

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; 6.0502.150; 6.0750.100; 6.0452.100; 6.0435.110; 6.0431.100; 6.0471.300; EN ISO 8467; DIN 38409-44

Summary

The determination of the physical and chemical parameters 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 the water quality. This bulletin describes how to determine the above mentioned parameters in a single analytical run.

Further important parameters in water analysis are the permanganate index (PMI) and the chemical oxygen demand (COD). Therefore, this Bulletin additionally 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 Pt 1000	6.0277.300
iAg-Titrode	6.0470.300
854 iConnect, 2×	2.854.0010
F selective electrode	6.0502.150
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	<p>Acetylactone and TRIS; $c(\text{acetylactone}) = 0.1 \text{ mol/L}$ 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. H₂O. 12 mL acetylactone is added and the solution is made up to the mark with dist. H₂O. This solution can only be used for a few days. It masks Fe³⁺ and Al³⁺ for a better differentiation of Ca²⁺ and Mg²⁺.</p>
Acetate buffer	<p>58 g NaCl is weighed into a 1 L volumetric flask and dissolved in approx. 500 mL dist. H₂O. 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. H₂O.</p>
Buffer pH 10	<p>54 g NH₄Cl and 350 mL $w(\text{NH}_3) = 25\%$ are dissolved in dist. H₂O and made up to 1 L with dist. H₂O.</p>

Standard solutions

Fluoride standard	<p>$\beta = 100 \text{ mg/L F}^-$ 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. H₂O. 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. H₂O.</p>
TRIS standard	<p>TRIS is dried over night 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 TRIS in dist. H₂O and filling up to the mark with dist. H₂O.</p>

Ca ²⁺ standard	<p>It is recommended to use a prepared standard (e.g., the certified Metrohm ion standard CaCl₂, 6.2301.070). Otherwise CaCO₃ is dried over night 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 CaCO₃ in approx. 100 mL dist. H₂O and adding drop by drop $c(\text{HCl}) = 5 \text{ mol/L}$, until all CaCO₃ is dissolved. The solution is then made up to 1 L with dist. H₂O.</p>
Cl ⁻ standard	<p>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 over night 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. H₂O.</p>
Conductivity standard	<p>It is recommended to use a prepared standard (e.g., the certified Metrohm conductivity standards 6.2324.010 or 6.2301.060).</p>

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 three times dipped into the standard.

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(HCl) = 0.1 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(EDTA) = 0.1 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(HNO₃) = 2 mol/L is added. After the addition of 40 mL of dist. H₂O, the solution is titrated using c(AgNO₃) = 0.01 mol/L until the first equivalence point. A threefold determination should be carried out.

Calibration of F-ISE

For the calibration of the F-ISE, an appropriate amount of fluoride standard is dosed into the titration vessel equipped with the F-ISE and LL ISE Reference electrode. The standard is then diluted up to 15 mL with dist. H₂O. 15 mL acetate buffer are 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 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 3 times for preconditioning into the sample. Then, the conductivity is measured.

5 to 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(HCl) = 0.1 mol/L.

Directly after the alkalinity determination, 15 mL of the auxiliary solution are added. The hardness of the sample solution is determined by titration with c(EDTA) = 0.1 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(HNO₃) = 2 mol/L are added and the titration of chloride with c(AgNO₃) = 0.01 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 dist. 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	9999 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} :	Titrant 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 instrument / software.

Example determinations

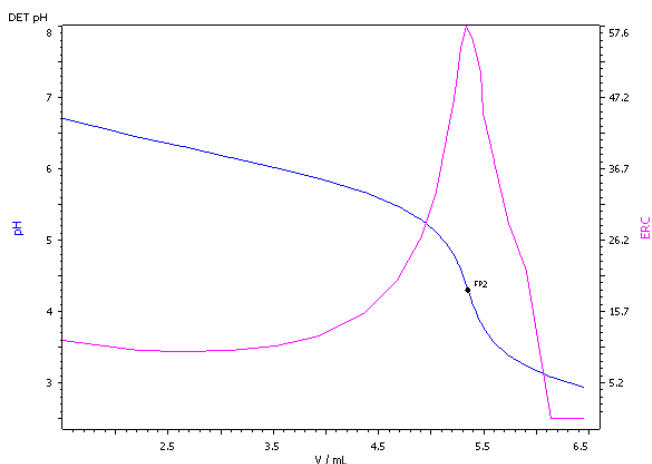


Fig. 1: Determination of the alkalinity

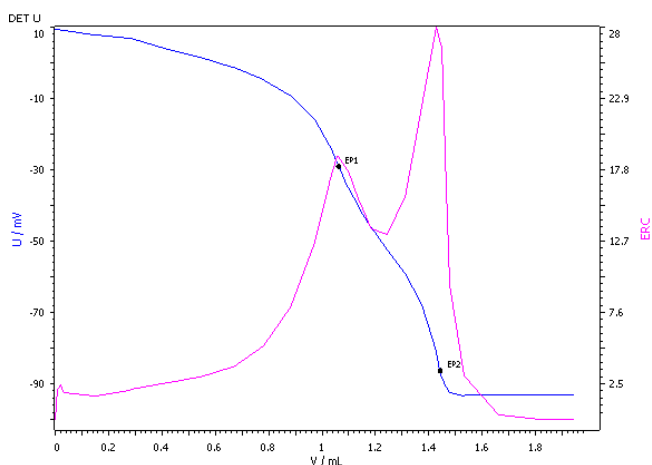


Fig. 2: Hardness determination

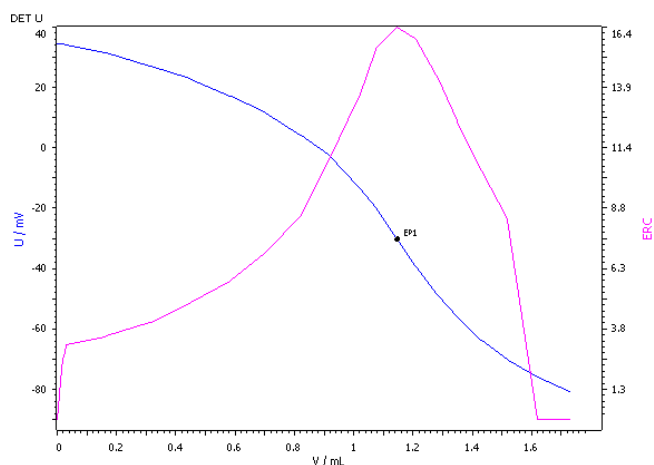


Fig. 3: Determination of the chloride content

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 Bulletin AB-301, AB-302, AB-303 and Metrohm Application Note AN-S-300.
- 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 to 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 are filled 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 are filled 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 aluminium foil and placed on the rack. The following steps are carried out by the system.

25 mL of blank 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. Then, 5 mL c(KMnO₄) = 2 mmol/L are added and the sample is stirred for 10 min.

5.5 mL c(Na₂C₂O₄) = 5 mmol/L are 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 are again added 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 aluminium 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 are added and the sample is stirred for another 10 min.

5.5 mL c(Na₂C₂O₄) = 5 mmol/L are 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
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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

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

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

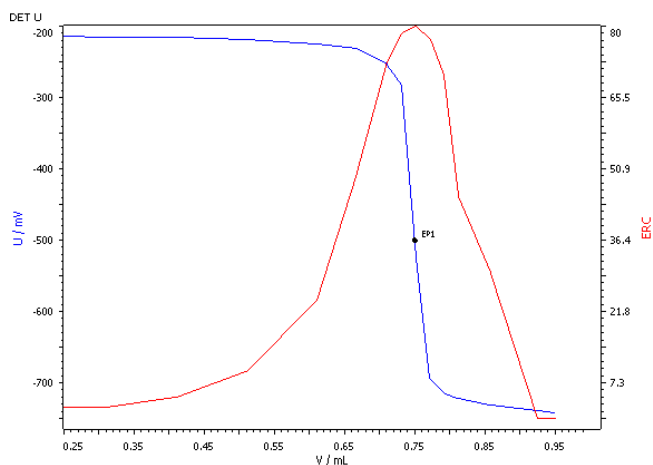


Fig. 4: Determination of the PMI of tap water.

Comments

- One determination takes about 30 minutes thereof 20 min are due to waiting times necessary for a complete reaction.
- To have better results, it is important to cover the beakers with aluminium foils. Without the foils the results will differ over the time because the samples stand open. The first blank after a longer standby time should be discarded; the value found is usually too high.
- To prevent manganese dioxide crystals 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 3 × (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, $K_2Cr_2O_7$, 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, $KCr(SO_4)_2 \cdot 12H_2O$, p.a.
- Ammonium iron(II) sulfate hexahydrate, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, p.a.
- Ultrapure water

Solutions

Reaction solution	$\beta(K_2Cr_2O_7) = 1.471$ g/L and $\beta(HgSO_4) = 20$ g/L in sulfuric acid If possible this solution should be directly bought from a distributor.
Ag_2SO_4 in sulfuric acid	$\beta(Ag_2SO_4) = 10$ g/L This solution should be prepared at least a day in advance.
$KCr(SO_4)_2$ solution	$\beta(KCr(SO_4)_2 \cdot 12 H_2O) = 25$ g/L
Titant	$c((NH_4)_2Fe(SO_4)_2 \cdot 6 H_2O) = 0.015$ mol/L

Sample preparation

For the blanks, 20 mL ultrapure water are 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 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. When the tubes have reached room temperature, they are positioned in the sample changer.

Analysis

Titer

10 mL of the reaction solution are dosed into a titration vessel, followed by 90 mL of ultrapure H_2O . 20 mL of sulfuric acid are 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 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 μ L
Max. increment	500 μ L
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

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

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

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

COD: Chemical oxygen demand in mg/L

EF_2 : Equivalence factor, here 8000 mg/mol
 V_s : Sample size in mL

Example

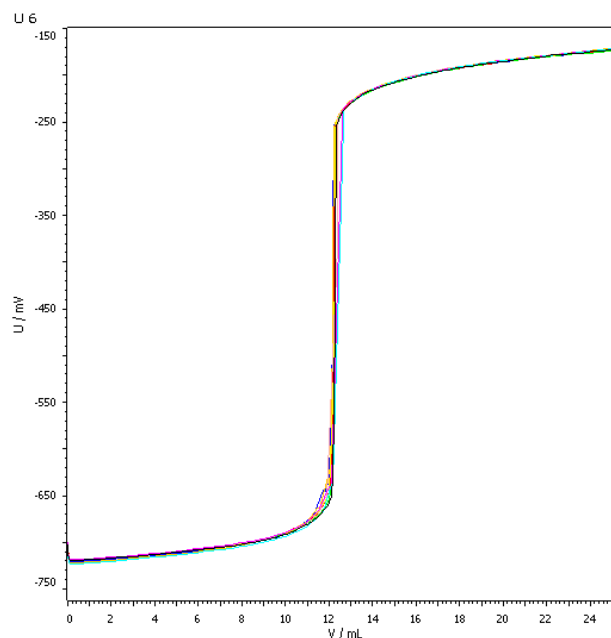


Fig. 5: Titration series indicating the high reproducibility for an automated COD determination (n = 9).

Comments

- Mercury(II) sulfate, potassium dichromate and silver sulfate are highly toxic. Handling those 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 depolluted 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

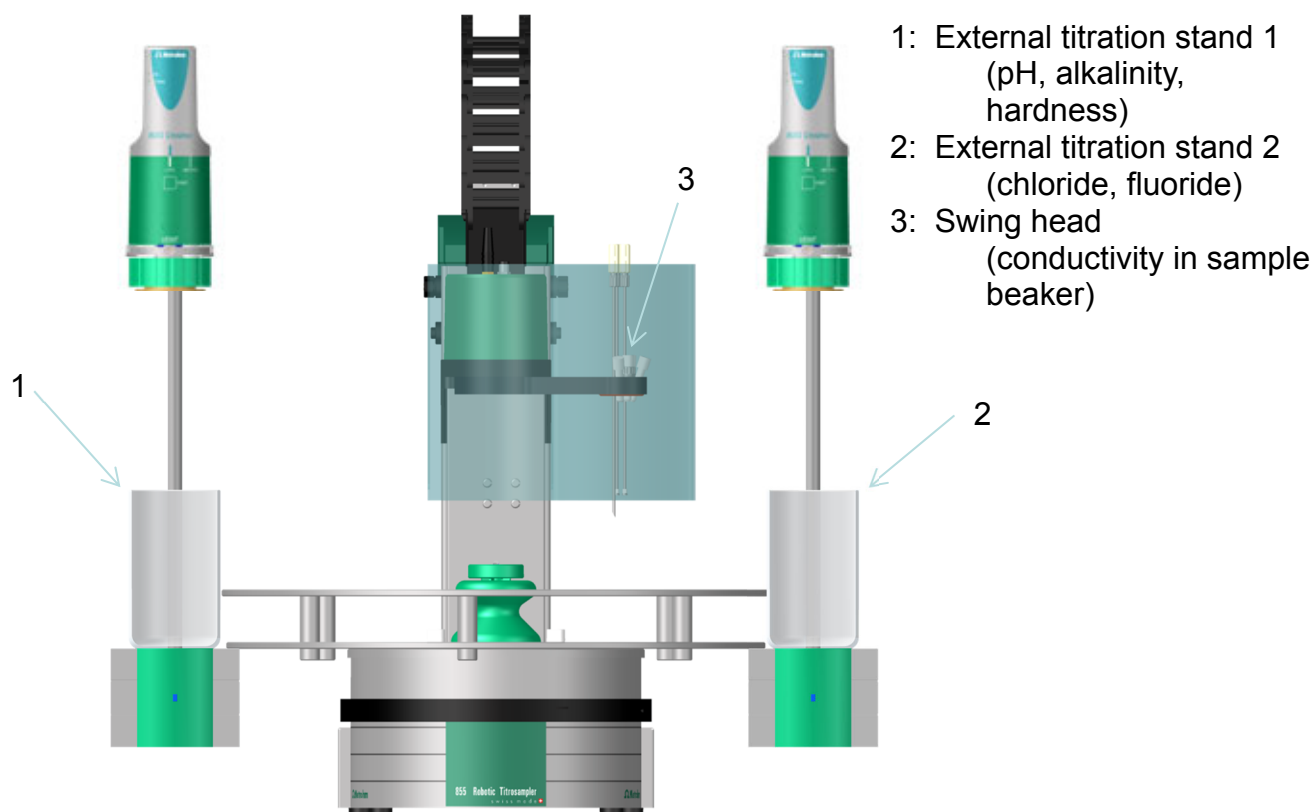


Fig. 6: Schematic view of the sample changer for the determination of the conductivity, pH, alkalinity, hardness, chloride and fluoride content.

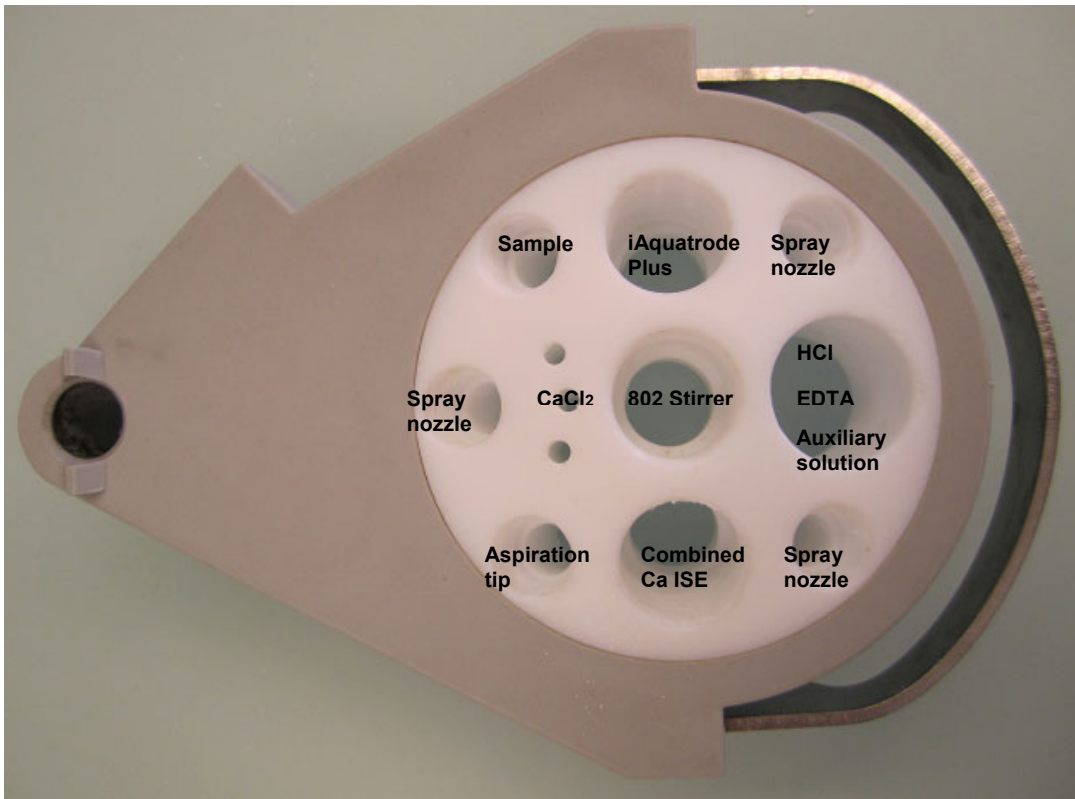


Fig. 7: Distribution of the electrodes and solutions for the determination of the pH, alkalinity and hardness in the external titration vessel 1. For the addition of HCl, EDTA, and the auxiliary solution a triburette was used.

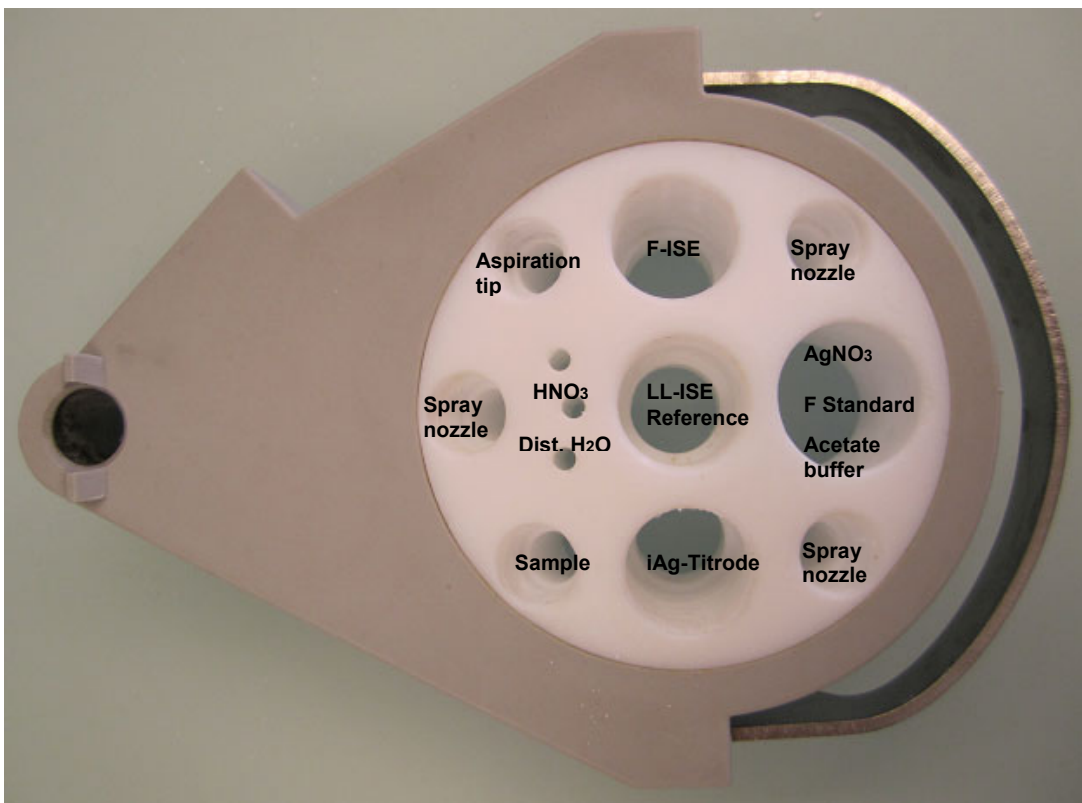


Fig. 8: Distribution of the electrodes and solutions for the determination of the chloride and fluoride content in the external titration vessel 2. For the addition of AgNO₃, F⁻ standard and the acetate buffer a triburette was used.