

Fully automated water analysis

Branch

General analytical chemistry; water, wastewater, environmental protection

Keywords

Water analysis; tap water; wastewater; automation; titration; conductivity; pH value; alkalinity; p value; m value; free chloride; total hardness; calcium hardness; magnesium hardness; fluoride; permanganate index; PMI; chemical oxygen demand; COD; branch 1; branch 2; Five-ring conductivity cell; combined Ca ISE; Aquatrode Plus; Ag-Titrode; F-ISE; LL ISE Reference; Combined Au-ring electrode; Micro Au Titrode; Pt-Titrode; 6.0915.100; 6.0510.100; 6.0277.300; 6.0470.300; 6.0750.100; 6.0452.100; 6.0435.110; 6.0431.100; 6.0471.300; 6.00500.300; 6.00500.600; EN ISO 8467; DIN 38409-44

Summary

The determination of the physical and chemical parameters such as electrical conductivity, pH value, p and m value (alkalinity), chloride content, the calcium and magnesium hardness, the total hardness, as well as fluoride content are necessary for evaluating water quality. This bulletin describes how to determine the above mentioned parameters in a single analytical run.

Additional important parameters in water analysis are the permanganate index (PMI) and the chemical oxygen demand (COD). Therefore, this Bulletin also describes the fully automated determination of the PMI according to EN ISO 8467 as well as the determination of the COD according to DIN 38409-44.

Conductivity, pH, alkalinity, hardness, chloride, fluoride

Instruments

- Sample changer with swing head
- External titration stand 2 ×
- Titrator with DET mode, 2 measuring interfaces
- Titrator or pH module for STDADD
- Conductivity module

- 50 mL burette 2 × (transfer 2 ×)
- 20 mL burette 4 × (alkalinity, hardness, fluoride 2 ×)
- 10 mL burette 1 × (hardness)
- 5 mL burette 3 × (chloride 2 ×, fluoride)
- Stirrer 2 ×

Electrodes

Five-ring conductivity measuring cell with Pt1000, $c = 0.7 \text{ cm}^{-1}$	6.0915.100
Combined Ca selective electrode	6.0510.100
iAquatrode Plus with Pt1000	6.0277.300
iAg-Titrode	6.0470.300
854 iConnect, 2 ×	2.854.0010
Combined dF-ISE with Pt1000	6.00500.300
Combined F-ISE with Pt1000	6.00500.600
LL ISE Reference electrode inner electrolyte: $c(\text{KCl}) = 3 \text{ mol/L}$ outer electrolyte: $c(\text{KCl}) = 3 \text{ mol/L}$	6.0750.100

Reagents

- Hydrochloric acid, $c(\text{HCl}) = 0.1 \text{ mol/L}$ and 5 mol/L volumetric solution
- EDTA, Titriplex, $c(\text{EDTA}) = 0.1 \text{ mol/L}$ volumetric solution
- Silver nitrate, $c(\text{AgNO}_3) = 0.01 \text{ mol/L}$ volumetric solution
- Nitric acid, $c(\text{HNO}_3) = 2 \text{ mol/L}$, purum
- Sodium hydroxide, $c(\text{NaOH}) = 5 \text{ mol/L}$, purum
- Ammonia, $w(\text{NH}_3) = 25\%$, purum
- Glacial acetic acid, CH_3COOH , purum
- Acetylacetone, purum
- Tris(hydroxymethyl)aminomethane, TRIS, Trizma Base, p.a.
- Calcium carbonate, CaCO_3 , p.a.
- Sodium fluoride, NaF , p.a.
- Sodium chloride, NaCl , p.a.
- Ammonium chloride, NH_4Cl , purum

Solutions

Auxiliary solution	Acetylacetone and TRIS; $c(\text{acetylacetone}) = 0.1 \text{ mol/L}$ and $c(\text{TRIS}) = 0.2 \text{ mol/L}$ 24.2 g of TRIS is weighed into a 1 L volumetric flask and dissolved in approx. 500 mL dist. H_2O. 12 mL acetylacetone is added and the solution is made up to the mark with dist. H_2O. This solution can only be used for a few days. It masks Fe^{3+} and Al^{3+} for a better differentiation of Ca^{2+} and Mg^{2+}.
Acetate buffer	58 g NaCl is weighed into a 1 L volumetric flask and dissolved in approx. 500 mL dist. H_2O. 57 mL of glacial acetic acid is added and after cooling down to room temperature, the pH of the mixture is adjusted to 5–5.5 using $c(\text{NaOH}) = 5 \text{ mol/L}$. The flask is then filled up to the mark with dist. H_2O.
Buffer pH 10	54 g NH_4Cl and 350 mL $w(\text{NH}_3) = 25\%$ are dissolved in dist. H_2O and made up to 1 L with dist. H_2O.

Standard solutions

Fluoride standard	$\beta = 100 \text{ mg/L F}^-$ stock solution 0.221 g of NaF is weighed in a 1 L volumetric flask and the flask is filled up to the mark with dist. H_2O. The solution is then transferred into a plastic bottle for storage. $\beta = 10 \text{ mg/L F}^-$ standard solution 100 mL of the stock solution is transferred into a new plastic flask and made up to 1 L with dist. H_2O.
TRIS standard	TRIS is dried overnight in a drying oven at 105°C and allowed to cool down in a desiccator for at least 1 h. A standard solution with $c(\text{TRIS}) = 0.1 \text{ mol/L}$ is prepared in a 1 L volumetric flask by dissolving 12.1 g of dried TRIS in dist. H_2O and filling up to the mark with dist. H_2O.

Ca^{2+} standard	It is recommended to use a prepared standard (e.g., the certified Metrohm ion standard CaCl_2, 6.2301.070). Otherwise CaCO_3 is dried overnight in a drying oven at 140°C and allowed to cool down in a desiccator for at least 2 h. A standard solution with $c(\text{CaCO}_3) = 0.1 \text{ mol/L}$ is prepared by suspending 10.0 g of dried CaCO_3 in approx. 100 mL dist. H_2O and adding drop by drop $c(\text{HCl}) = 5 \text{ mol/L}$, until all CaCO_3 is dissolved. The solution is then made up to 1 L with dist. H_2O.
Cl^- standard	It is recommended to use a prepared standard (e.g., the certified Metrohm ion standard KCl, 6.2301.060). Otherwise NaCl is ground to fine powder in a mortar, dried overnight in a drying oven at 140°C, and allowed to cool down in a desiccator for at least 2 h. A standard solution with $c(\text{NaCl}) = 0.1 \text{ mol/L}$ is prepared by dissolving 5.9 g NaCl in 1 L of dist. H_2O.
Conductivity standard	It is recommended to use a prepared standard (e.g., the certified Metrohm conductivity standards 6.2324.010 or 6.2301.060).

Sample preparation

No sample preparation is required.

Analysis

As the system is rather complex, a scheme can be found in the appendix, as well as the arrangement of different solutions and electrodes on the two titration lids.

To avoid interferences between combined electrodes, it is important that combined electrodes which measure in the same titration vessel are not connected at the same measuring input.

Cell constant

A sample beaker and the measuring cell are rinsed with the conductivity standard. The sample beaker is then filled with standard and placed on the rack. Before calibration, the conductivity cell is dipped in to the standard three times.

Titer of HCl

An appropriate volume of the prepared TRIS standard solution and approx. 40 mL of dist. H₂O are dosed into the titration vessel equipped with the iAquatrode Plus and titrated using $c(\text{HCl}) = 0.1 \text{ mol/L}$ until the first equivalence point. A threefold determination should be carried out.

Titer of EDTA

An appropriate volume of the prepared CaCO₃ standard solution is dosed into the titration vessel equipped with the combined Ca ISE. After the addition of 30 mL of dist. H₂O and 10 mL auxiliary solution, the solution is titrated using $c(\text{EDTA}) = 0.1 \text{ mol/L}$ until the first equivalence point. A threefold determination should be carried out.

Titer of AgNO₃

An appropriate volume of the prepared NaCl standard solution is dosed into the titration vessel equipped with the iAg-Titrode and 1 mL of $c(\text{HNO}_3) = 2 \text{ mol/L}$ is added. After the addition of 40 mL of dist. H₂O, the solution is titrated using $c(\text{AgNO}_3) = 0.01 \text{ mol/L}$ until the first equivalence point. A threefold determination should be carried out.

Calibration of F-ISE

For the calibration of the combined F-ISE, an appropriate amount of fluoride standard is dosed into the titration vessel. The standard is then diluted up to 15 mL with dist. H₂O. Then 15 mL acetate buffer is added and the concentration is measured.

The concentration of the standards should be chosen in such a way that the expected sample concentration lies within the calibration range. At least four different concentrations should be measured.

Sample

For this automated system, pH, p value, m value, calcium hardness, as well as magnesium hardness are measured in parallel to the chloride and fluoride content.

Beakers filled with an appropriate amount of sample are placed on the rack. First, the conductivity cell is dipped three times for preconditioning into the sample. Then, the conductivity is measured.

Between 5–10 mL of sample solution is transferred into both external titration vessels to prerinse all parts with fresh sample. All tubes have to be filled with sample after this

procedure. The external titration vessels are then cleaned before determination.

For the determinations of alkalinity and hardness, a total volume of 100 mL sample is transferred into the first external titration vessel. After pH measurement, the p and m values are determined by a DET titration with fixed endpoints (FP) at pH 8.2 and 4.3 using $c(\text{HCl}) = 0.1 \text{ mol/L}$.

Directly after the alkalinity determination, 15 mL of the auxiliary solution is added. The hardness of the sample solution is determined by titration with $c(\text{EDTA}) = 0.1 \text{ mol/L}$. As the pH is lowered during the alkalinity measurement, it is important to check whether the auxiliary solution is capable of keeping the pH at the required level of 8.5.

At the same time, a total volume of 75 mL sample is dosed into the second external titration vessel. 2 mL of $c(\text{HNO}_3) = 2 \text{ mol/L}$ is added and the titration of chloride with $c(\text{AgNO}_3) = 0.01 \text{ mol/L}$ is started. After cleaning, another 15 mL sample and 15 mL acetate buffer are dosed into the external titration vessel for the fluoride determination.

At the end of all the titrations, both external titration vessels are cleaned using pumps while the conductivity cell is dip rinsed in distilled water.

Parameters

Conductivity

Mode	MEAS Cond
Measurement	Time controlled (no drift control)
Measuring time	30 s
Measuring interval	2 s

pH measurement

Mode	MEAS pH
Drift	2 mV/min
Min. waiting time	10 s
Max. waiting time	110 s

Alkalinity

Mode	DET pH
Drift	50 mV/min
Max. waiting time	26 s
Meas. point density	4
Min. increment	10 μL
EP criterion	5
EP recognition	all
Fix point 1	8.2
Fix point 2	4.3

Hardness

Mode	DET U
Drift	50 mV/min
Max. waiting time	26 s
Meas. point density	4
Min. increment	10 µL
Max. increment	100 µL
EP criterion	5
EP recognition	all

Chloride

Mode	DET U
Start volume	1 mL
Drift	50 mV/min
Max. waiting time	26 s
Meas. point density	4
Min. increment	10 µL
EP criterion	5
EP recognition	greatest

Fluoride

Mode	MEAS Conc
Signal drift	0.5 mV/min
Min. waiting time	30 s
Max. waiting time	215 s
Measuring interval	0.5 s

Calculations

Cell constant

$$\text{Cell constant} = \frac{\sigma_{\text{nom}}}{\sigma_{\text{meas}}}$$

Cell constant: The current cell constant

σ_{nom} : The nominal conductance

σ_{meas} : The measured conductance

Titer

$$\text{Titer} = \frac{V_{\text{Std}} \times C_{\text{Std}}}{V_{\text{EP1}} \times C_{\text{Titrant}}}$$

Titer: Correction factor (dimensionless) for the exact concentration of the titrant

V_{Std} : Added volume of standard solution in mL

C_{Std} : Exact concentration of standard solution in mol/L

V_{EP1} : Titrant consumption until the first equivalence point in mL

C_{Titrant} : Concentration of titrant in mol/L

Alkalinity

$$\text{p-value} = \frac{V_{\text{FP1}} \times C_{\text{HCl}} \times f \times 1000}{V_{\text{s}}}$$

p-value: Amount of carbonate in the sample in mmol/L

V_{FP1} : Titrant consumption until the first fixed endpoint (pH = 8.2) in mL

C_{HCl} : Concentration of titrant in mol/L; here $c(\text{HCl}) = 0.1 \text{ mol/L}$

f: Correction factor («titer»), dimensionless

1000: Conversion factor to obtain result in mmol/L

V_{s} : Sample size in mL

$$\text{m-value} = \frac{V_{\text{FP2}} \times C_{\text{HCl}} \times f \times 1000}{V_{\text{s}}}$$

m-value: Amount of total alkalinity in the sample in mmol/L

V_{FP2} : Titrant consumption until the second fixed endpoint (pH = 4.3) in mL

Hardness

$$\text{Ca hardness} = \frac{V_{\text{EP1}} \times C_{\text{EDTA}} \times f \times 1000}{V_{\text{s}}}$$

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 $c(\text{EDTA}) = 0.1 \text{ mol/L}$

f: Correction factor («titer»), dimensionless

1000: Conversion factor to obtain result in mmol/L

V_{s} : Sample size in mL

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

Mg hardness: Amount of magnesium in the sample in mmol/L

V_{EP2} : Titrant consumption until the second equivalence point in mL

$$\text{Total hardness} = \frac{V_{\text{EP2}} \times C_{\text{EDTA}} \times f \times 1000}{V_{\text{s}}}$$

Total hardness: Total hardness of the sample in mmol/L

Chloride

$$Cl = \frac{V_{EP1} \times c_{AgNO_3} \times M_A \times f \times 1000}{V_s}$$

Cl:	Amount of chloride in the sample in mg/L
V_{EP1} :	Titration consumption until the first equivalence point in mL
c_{AgNO_3} :	Concentration of titrant in mol/L; here $c(AgNO_3) = 0.01$ mol/L
M_A :	Molar mass of analyte; here 35.45 g/mol
f:	Correction factor («titer»), dimensionless
1000:	Conversion factor to obtain result in mg/L
V_s :	Sample size in mL

Fluoride

The result is automatically calculated by the software.

Example determinations

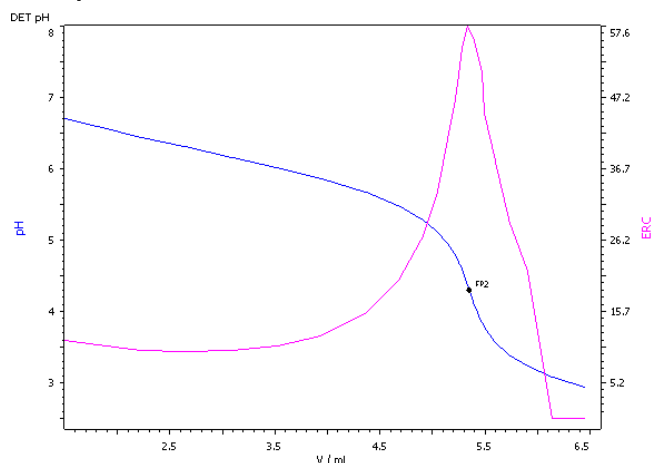


Fig. 1: Determination of the alkalinity

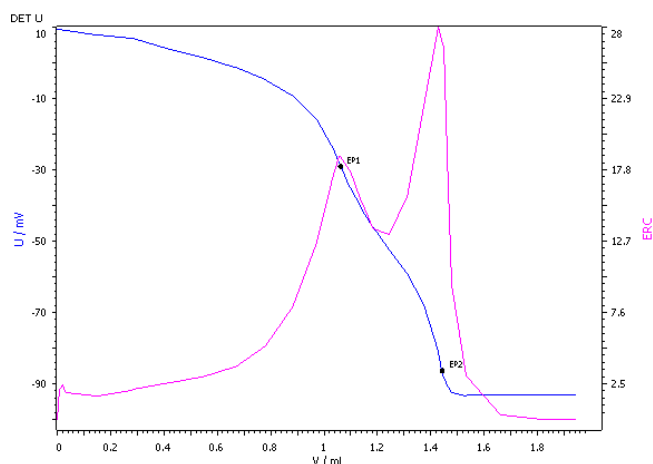


Fig. 2: Hardness determination

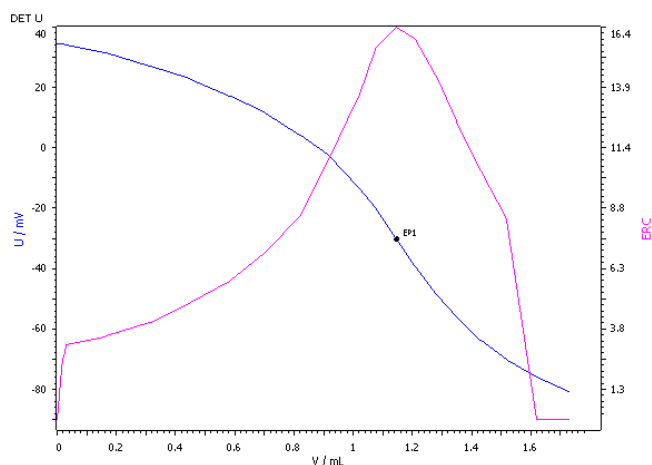


Fig. 3: Determination of the chloride content

Comments

- It takes about 15 minutes to measure all parameters.
- The beakers must be filled with a minimum of 250 mL sample to carry out all determinations.
- Automated systems, including ion chromatography for water analysis, are also offered by Metrohm under the name «TitrIC». For further information see Metrohm Application Note AN-S-387.
- The conductivity measuring cell can be cleaned using the polishing set 6.2802.000.
- The volume needed to reach the equivalence point should lie between 10–90% of the burette volume containing the titrant.

References

- Metrohm Application Bulletin AB- 221
Standard methods in water analysis

Permanganate Index according to EN ISO 8467

filled up to the mark with dist.
H₂O.

Instruments

- Sample changer with swing head
- External titration stand
- Titrator with DET mode
- Stirrer
- 50 mL burette (Transfer)
- 10 mL burette 2 × (Na₂C₂O₄ and KMnO₄)
- Titration vessel with thermostat jacket
- Thermostat

Electrodes

Pt- Titrode or iPt-Titrode with 854 iConnect	6.0431.100 6.0471.300 2.854.0010
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Reagents

- Sulfuric acid, concentrated, purum
- Disodium oxalate, Na₂C₂O₄, p.a.
- Potassium permanganate, c(KMnO₄) = 2 mol/L volumetric solution

Solutions

Oxalate solution c(Na ₂ C ₂ O ₄) = 5 mmol/L	Disodium oxalate is dried at 120 °C and allowed to cool down in a desiccator. 0.67 g is dissolved in 1 L dist. H ₂ O.
KMnO ₄ solution, c(KMnO ₄) = 2 mmol/L	The volumetric solution is diluted 1:10 with dist. H ₂ O.
Sulfuric acid, c(H ₂ SO ₄) = 2 mol/L	500 mL dist. H ₂ O is put into a 1 L volumetric flask, 110 mL conc. H ₂ SO ₄ is added. c(KMnO ₄) = 2 mmol/L solution is added until a slight pink color remains. After cooling down, the flask is filled up to the mark with dist. H ₂ O.
Sulfuric acid, c(H ₂ SO ₄) = 7.5 mol/L	500 mL dist. H ₂ O is put into a 1 L volumetric flask. Approx. 420 mL conc. H ₂ SO ₄ is added. After cooling down, the flask is

Sample preparation

Before the determination can be started, the thermostat connected to the titration vessel must be heated up to approximately 110 °C.

To all samples, blanks, and standards, 5 mL c(H₂SO₄) = 7.5 mol/L should be added in advance.

Analysis

Blank and standardization

Blank samples are covered with aluminum foil and placed on the rack. The following steps are carried out by the system.

25 mL of blank sample is pipetted into the titration vessel. The pipetting loop is rinsed with 5 mL c(H₂SO₄) = 2 mol/L and the rinsing solution is added to the titration vessel. The sample solution is heated for 10 min according to DIN EN ISO 8467. Then, 5 mL c(KMnO₄) = 2 mmol/L is added and the sample is stirred for 10 min.

5.5 mL c(Na₂C₂O₄) = 5 mmol/L is added and the excess is back-titrated with c(KMnO₄) = 2 mmol/L. The consumption for the first equivalence point is the blank value.

To standardize the titrant, 5.5 mL c(Na₂C₂O₄) = 5 mmol/L is added again and another back-titration with c(KMnO₄) = 2 mmol/L is carried out. The consumption for the first equivalence point corresponds to the titer value.

The titration vessel is then automatically cleaned and emptied.

Sample

The samples are covered with aluminum foil and placed on the rack. The following steps are carried out by the system.

25 mL of sample are pipetted into the titration vessel. The pipetting loop is rinsed with 5 mL c(H₂SO₄) = 2 mol/L and the rinsing solution is added to the titration vessel. The sample solution is heated for 10 min according to DIN EN ISO 8467. 5 mL c(KMnO₄) = 2 mmol/L is added and the sample is stirred for another 10 min.

5.5 mL c(Na₂C₂O₄) = 5 mmol/L is added and the excess is back-titrated with c(KMnO₄) = 2 mmol/L. The consumption for the first equivalence point corresponds to the permanganate index (PMI).

The titration vessel is then automatically cleaned and emptied.

Parameters

Method	DET U
Start volume	0.05 mL
Stirring rate	6
Signal drift	50 mV/min
Min. waiting time	2 s
Max. waiting time	26 s
Meas. point density	0
Min. increment	20 µL
Max. increment	100 µL
EP criterion	50
Stop EP	1
Volume after EP	0.2 mL

Calculations

Blank = $V_{EP1}(\text{Blank})$

Blank: Volume for blank in mL

$V_{EP1}(\text{Blank})$: Titrant consumption until the first equivalence point in mL for the blank determination

$k = V_{EP1}(\text{Std}) + V_{KMnO_4} - \text{Blank}$

k: Value of the standardization in mL

$V_{EP1}(\text{Std})$: Titrant consumption until the first equivalence point in mL for the standardization determination

V_{KMnO_4} : End volume of $KMnO_4$ needed for the blank determination in mL

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

PMI: Permanganate index in mg/L

V_{EP1} : Titrant consumption until the first equivalence point in mL

$V_{Na_2C_2O_4}$: 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

V_s : Sample size in mL

Example determination

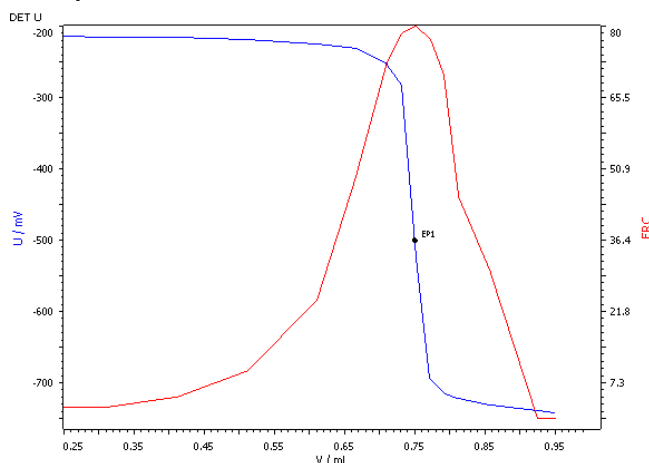


Fig. 4: Determination of the PMI of tap water.

Comments

- One determination takes about 30 minutes, out of which 20 min is attributed to waiting times necessary for a complete reaction.
- To have better results, it is important to cover the beakers with aluminum foil. Without the foil covers the results will differ over the time because the samples are exposed. The first blank after a longer standby time should be discarded since the value found is usually too high.
- To prevent manganese dioxide crystals gathering in the burette, it is recommended to use high, narrow bottles, and the aspiration tip of the burette 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.

References

- EN ISO 8467
Water quality – determination of permanganate index

Chemical Oxygen Demand according to DIN 38409-44

Instruments

- Sample changer
- Titrator with DET mode
- Stirrer
- Burette 2 mL (chromium(III) potassium solution)
- Burette 20 mL $\times$ (sample, potassium dichromate, titrant)
- Burette 50 mL (ultrapure water)

Electrodes

Combined Au-ring electrode or Micro Au Titrode	6.0452.100 6.0435.110
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Reagents

- Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, p.a.
- Mercury sulfate, HgSO_4 , p.a.
- Sulfuric acid, H_2SO_4 , p.a.
- Silver(I) sulfate, Ag_2SO_4 , p.a.
- Chromium(III) potassium sulfate dodecahydrate, $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, p.a.
- Ammonium iron(II) sulfate hexahydrate, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, p.a.
- Ultrapure water

Solutions

Reaction solution	$\beta(\text{K}_2\text{Cr}_2\text{O}_7) = 1.471 \text{ g/L}$ and $\beta(\text{HgSO}_4) = 20 \text{ g/L}$ in sulfuric acid If possible, this solution should be bought directly from a distributor.
Ag_2SO_4 in sulfuric acid	$\beta(\text{Ag}_2\text{SO}_4) = 10 \text{ g/L}$ This solution should be prepared at least a day in advance.
$\text{KCr}(\text{SO}_4)_2$ solution	$\beta(\text{KCr}(\text{SO}_4)_2 \cdot 12 \text{ H}_2\text{O}) = 25 \text{ g/L}$
Titant	$c((\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6 \text{ H}_2\text{O}) = 0.015 \text{ mol/L}$

Sample preparation

For the blanks, 20 mL ultrapure water is added instead of 20 mL sample solution.

The sample volume is added into the reaction tube, followed by 0.5 mL of chromium(III) potassium sulfate solution and 10 mL of reaction solution.

40 mL of silver(I) sulfate in sulfuric acid is 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. When the tubes have reached room temperature, they are positioned in the sample changer.

Analysis

Titer

10 mL of the reaction solution is dosed into a titration vessel, followed by 90 mL of ultrapure H_2O . 20 mL of sulfuric acid is added under stirring. The solution is stirred for 10 min followed by the titration with ammonium iron(II) sulfate solution. After the titration, the vessel is cleaned, and all waste solution is removed using the pumps.

Blank

The prepared blank is stirred for 20 s before titration with ammonium iron(II) sulfate solution. After the titration the vessel is cleaned, and all waste solution is removed using the pumps.

Sample

The prepared sample solution is stirred for 20 s before titration with ammonium iron(II) sulfate solution. After the titration the vessel is cleaned, and all waste solution is removed using the pumps.

Parameters

Titer

Method	DET U
Start volume	10 mL
Pause	20 s
Signal drift	10 mV/min
Min. waiting time	5 s
Max. waiting time	20 s
Meas. point density	2
Min. increment	50 μL
Max. increment	500 μL
EP criterion	50
EP recognition	greatest

Blank

Method	DET U
Start volume	10 mL
Pause	20 s
Signal drift	10 mV/min
Min. waiting time	5 s
Max. waiting time	20 s
Meas. point density	2
Min. increment	25 µL
Max. increment	500 µL
EP criterion	50
EP recognition	greatest

Sample

Method	DET U
Signal drift	10 mV/min
Min. waiting time	5 s
Max. waiting time	20 s
Meas. point density	2
Min. increment	25 µL
Max. increment	500 µL
EP criterion	50
EP recognition	greatest

Calculations

Blank = V_{EP1}

Blank: Volume for blank in mL

V_{EP1} : Titrant consumption until the first equivalence point in mL

$$f = \frac{V_{K_2Cr_2O_7} \times c_{K_2Cr_2O_7} \times EF_1}{V_{EP1} \times c_{(NH_4)_2Fe(SO_4)_2}}$$

f: Value for titer

$V_{K_2Cr_2O_7}$: Prepared volume of potassium dichromate solution in mL

$c_{K_2Cr_2O_7}$: Exact concentration of the potassium dichromate solution in mol/L

EF_1 : Equivalence factor; here 6

$c_{(NH_4)_2Fe(SO_4)_2}$: Concentration of the ammonium iron(II) sulfate solution in mol/L

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

COD: Chemical oxygen demand in mg/L

EF_2 : Equivalence factor; here 8000 mg/mol

V_s : Sample size in mL

Example

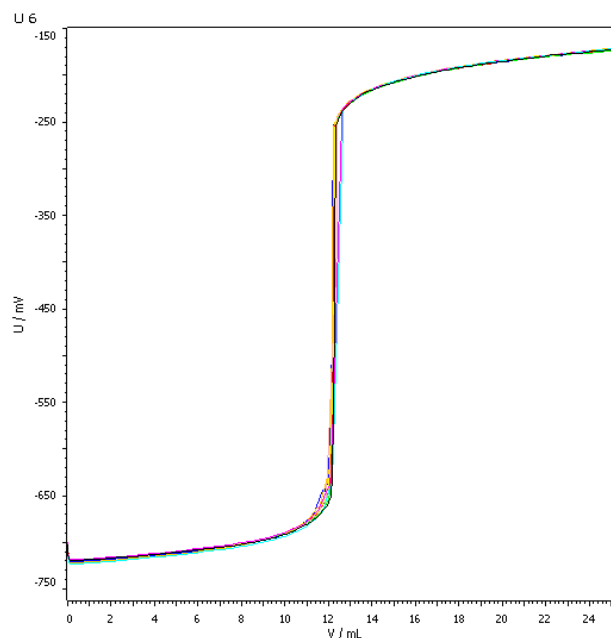


Fig. 5: Titration series indicating the high reproducibility for an automated COD determination (n = 9).

Comments

- Mercury(II) sulfate, potassium dichromate and silver sulfate are highly toxic. Handling these substances requires a totally safe and careful operation process.
- All disposed chemicals have to be collected in a canister. Because of the high toxic composition, this waste has to be disposed of by a professional chemical waste management company.
- Only ultrapure water should be used to assure a minimal contamination.

References

- DIN 38409-44
German standard methods for the examination of water, waste water and sludge; parameters characterizing effects and substances (group H); determination of the chemical oxygen demand (COD), ranging from 5 to 50 mg/L

Author

Competence Center Titration

Metrohm International Headquarters

Appendix

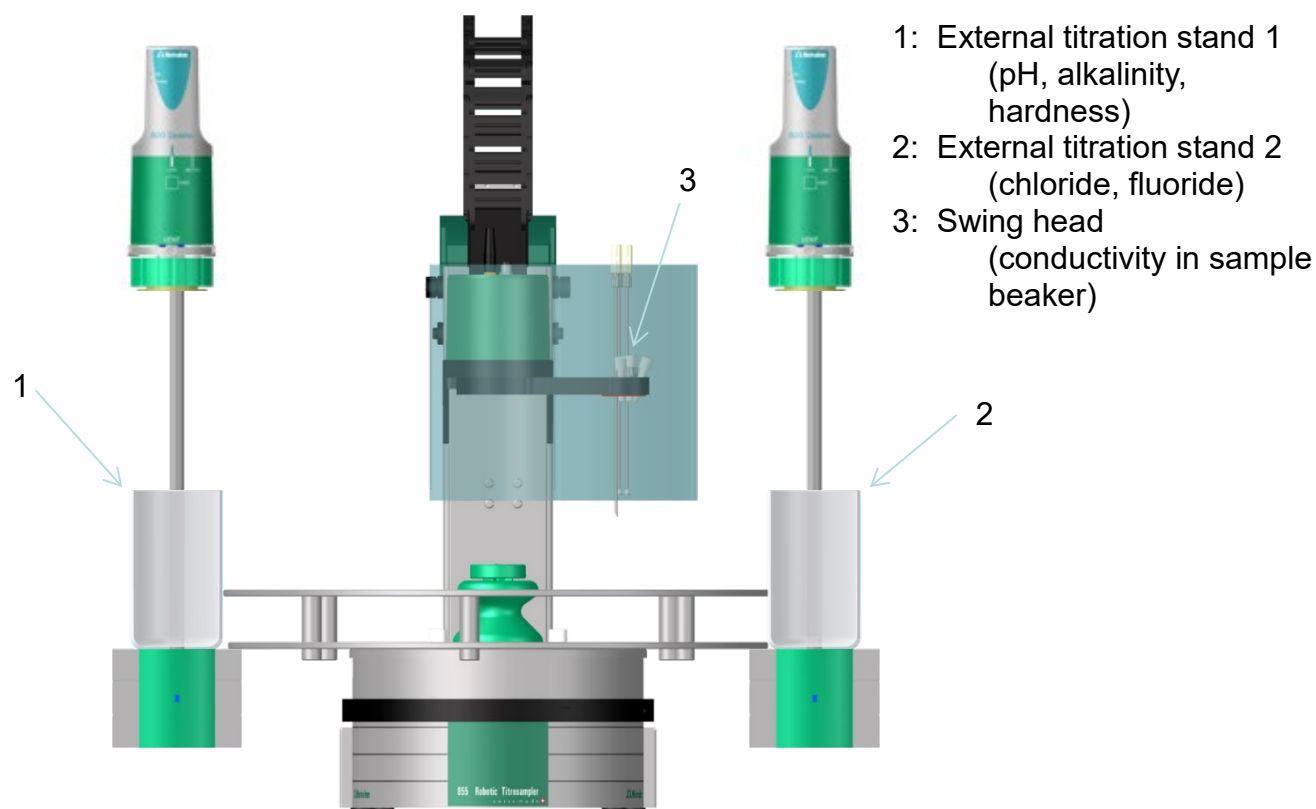


Fig. 6: Schematic view of the sample changer for the determination of the conductivity, pH, alkalinity, hardness, chloride, and fluoride content.

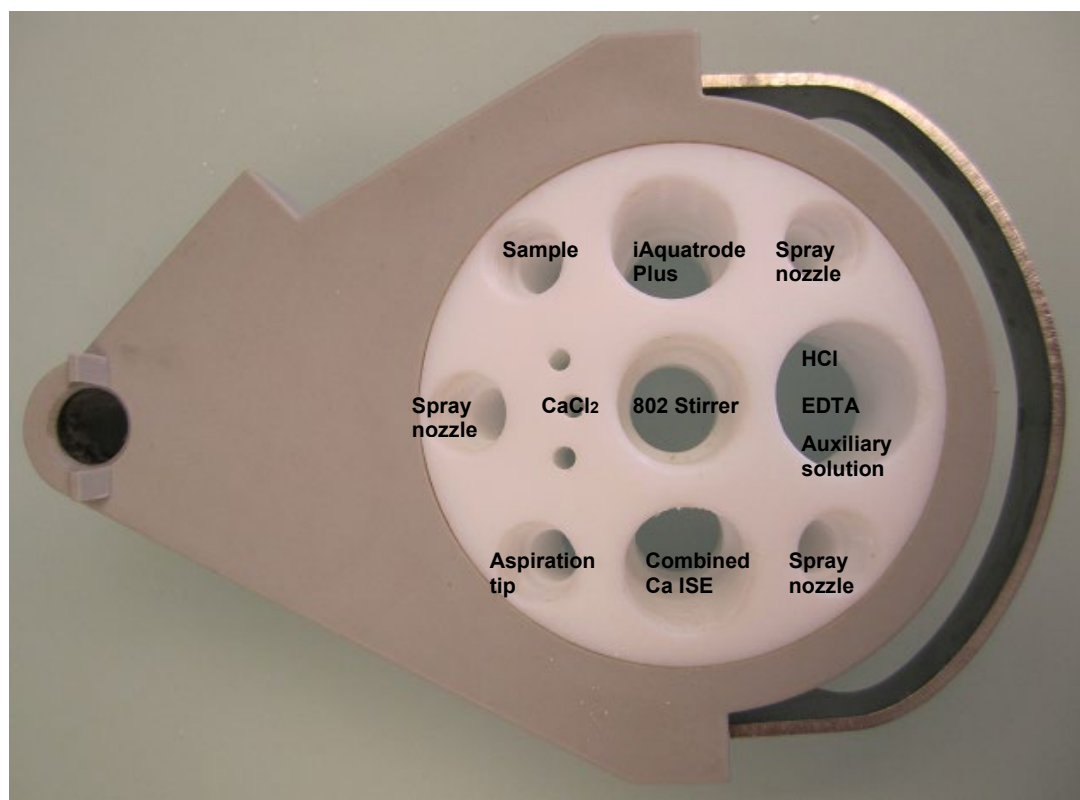


Fig. 7: Distribution of the electrodes and solutions for the determination of the pH, alkalinity, and hardness in the external titration vessel 1. For the addition of HCl, EDTA, and the auxiliary solution, a triburette was used.

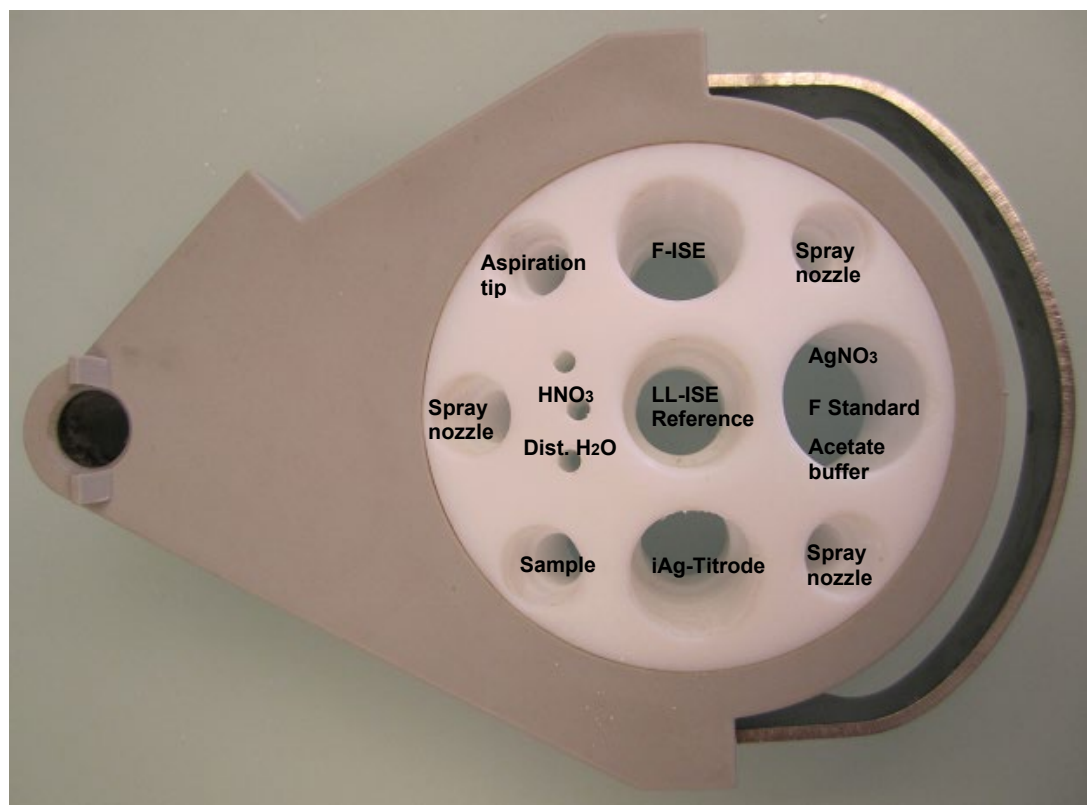


Fig. 8: Distribution of the electrodes and solutions for the determination of the chloride and fluoride content in the external titration vessel 2. For the addition of AgNO₃, F⁻ standard, and the acetate buffer, a triburette was used.