| Peak potential Sb | approx. –0.16 V |

The concentration in the sample is determined by means of two standard additions.

## Example

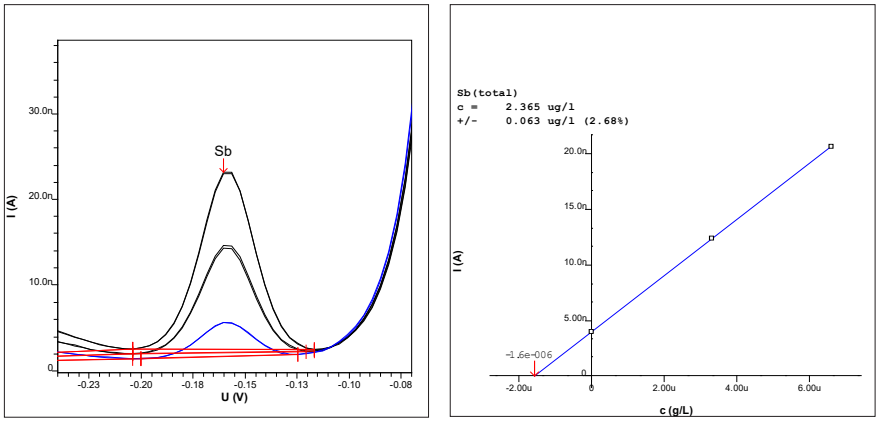



*Figure 71: Total antimony in drinking water: Voltammograms and standard addition curve*

The concentration of total antimony in the drinking water sample is 2.4 µg/L.

### Metrohm literature

Application Bulletin AB-074: «Determination of antimony, bismuth, and copper by anodic stripping voltammetry»

# 5.17 Determination of platinum and rhodium with VA using the Multi-Mode Electrode pro

## General remarks

The determination of platinum and rhodium traces has gained strongly in interest since the 1990s. The emission of these metals from automotive exhaust catalysts has increased their occurrence, especially near highly frequented roads. The contents normally range in the lower ng/L.

Two extremely sensitive catalytic adsorptive stripping voltammetric methods are described that allow to determine 0.1 ng/L platinum or 0.5 ng/L rhodium. Both methods are extremely sensitive towards interferences by organic water constituents. All water samples, including drinking water, must therefore be digested.

## Instruments

VA instrument with Multi-Mode Electrode pro



## Sample preparation

Add 50–100 µL hydrogen peroxide w($H_2O_2$) = 30% to 10 mL acidified sample. The quartz tubes are irradiated for 90 min at 90 °C in the UV Digester. After cooling to room temperature, the digested samples can be transferred directly to the polarographic vessel.

# Determination of platinum

## Reagents

Use only reagents for trace analysis (e.g., Merck Suprapur, Honeywell Fluka TraceSelect) and ultrapure water (resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)).

- Supporting electrolyte: c($H_2SO_4$) = 0.72 mol/L + c(HCHO) = 6.7 mmol/L + c(hydrazine sulfate) = 3 mmol/L in ultrapure water. Prepare the solution fresh daily.
- Standard solution: β(Pt(IV)) = 1 g/L: This solution is commercially available.
- Standard solution: β(Pt(IV)) = 1 µg/L in c(HCl) = 0.1 mol/L

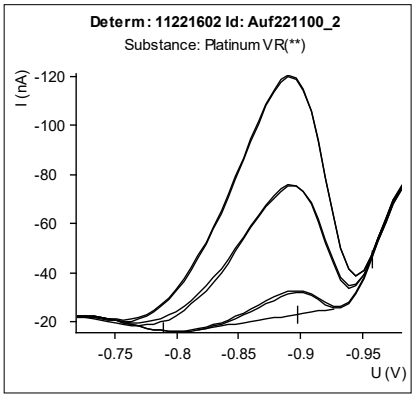
## Analysis

Add 10 mL digested sample and 1.5 mL supporting electrolyte in the measuring vessel. Deaerate for 5 min and record the voltammogram applying the following conditions:

| | |
|---|---|
| Working electrode | HMDE |
| Mode | DP – Differential Pulse |
| Deposition time | 120 s |
| Deposition potential | –0.6 V |
| Start potential | –0.6 V |
| End potential | –1.1 V |
| Peak potential Pt | approx. –0.88 V |

The concentration in the sample is determined by means of two standard additions.

## Example



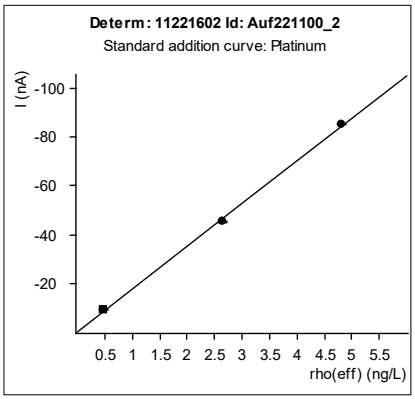




*Figure 72: Platinum in drinking water: Voltammograms and standard addition curve*

The concentration of platinum in the drinking water sample is 0.6 ng/L.

## Remarks

- It is mandatory to use a glassy carbon (GC) electrode as auxiliary electrode.
- It is strongly recommended to use all electrodes and vessels exclusively for the platinum and rhodium determination.
- With a deposition time of 60 s the linear range ends at 200 ng/L platinum. For samples with higher contents the sample is diluted with ultrapure water.
- With high nitrate contents the platinum peak disappears in the ascending baseline. At 10 g/L $NO_3^-$ the recovery rate for 5 ng/L platinum is approx. 50%.
- Determine the blank value of the chemicals with ultrapure water and take it into account when calculating the result. In this example the blank value was approx. 1 ng/L platinum.

# Determination of rhodium

## Reagents



Use only reagents for trace analysis (e.g., Merck Suprapur, Honeywell Fluka TraceSelect) and ultrapure water (resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)).

- Hydrochloric acid, w(HCl) = 30%, for trace analysis, CAS 7647-01-0
- Formaldehyde solution: w(HCHO) = 37%, CAS 50-00-0
- Standard solution: β(Rh(III)) = 1 g/L: This solution is commercially available.
- Standard solution: β(Rh(III)) = 1 µg/L in c(HCl) = 0.1 mol/L

## Analysis

Add 10 mL digested sample, 100 µL w(HCl) = 30%, and 10 µL w(HCHO) = 37% in the measuring vessel. Deaerate for 5 min and record the voltammogram applying the following conditions:

| | |
|---|---|
| Working electrode | HMDE |
| Mode | DP – Differential Pulse |
| Deposition time | 60 s |
| Deposition potential | –0.7 V |
| Start potential | –0.9 V |
| End potential | –1.23 V |
| Peak potential Rh | approx. –1.15 V |

The concentration in the sample is determined by means of two standard additions.

## Remarks

- With a deposition time of 60 s the linear range extends to 500 ng/L rhodium. For samples with higher contents the sample is diluted with ultrapure water.
- As the rhodium peak lies in the area where hydrogen evolution starts, it is recommended to evaluate only the front half of the peak.
- Determine the blank value of the chemicals with ultrapure water and take it into account when calculating the result. In this example the blank value was approx. 1 ng/L rhodium.

## Example

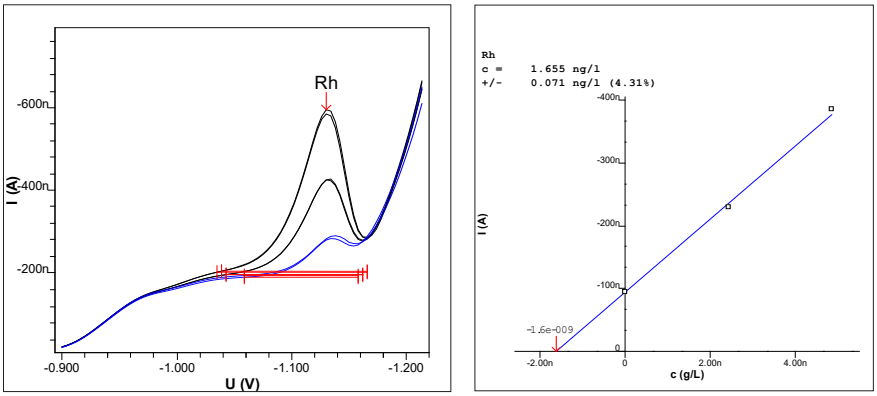



*Figure 73: Rhodium in drinking water: Voltammograms and standard addition curve*

The concentration of rhodium in the drinking water sample is 1.7 ng/L.

### Metrohm literature

Application Bulletin AB-220: «Determination of platinum and rhodium in the ultratrace range by adsorptive stripping voltammetry»

# 6 Specific water constituents

## 6.1 Ion chromatography: NTA, EDTA, and DTPA



### General remarks

The procedure described below allows the determination of the dissolved complexing agents nitrilotriacetic acid (NTA), ethylenedinitrilotetraacetic acid (EDTA), and diethylenetrinitrilopentaacetic acid (DTPA) by means of liquid chromatography (DIN 38413-8).

NTA, EDTA, and DTPA are complexed by iron(III) ions; this is followed by separation on a reversed-phase column by means of ion-pair chromatography. The eluent contains nitric acid, tetrabutylammonium hydrogensulfate (TBA-$HSO_4$), tetrabutylammonium hydroxid (TBAOH), and methanol. The detection of the complexing agents is carried out by UV/VIS detection. Before the detection a suppressor removes the excess of free iron(III).

### Sample preparation

The samples have to be derivatized before the analysis. This is done as follows: add 1 part derivatization solution (e.g., 1 mL) to 20 parts of sample (e.g., 20 mL), seal, and keep at 60 °C for 20 minutes under stirring.

All water samples should be filtered through a filter with 0.2 µm pore size.

### Analysis

Quantification is carried out by means of an external multipoint calibration covering the concentration range concerned. To obtain the required concentrations, the standards are diluted with ultrapure water.

Like the samples, the standard solutions have to be derivatized before injection as described under «Sample preparation» beforehand.

# Examples

## NTA, EDTA, and DTPA in water

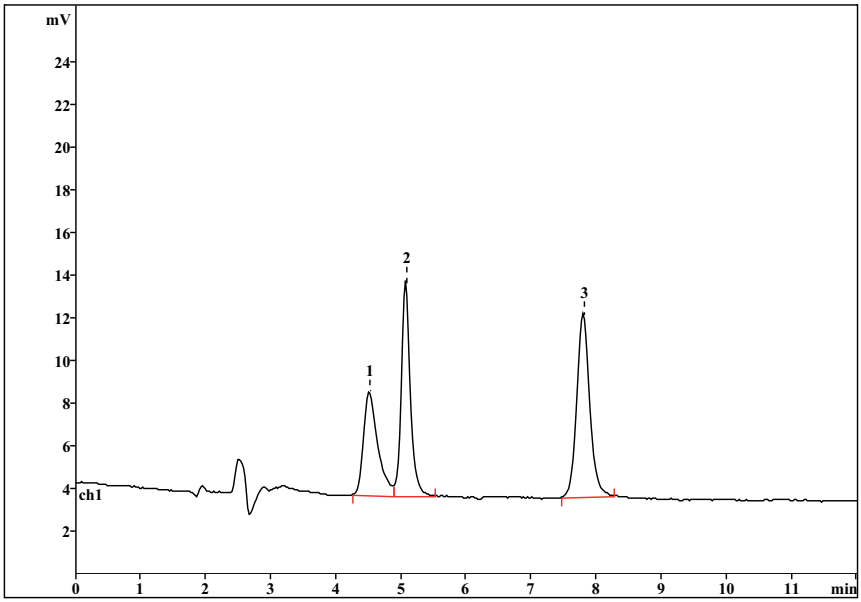



*Figure 74: NTA, EDTA, and DTPA in water*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/L] |
|---|---|---|---|
| 1 | NTA | 4.5 | 0.48 |
| 2 | EDTA | 5.1 | 0.50 |
| 3 | DTPA | 7.8 | 0.98 |

| | |
|---|---|
| Instrument | Compact or Professional IC instrument with a UV/VIS Detector |
| Column | Prontosil 120-5-C18 AQ, 250 mm (reversed phase column) |
| Eluent | c($HNO_3$) = 0.5 mmol/L (CAS 7697-37-2)<br>c(TBAOH) = 2.5 mmol/L (CAS 2052-49-5)<br>c(TBA-$HSO_4$) = 7.5 mmol/L (CAS 32503-27-8)<br>c(methanol) = 5% v/v (CAS 67-56-1) |
| Pre-column reagent | c($Fe(III)(NO_3)_3$) = 37 mmol/L (CAS 782-61-8)<br>c(TBA-$HSO_4$) = 130 mmol/L (CAS 32503-27-8) |
| Flow | 1.0 mL/min |
| Injection volume | 100 µL |

## Metrohm literature

IC Application Note AN-S-036: «The use of the MSM in the determination of NTA, EDTA, and DTPA in water samples»



## Additional literature

DIN 38413-8: «Determination of nitrilotriacetic acid (NTA), ethylenedinitrilotetraacetic acid (EDTA) and diethylenetrinitrilopentaacetic acid (DTPA) by liquid chromatography»

EN 13368-1: «Fertilizers – Determination of chelating agents in fertilizers by ion chromatography – Part 1: EDTA, HEDTA and DTPA»

EN 13368-2: «Fertilizers – Determination of chelating agents in fertilizers by chromatography – Part 2: Determination of Fe chelated by o,o-EDDHA,o,o-EDDHMA and HBED by ion-pair chromatography»

EN 13368-3: «Fertilizers – Determination of chelating agents in fertilizers by chromatography – Part 3: Determination of [S,S]-EDDS by ion pair chromatography»

# 7 Examples of automation



## 7.1 Ion chromatography

### Metrohm Inline Ultrafiltration

In modern ion chromatography it is recommended to filter all samples before injection. Separating columns with a particle size below 10 µm require absolutely particle-free sample solutions. Unfiltered solutions can cause increased column pressures and therefore, in some cases, result in a vastly reduced  reduced column lifetime.

Manual filtration is usually carried out by using disposable filter cartridges with a pore size of 0.45 µm or less. These become blocked very quickly, particularly with samples containing very fine particles. Sample changers with filter caps are used as an alternative. In this case, the pore size is most often larger than those of disposable filters. These filter caps are expensive and do not fully prevent the risk of blockage. Additionally, they can be a source of contamination if not treated with care.

The Inline Ultrafiltration combines inline filtration with automatic sample introduction. To apply Metrohm Inline Ultrafiltration, the IC system needs a dual-channel peristaltic pump or two Dosinos for sample feed and filtrate loading to the injection device.

The samples are placed directly on the sample precessor. Through sample processing, the sample is led into the lower chamber of the ultrafiltration cell and along the membrane to the waste using a pumping device. The peristaltic pump or the Dosino respectively create a vacuum in the upper chamber and this draws the sample solution through the ultrafiltration membrane. The filtered sample solution enters the injection loop and is then injected. Around 25% of the original solution is removed as filtrate. The rest flows into the waste container. This, together with the geometrical arrangement of the cell, prevents to a large extent the formation of a filter cake that would block the membrane. As the sample is rinsed out with ultrapure water after its injection, a multitude of samples can be measured with the same filter – without remarkable cross contamination from one sample to the next. This is incredibly useful for users, as they can use the membrane for many samples without the need to interfere with the analysis process. This is truly helpful automation.

Inline Ultrafiltration is particularly suitable for samples with a low to medium load, such as drinking water, surface water, wastewater, digestion solutions, extracts, etc.

Particle-free samples can be injected directly. Those with a high load such as juices containing fruit pulp, emulsions, and dispersions should be processed by Inline Dialysis (see next paragraph).

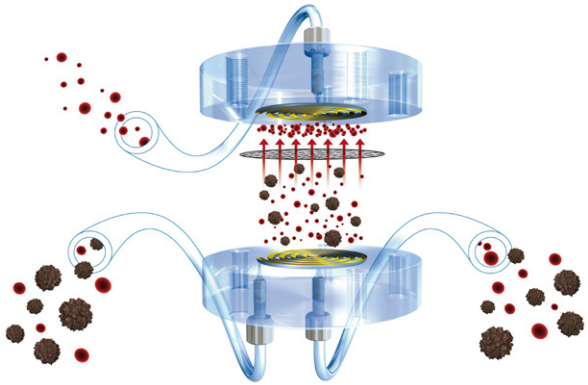


*Figure 75: The ultrafiltration cell is the heart of the Inline Ultrafiltration setup. The membrane prevents particles from getting onto the separation column.*

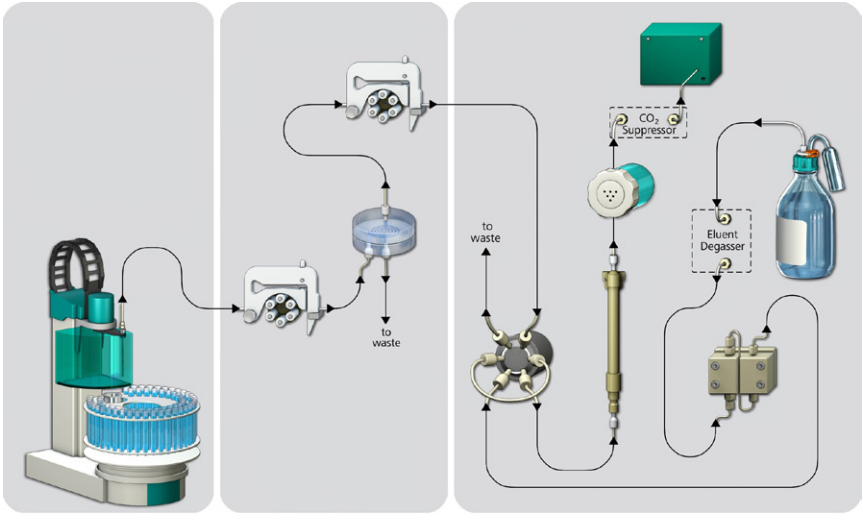



*Figure 76: Inline Ultrafiltration setup in an ion chromatography system applying sequential suppression.*

## Example

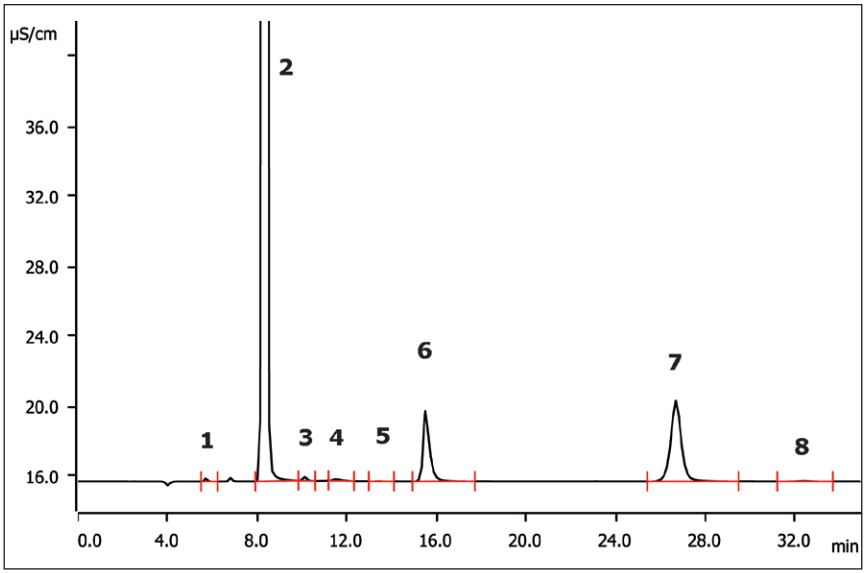



*Figure 77: Chromatogram of anions after chemical suppression in wastewater applying Inline Ultrafiltration.*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/kg] |
|---|---|---|---|
| 1 | Fluoride | 5.7 | n.q. |
| 2 | Chloride | 8.4 | 102.7 |
| 3 | Nitrite | 10.1 | n.q. |
| 4 | System peak | – | – |
| 5 | Bromide | 13.4 | n.q. |
| 6 | Nitrate | 15.5 | 21.5 |
| 7 | Sulfate | 26.7 | 29.7 |
| 8 | Phosphate | 32.4 | n.q. |

n.q. = not quantified

| | |
|---|---|
| Instrument | Any IC system with a dual-channel peristaltic pump or two Dosinos |
| Column | 6.01032.430 Metrosep A Supp 17 - 250/4.0 |
| Eluent | $c(Na_2CO_3)$ = 5.0 mmol/L (CAS 497-19-8)<br>$c(NaHCO_3)$ = 0.2 mmol/L (CAS 144-55-8) |
| Flow | 0.76 mL/min |
| Suppressor regenerant | $c(H_2SO_4)$ = 100 mmol/L (CAS 7664-93-9) |
| Suppressor rinsing | STREAM |
| Injection volume | 10 µL |
| Column temperature | ambient |

## Metrohm Inline Dialysis

Ion chromatography is an accepted method for simultaneously determining various anions and cations in water samples and various other matrices. Some of these sample matrices require complex and labor-intensive preparation steps before the determination itself can be carried out.

Metrohm Inline Dialysis allows a considerable rationalization of the whole analysis. The only demands placed on the sample: it must either be present in liquid form or capable of being brought into a liquid form and must be largely homogeneous. If larger particles are present, they must be removed by centrifugation. Thanks to this special stopped-flow method a virtually complete dialysis rate is achieved. This means that the acceptor solution has the same ion concentrations as the original sample (equilibrium dialysis). The acceptor solution is then injected directly into the ion chromatograph and analyzed. If the system is programmed so that the next sample is dialyzed while the previous sample is being determined (nested), then the total analysis time corresponds to that of a direct injection.

In the food industry, for example, it is possible to determine the ionic contents of milk and dairy products very simply. The time-consuming clarification with Carrez reagents is no longer necessary. With Metrohm Inline Dialysis, emulsions, juice dispersions, and even freshly pressed orange with fruit pulp no longer present any problems.


*Figure 78: Top view of the low-volume dialysis cell, the simple but highly efficient purification system for complex samples.*

## The method in detail

The method involves four steps. Ultrapure water is normally used as the acceptor solution for anion determinations, while diluted nitric acid is employed for cation determinations. Inline dialysis requires a total ion concentration of at least 1 mg/L. For samples with a lower total ion concentration the completeness of the dialysis cannot be guaranteed. However, such samples do usually not need to be dialyzed.

### Step 1: Conditioning

The dialysis cell is conditioned, i.e. both the sample solution and the acceptor solution are pumped through the cell. This step removes any traces of the previous sample from the two channels.

### Step 2: Dialysis

The sample solution continues to flow through the cell, while the acceptor solution remains stationary in a closed circuit. In this configuration, ions can diffuse through the membrane. The driving force is the concentration difference. As the sample solution is continuously renewed, the ion concentrations in the sample solution and the acceptor solution are equal when equilibrium is reached. This equilibrium is normally achieved with a sufficient degree of accuracy after 5–10 minutes (depending on the used dialysis cell).

### Step 3: Transfer

After the dialysis, the peristaltic pump on the sample side is stopped while the one on the acceptor side is started, transferring the acceptor solution fraction to the sample loop of the injector.



### Step 4: Sample injection

As soon as the purified sample is in the sample loop it is injected the analysis itself starts. The next sample can be dialyzed, while the current sample is being analyzed. In this way, the duration of the analysis is reduced to the time required for running the chromatogram.

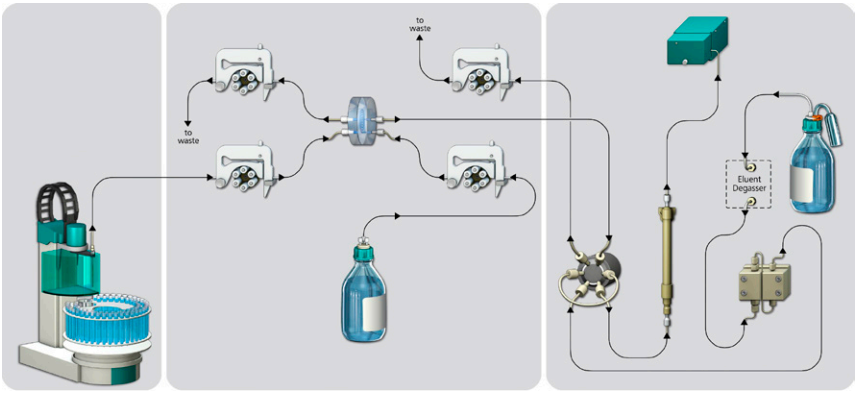



*Figure 79: Inline Dialysis setup in an ion chromatography system. Only diffusion shall be the driving force in Inline Dialysis. To avoid filtration effects, no pressure differences between the sample and acceptor channel are allowed. Therefore, the setup with two dual-channel peristaltic pumps is required. Sample and acceptor flows are securely stopped when the respective peristaltic pump stops.*

## Example

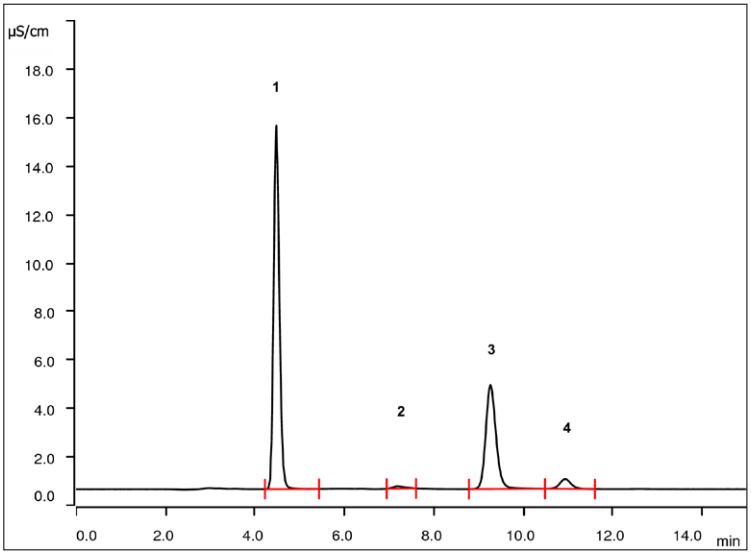



*Figure 80: Determination of anions in milk applying Inline Dialysis.*

| Peak no. | Component | $t_R$ [min] | Conc. [mg/kg] |
|---|---|---|---|
| 1 | Chloride | 4.5 | 876 |
| 2 | Nitrate | 7.2 | 39 |
| 3 | Phosphate | 9.3 | 1537 |
| 4 | Sulfate | 10.9 | 88 |

| | |
|---|---|
| Instrument | Any IC system with two dual-channel peristaltic pumps |
| Column | 6.1006.510 Metrosep A Supp 5 - 100/4.0 |
| Eluent | c($Na_2CO_3$) = 3.2 mmol/L (CAS 497-19-8)<br>c($NaHCO_3$) = 1.0 mmol/L (CAS 144-55-8) |
| Flow | 0.7 mL/min |
| Suppressor regenerant | c($H_2SO_4$) = 100 mmol/L (CAS 7664-93-9) |
| Suppressor rinsing | STREAM |
| Injection volume | 20 µL |
| Column temperature | ambient |

# 7.2 TitrIC



New possibilities in ion analysis through the unique combination of titration, direct measurement, and ion chromatography: TitrIC fully enables the automatic analysis of drinking water. All ionic components are determined quickly, reliably, and reproducibly. Results are presented as a single report or stored in the integral database.

As this monograph shows, the determination of ionic components in water samples involves four fields: direct measurement, ion chromatography, titration, and voltammetry. Metrohm accepted the challenge of combining these methods in a single system in 1998, and the first TitrIC system was introduced. Rapid advances in instrument development have allowed Metrohm to present a new version of the extremely powerful TitrIC system, in which direct measurement, titration, and ion chromatography are incorporated in a single analytical unit.

TitrIC flex is available in two main versions.

| Determinations | TitrIC flex I | TitrIC flex II |
|---|---|---|
| **pH value** | • | • |
| **Temperature** | • | • |
| **Conductivity** | • | • |
| **p + m value** | • | • |
| **Hardness** (Calcium/Magnesium) | • | • |
| **Cation IC:**<br>Lithium, sodium, ammonium, magnesium, calcium ... | – | • |
| **Anion IC:**<br>Fluoride, chloride, bromide, nitrite, nitrate, phosphate, sulfate … | • | • |
| **Molar concentrations of all cations** | – | • |
| **Molar concentrations of all anions** | • | • |
| **Ionic balance** | – | • |

TitrIC first determines the temperature and conductivity of the sample. Then the sample is introduced into the IC system after passing through the Inline Ultrafiltration cell. At the same time the pH value is measured followed by titration, that determines the p- and m-values. Calcium and magnesium, which are used to calculate total hardness, can be determined by titration or ion chromatography.

Ion chromatography determines all the inorganic ions contained in the sample. This comprises the halides fluoride, chloride, bromide, and iodide and their oxidized and partly toxic compounds such as chlorite, chlorate, and bromate. The nutrient anions nitrite, nitrate, and phosphate are also determined, as is sulfate. If present, organic anions such as formate, acetate, or propionate can also be quantified. As far as cations are concerned, all alkali and alkaline earth metals are determined. The titrimetric carbonate/hydrogen carbonate content completes the data required for the ion balance. For each sample it is possible to decide whether to do just a titration, only determine conductivity, only use ion chromatography, or to run all methods in parallel. The TitrIC system is highly flexible and can easily be adapted to the user's application requirements.

### Metrohm literature

Application Bulletin AB-436: «Installation instructions TitrIC flex I»
Application Bulletin AB-437: «Installation instructions TitrIC flex II»

## Report

### TitrIC flex II

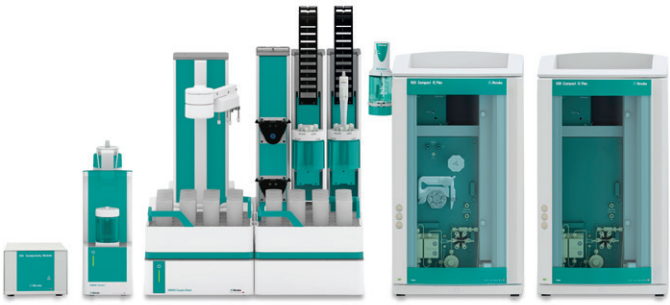


*Figure 81: TitrIC flex II*

| Ion chromatography | | Titration / Calculation | |
|---|---|---|---|
| Fluoride | 0.080 mg/L | Conductivity | 537.8 µS/cm |
| Chloride | 1.918 mg/L | Temperature | 25.4 °C |
| Nitrate | 27.719 mg/L | pH value | 7.68 |
| Sulfate | 4.216 mg/L | m-value | 5.317 mmol/L |
| Sodium | 2.498 mg/L | p-value | 0.0 mmol/L |
| Potassium | 0.413 mg/L | Total hardness | 2.924 mmol/L |
| Calcium | 80.773 mg/L | Sum of anions | 0.59 mEq/L |
| Magnesium | 22.091 mg/L | Sum of cations | 5.97 mEq/L |
| Ion difference | 0.07 mEq/L | Ion balance | 0.55 % |

## Flow chart

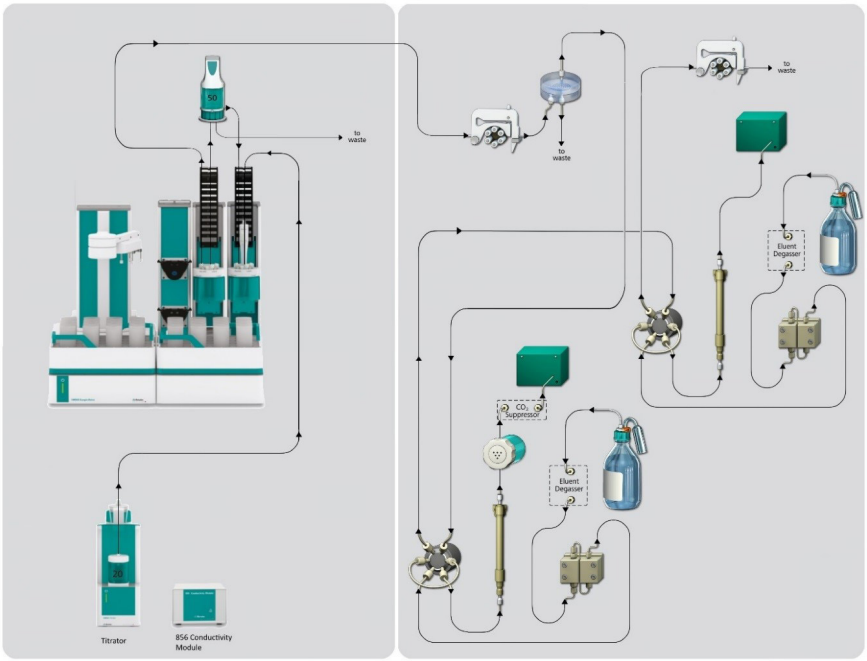



*Figure 82: Schematic of the fully automated TitrIC system for water analysis.*

# 8 Appendix



## Metrohm monographs dealing with the analytical methods used

**You can obtain these monographs free of charge from your Metrohm distributor or download them from www.metrohm.com.**

- Conductometry
- Practical ion chromatography – an introduction
- Sample preparation techniques for ion chromatography
- Practical titration – a training manual for titrimetric analysis
- Introduction to Polarography and Voltammetry

## Drinking water quality requirements

Maximum permissible values

| Parameter | WHO | EU | US EPA |
|---|---|---|---|
| pH value | | 6.5–9.5****) | |
| Electrical conductivity | | 2500 µS/cm****) | |
| Chlorine | 5 mg/L | | 4 mg/L |
| Oxidizability | | 5 mg/L $O_2$****) | |
| Al | | 200 µg/L****) | 50–200 µg/L ***) |
| Ammonium | | 0.5 mg/L****) | |
| As | 10 µg/L | 10 µg/L | 10 µg/L |
| Ba | 0.7 mg/L | | 2 mg/L |
| Cd | 3 µg/L | 5 µg/L | 5 µg/L |
| Cr(total) | 50 µg/L | 25 µg/L | 100 µg/L |
| Cu | 2 mg/L | 2 mg/L | 1 mg/L***) |
| | | | 1.3 mg**) |
| Fe | | 0.2 mg/L****) | 0.3 mg/L***) |
| Hg | 6 µg/L | 1 µg/L | 2 µg |
| Mn | | 50 µg/L****) | 50 µg/L***) |
| Na | | 200 mg/L****) | |
| Ni | 70 µg/L | 20 µg/L | |
| Pb | 10 µg/L | 5 µg/L | 15 µg/L**) |
| Sb | 20 µg/L | 10 µg/L | 6 µg/L |
| Se | 40 µg/L | 20 µg/L | 50 µg/L |
| Tl | | | 2 µg/L |
| U | 30 µg/L*) | 30 µg/L | 30 µg/L |
| Zn | | | 5 mg/L***) |

| | | | |
|---|---|---|---|
| Bromate | 10 µg/L | 10 µg/L | 10 µg/L |
| Chloride | | 250 mg/L****) | 250 mg/L***) |
| Chlorite | 0.7 mg/L*) | 0.25 mg/L | 1 mg/L |
| Chlorate | 0.7 mg/L*) | 0.25 mg/L | |
| Cyanide | | 50 µg/L | 200 µg/L |
| Dichloroacetic acid | 50 µg/L*) | | |
| Fluoride | 1.5 mg/L | 1.5 mg/L | 2 mg/L***) |
| Haloacetic acids | | 60 µg/L | |
| Nitrate | 50 mg/L | 50 mg/L | 10 mg/L |
| Nitrite | 3 mg/L | 0.5 mg/L | 1 mg/L |
| Sulfate | | 250 mg/L****) | 250 mg/L***) |

*) Provisional guideline value
**) Action level
***) Secondary Drinking Water Regulations
****) Indicator parameter

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8.108.5071EN – 2021-02

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