
Application Bulletin

Of interest to: General analytical laboratories; Water analysis

A B E G I K 1, 2, 7

Standard methods in water analysis – use of Metrohm instruments

Summary

This bulletin gives a survey of standard methods from the field of water analysis. You will also find the analytical instruments required for the respective determinations and references to the corresponding Metrohm Application Bulletins and Application Notes. The following parameters are dealt with: electrical conductivity, pH value, fluoride, ammonium and Kjeldahl nitrogen, anions and cations by means of ion chromatography, heavy metals and NTA/EDTA by means of voltammetry, chemical oxygen demand (COD), water hardness, free chlorine as well as a few other water components.

Abbreviations

- **AOAC** Official Methods of Analysis of the Association of Official Analytical Chemists (USA)
- **ASTM** American Society for Testing and Materials
- **Schweizerisches Lebensmittelbuch** Schweizer Methoden für Lebensmittel- und verwandte Analysen
- **EPA** United States Environmental Protection Agency
- **DIN** Deutscher Normenausschuss
- **ISO** International Organization for Standardization
- **ISWS** Illinois State Water Survey
- **USP** United States Pharmacopoeia

1. Electrical conductivity

Official methods

- **AOAC** 973.40 (1990)
Specific conductance of water.
- **Schweizerisches Lebensmittelbuch**, Kapitel 27 Trinkwasser
2.3 Bestimmung der spezifischen elektrischen Leitfähigkeit.
- **EPA** 120.1 (1983)
Conductance (Specific conductance, μmhos at 25 °C).
- **DIN** 38404 Teil 8 (1982)
Physikalische und physikalisch-chemische Kenngrößen. Bestimmung der elektrischen Leitfähigkeit.

- **ISO 7888: 1985**
Water quality – Determination of electrical conductivity.
- **USP (645)**
Water conductivity.

Instruments and accessories

- 712 Conductometer with 6.0908.110 conductivity measuring cell
- 6.2301.060 conductivity standard: c(KCl) = 0.1000 mol/L

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2. pH value

Official methods

- **AOAC 973.41 (1990)**
pH of water.
- **Schweizerisches Lebensmittelbuch**, Kapitel 27 Trinkwasser
2.2 Bestimmung des pH-Wertes.
- **DIN 38404 Teil 5 (1983)**
Physikalische und physikalisch-chemische Kenngrößen. Bestimmung des pH-Wertes.
- **EPA 150.1 (1983)**
pH (Electrometric).
- **ISO 10523: 1994**
Water quality – Determination of pH.

Instruments and accessories

- 691, 704, 713 or 744 pH Meter
- 6.0255.100 combined LL double-junction pH glass electrode or
6.0235.100 LL Porotrode or
6.0239.100 combined LL pH glass electrode
with 6.2104.020 electrode cable
- 6.2302.010 buffer set: 50 mL each concentrate pH = 4.00, pH = 7.00, c(KCl) = 3 mol/L

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3. Fluoride

Official methods

- **ASTM D 1179-A**
Fluoride Ion in Water using Distillation.
- **ASTM D 1179-B**
Fluoride Ion in Water using ISE.
- **ASTM D 3868**
Fluoride Ions in Saline Water.

- **Schweizerisches Lebensmittelbuch**, Kapitel 27 Trinkwasser
4.5 Bestimmung von Fluorid, Potentiometrie.
- **DIN 38405 Teil 1** (1982)
Bestimmung des Fluoridions mittels Fluorid-ionensensitiver Elektrode.
- **EPA 340.2** (1983)
Fluoride (Potentiometric, ion-selective electrode).
- **ISO 10359-1**: 1992
Water quality – Determination of fluoride – Part 1: Electrochemical probe method for potable and lightly polluted water.

Instruments and accessories

- 692 pH/Ion Meter with 2.728.0040 Magnetic Stirrer
- 776 Dosimat including 6.3014.223 Exchange Unit, with 6.2138.010 cable for automatic standard additions
- 6.0502.150 ion-selective fluoride electrode with 6.2104.020 electrode cable
- 6.0733.100 LL Ag/AgCl reference electrode with 6.2106.020 electrode cable
- 6.2301.030 NaF ion standard: $c(\text{NaF}) = 0.1000 \text{ mol/L}$
- 6.2308.020 electrolyte solution: $c(\text{KCl}) = 3 \text{ mol/L}$

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4. Ammonium and Kjeldahl nitrogen

Official methods

- **EPA 350.2** (1983)
Nitrogen, Ammonia (Colorimetric, titrimetric, potentiometric - distillation procedure).
- **EPA 350.3** (1983)
Nitrogen, Ammonia (Potentiometric, ion-selective electrode).
- **EPA 351.3** (1983)
Nitrogen, Kjeldahl, Total (Colorimetric, titrimetric, potentiometric).
- **EPA 351.4** (1983)
Nitrogen, Kjeldahl, Total (Potentiometric, ion-selective electrode).
- **ISO 6778**: 1984
Water quality – Determination of ammonium – Potentiometric method.

Instruments and accessories

- 692 pH/Ion Meter with 2.728.0040 Magnetic Stirrer
- 776 Dosimat including 6.3014.223 Exchange Unit, with 6.2138.010 cable for automatic standard additions
- 6.0506.010 NH_3 selective electrode

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and/or

- 702 SET/MET Titrino, 716 DMS Titrino, 719 SET Titrino, 736 GP Titrino, 751 GPD Titrino or 785 DMP Titrino with 2.728.0040 Magnetic Stirrer and 6.3014.213 Exchange Unit
- 6.0239.100 combined LL pH glass electrode with 6.2104.020 electrode cable

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5. Anions and cations by means of ion chromatography

Official methods

- **ASTM D 4327-97 (1997)**
Standard Test Method for Anions in Water by Chemically Suppressed Ion Chromatography.
- **ASTM D 5085-95 (1995)**
Standard Test Method for Determination of Chloride, Nitrate and Sulfate in Atmospheric Wet Deposition by Chemically Suppressed Ion chromatography.
- **ASTM D 5542-94 (1994)**
Standard Test Method for Trace Anions in High Purity Water by Ion Chromatography.
- **ASTM D 5996-96 (1996)**
Standard Test Method for Measuring Anionic Contaminants in High Purity Water by On-Line Ion Chromatography.
- **AOAC 993.30**
Inorganic Anions in Water.
- **Schweizerisches Lebensmittelbuch**, Kapitel 27 Trinkwasser
4.4 Chlorid, Nitrat, Sulfat mittels Ionenchromatographie (1988).
- **DIN 38405 Teil 19 (1988)**
Anionen. Bestimmung der Anionen Fluorid, Chlorid, Nitrit, Orthophosphat, Bromid, Nitrat und Sulfat in wenig belasteten Wässern mit der Ionenchromatographie.
- **DIN 38405 Teil 20 (1989)**
Anionen. Bestimmung der gelösten Anionen Bromid, Chlorid, Nitrat, Nitrit, Phosphat (ortho) und Sulfat in Abwasser mit der Ionenchromatographie.
- **EPA 300.0**
The determination of inorganic anions in water by ion chromatography.
- **ISO 276: 1993**
Water quality – Determination of dissolved chlorate, chloride and chlorite by liquid chromatography of ions - Part 4: Method for water of low contamination
- **ISO 10304-1: 1992**
Water quality – Determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulfate ions using liquid chromatography of ions – Part 1: Method for water with low contamination.
- **ISO 10304-2: 1995**
Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 2: Determination of bromide, chloride, nitrate, nitrite, orthophosphate and sulfate in waste water.

- **ISO 10304-3: 1997**
Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 3: Determination of chromate, iodide, sulfite, thiocyanate and thio-sulfate.
- **ISO 10304-4: 1997**
Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 4: Determination of chlorate, chloride and chlorite in water with low contamination.
- **ISO 14911: 1998**
Water quality – Determination of dissolved Li, Na, ammonium, K, Mn(II), Ca, Mg, Sr and Ba using ion chromatography – Method for water and waste water.
- **ISWS 300.6 (1986)**
Chloride, orthophosphate, nitrate and sulfate in wet deposition by ion chromatography.
- **ISWS 300.7 (1986)**
Dissolved sodium, ammonium, potassium, magnesium and calcium by ion chromatography.

Instruments and accessories

- 2.761.0020 Compact IC with Metrohm Suppressor Module MSM
or
- 2.732.0X10 IC Detector
- 2.733.0X30 IC Separation Center with Metrohm Suppressor Module MSM
- 2.709.0X10 IC Pump
- 752 IC Pump Unit
- 6.2620.150 Pulsation dampener
- 2.762.00X0 IC Interface including Metrodata IC-Net 2.0 software

- Possibly 791 VA Detector with 6.0807.000 mini carbon paste electrode (for the electrochemical detection of nitrite traces)
- Possibly 766 IC Sample Processor

Recommended IC separation columns:

- For the determination of anions:
6.1006.040 Metrosep Anion Dual 1, possibly 6.1006.200 preconcentration cartridge
- For the determination of cations:
6.1010.000 Metrosep Cation 1-2, possibly 6.1010.010 precolumn cartridge

Different Metrohm Application Bulletins and Application Notes

6. Polarographic/voltammetric determinations

Official methods

- **ASTM D 3557-95** (1995)
Standard Test Methods for Cadmium in Water.
- **ASTM D 3559-96** (1996)
Standard Test Methods for Lead in Water.
- **Schweizerisches Lebensmittelbuch**, Kapitel 27 Trinkwasser
Polarographische Bestimmung von Kupfer, Blei, Cadmium und Zink.
- **DIN 38406 Part 16** (1990)
Determination of 7 metals by voltammetric methods (Zn, Cd, Pb, Cu, Tl, Ni, Co). Water analysis.
- **DIN 38413 Teil 5** (1990)
Einzelkomponenten. Bestimmung von Ethylendinitrilotetraessigsäure (EDTA) und Nitritotriessigsäure (NTA) mittels Polarographie.
- **EPA 7063** (1996)
Arsenic in aqueous samples and extracts by anodic stripping voltammetry (ASV).
- **EPA 7472** (1996)
Mercury in aqueous samples and extracts by anodic stripping voltammetry (ASV).

Instruments and accessories

- 757 VA Computrace
or
- 746 VA Trace Analyzer with 747 VA Stand
- Possibly 705 UV Digester

Different Metrohm Application Bulletins and Application Notes

7. Chemical oxygen demand (COD)

Official methods

- **EPA 410.1** (1983)
Chemical Oxygen Demand (Titrimetric, mid-level).
- **EPA 410.2** (1983)
Chemical Oxygen Demand (Titrimetric, low-level).
- **EPA 410.3** (1983)
Chemical Oxygen Demand (Titrimetric, high-level for saline waters).
- **ISO 6010: 1989**
Water quality. Determination of the Chemical Oxygen Demand.

Instruments and accessories

- 702 SET/MET Titrino, 716 DMS Titrino, 736 GP Titrino, 751 GPD Titrino or 785 DMP Titrino or 726 or 796 Titroprocessor
- 730 Sample Changer

As far as additional accessories are concerned, please ask for an offer.

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8. Water hardness**Official methods**

- **ASTM 314** (1985)
Hardness (water hardness).
- **ASTM D 511-93** (1998)
Standard Test Methods for Calcium and Magnesium in water.
- **Schweizerisches Lebensmittelbuch**, Kapitel 27 Trinkwasser
6.1 Bestimmung der Gesamthärte; 6.2 Säureverbrauch bis pH = 4,3 bzw. 8,2.
- **DIN 38406 Teil 3** (1982)
Kationen (Gruppe E). Bestimmung von Calcium und Magnesium.
- **EPA 130.2** (1983)
Hardness, total (mg/L as CaCO₃). Titrimetric, EDTA.
- **EPA 305.2** (1983)
Acidity (Titrimetric).
- **EPA 310.1** (1983)
Alkalinity (Titrimetric, pH = 4.5).
- **ISO 6058: 1984**
Water quality – Determination of calcium content – EDTA titrimetric method.
- **ISO 6059: 1984**
Water quality – Determination of the sum of calcium and magnesium – EDTA titrimetric method.

Instruments and accessories

- 702 SET/MET Titrino, 716 DMS Titrino, 736 GP Titrino, 751 GPD Titrino or 785 DMP Titrino or 726 or 796 Titroprocessor
- Possibly 730 Sample Changer
- 6.0255.100 combined LL double-junction pH glass electrode or 6.0235.100 LL Porotrode
- 6.0504.100 ion-selective calcium electrode with 6.0726.100 double-junction Ag/AgCl reference electrode
- Possibly 6.5501.01X Spectrode 610 nm

As far as additional accessories are concerned, please ask for an offer.

Metrohm Application Bulletins No. 125 and 178

Metrohm Application Notes T-52 and T-57

9. Free chlorine

Official methods

- **EPA 330.1** (1983)
Chlorine, total residual (Titrimetric, amperometric).
- **EPA 330.2** (1983)
Chlorine, total residual (Titrimetric, back, iodometric).
- **EPA 330.3** (1983)
Chlorine, total residual (Titrimetric, iodometric).

Instruments and accessories

- 702 SET/MET Titrino, 716 DMS Titrino, 736 GP Titrino, 751 GPD Titrino or 785 DMP Titrino or 726 or 796 Titroprocessor
- Depending on the chosen method 6.0308.100 double Pt wire electrode or 6.0430.100 Pt Titrode

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Additional literature:

- E. Barbolani, G. Piccardi, F. Pantani
Potentiometric titration of chlorine and its oxy compounds in water
Anal. Chim. Acta 132 (1981) 223–228.
- G. Gordon, W. J. Cooper, R. G. Rice, G. E. Pacey
Methods of measuring disinfectant residuals
J. AWWA (1988) 94–108.

10. Other titrimetric determinations (bromide, chloride, sulfate, sulfide)

Official methods

- **EPA 320.1** (1983)
Bromide (Titrimetric).
- **EPA 325.3** (1983)
Chloride (Titrimetric).
- **EPA 376.1** (1983)
Sulfide (Titrimetric).

Instruments and accessories

- 702 SET/MET Titrino, 716 DMS Titrino, 736 GP Titrino, 751 GPD Titrino or 785 DMP Titrino or 726 or 796 Titroprocessor
- 6.0430.100 Ag Titrode with Ag₂S coating
- 6.5501.00X Spectrode 525 nm

Metrohm Application Bulletins No. 25, 130 and 178
Metrohm Application Notes T-1, T-7, T-32 and T-53