

Application Bulletin 143/3 e

Determination of complexing agents in detergents

Branch

General analytical chemistry; detergents, surfactants, cosmetics

Keywords

Detergents; titration; potentiometric titration; EDTA; NTA; citrate; complexing agent; chelating agent; soap; washing agents; ethylenediaminetetraacetic acid; nitrilotriacetate; branch 1; branch 12; Cu ISE; 6.0502.140; ASTM; D4608; D4954; D1767; ISO; ISO 4325

Summary

Application Bulletin No. 76 describes the polarographic determination of small concentrations (1–100 mg/L) of NTA and EDTA in water. In certain countries, legislation has been introduced requiring that phosphates in washing agents should be replaced. Therefore, complexing agents such as NTA, EDTA, and citrate have become more and more important as complexing agents and builders.

This bulletin describes the determination of higher (>100 mg/L) concentrations of complexing agents in washing agents by potentiometric titration. The ion-selective copper electrode (Cu-ISE) is used as indicator electrode. Other components normally found in washing agents do not interfere with this determination.

Determination of EDTA

Summary

The EDTA determination is based on the ASTM D1767 using copper sulfate as titrant. Instead of a photometric titration the EDTA content is determined potentiometrically.

Instruments

- Titrator with SET and MET mode
- 10 mL buret, 2x
- Stirrer

Electrode

Cu ISE	6.0502.140
Unitrode with Pt1000 (Head U)	6.0258.600

Reagents

- Copper sulfate pentahydrate, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, p.a.
- Glacial acetic acid, CH_3COOH , p.a.
- Ethylenediaminetetraacetic acid disodium salt dihydrate, EDTA, p.a.
- Ammonium acetate, $\text{NH}_4\text{CH}_3\text{COO}$, p.a.

Solutions

Titrant	$c(\text{CuSO}_4) = 0.01 \text{ mol/L}$ 2.497 g $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ is weighed into a 1 L volumetric flask and dissolved in deion. H_2O . The flask is then filled up to the mark with deion. H_2O .
Acetate buffer	116 g ammonium acetate is weighed into a 1 L volumetric flask and dissolved in deion. H_2O . 86 mL glacial acetic acid is added. The flask is then filled up to the mark with deion. H_2O .

Standard solution

c(EDTA) = 0.01 mol/L	EDTA is dried over night in a drying oven at 105 °C and allowed to cool down in a desiccator for at least 1 h. 0.372 g EDTA is weighed into a 100 mL volumetric flask and dissolved in deion. H ₂ O. The flask is then filled up to the mark with deion. H ₂ O.
-------------------------	--

Sample preparation

No sample preparation is required. In some cases the removal of fatty acids by filtration through a wet filter paper leads to sharper equivalence points.

Analysis

Titer

5 mL of the EDTA standard solution is pipetted into a titration vessel. About 75 mL deion. H₂O and 5 mL acetate buffer are added. The sample is then titrated with c(CuSO₄) = 0.01 mol/L until after the equivalence point.

Sample

A 3–5 g portion of sample (approx. 1% EDTA content) is weighed into a titration vessel. About 75 mL deion. H₂O is added and the pH is adjusted to approximately 5 with glacial acetic acid using a SET titration. The sample is then titrated with c(CuSO₄) = 0.01 mol/L until after the equivalence point.

Parameters

Titer and Sample

Mode	MET U
Stirring rate	8
Signal drift	30 mV/min
Max. waiting time	32 s
Volume increment	0.05 mL
Stop volume	10 mL
EP criterion	30 mV
EP recognition	greatest

Sample - SET pH

Mode	SET pH
Stirring rate	8
EP at pH	5.0
Dynamics	2
Max. rate	10 mL/min
Min. rate	25 µL/min
Stop criterion	Drift
Stop drift	20 µL/min

Calculation

Titer

$$f = \frac{V_{\text{EDTA}} \times c_{\text{EDTA}}}{V_{\text{EP1}} \times c_{\text{CuSO}_4}}$$

f: Titer of the copper sulfate solution; c(CuSO₄) = 0.01 mol/L

V_{EDTA}: Volume of EDTA standard solution in mL

c_{EDTA}: Exact concentration of the EDTA standard solution in mol/L

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

c_{CuSO₄}: Concentration of the titrant in mol/L; here c(CuSO₄) = 0.01 mol/L

Sample

$$w_{\text{EDTA}} = \frac{V_{\text{EP1}} \times c_{\text{CuSO}_4} \times f \times M_{\text{A}} \times 0.1}{m_{\text{s}}}$$

w_{EDTA}: Content of EDTA in %

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

c_{CuSO₄}: Concentration of the titrant in mol/L; here c(CuSO₄) = 0.01 mol/L

f: Titer of CuSO₄

M_A: Molecular weight of the analyte (EDTA); 372.24 g/mol

m_s: Sample size in g

0.1: Conversion factor

Example determination

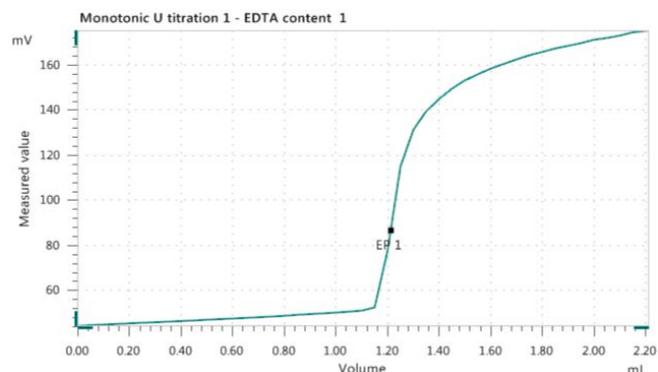


Fig. 1: Titration curve of the determination of EDTA in detergents.

Comments

- For Titrandos, the internal reference electrode of the Unitrode can be used for the Cu ISE with the strand 6.2106.020.
- For the OMNIS Titrators, the internal reference of the Unitrode is automatically used for the Cu ISE when both electrodes are connected to the same analog measuring module.
- Other chelating agents which react with copper (e.g., citrate, formate, NTA and phosphate) interfere with this determination.
- For a separate determination of EDTA apart from other chelating agents, please refer to AB-076 - Polarographic determination of nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA) according to DIN 38413 part 5
- The advantage of the potentiometric titration over the photometric titration is that no indicator solution is necessary and the equivalence point is not influenced by turbidity.
- The ISO 4325 is very similar to ASTM D1767. The main difference is the titration at elevated temperature.
- For detergents which strongly foam upon the addition of the glacial acetic acid, a larger portion should be dissolved in approx. 100 mL deion. H₂O. The pH of this solution is then adjusted to 7 using glacial acetic acid (strong foam formation). The neutralized solution is then quantitatively transferred into a 500 mL volumetric flask and made up the mark with deion. H₂O. This stock solution should then be used for the titration.

References

- ASTM D1767-89(2009)
Standard Test Method for Ethylene Diamine Tetraacetate (EDTA) in Soaps or Synthetic Detergents
- ISO 4325:1990
Soaps and detergents -- Determination of chelating agent content -- Titrimetric method

Determination of NTA

Summary

The nitrilotriacetate (NTA) content is determined in accordance with ASTM D4954 by a back-titration of an excess of cupric nitrate.

Instruments

- Titrator with SET and MET mode
- 20 mL buret, 2x (NTA, NaOH)
- 50 mL buret (EDTA)
- Stirrer

Electrode

Cu ISE	6.0502.140
Unitrode with Pt1000 (Head U)	6.0258.600

Reagents

- Cupric nitrate trihydrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$, p.a.
- Nitric acid, HNO_3 , conc, p.a.
- Ethylenediaminetetraacetic acid disodium salt dehydrate, EDTA, p.a.
- Sodium acetate trihydrate, $\text{NaCH}_3\text{COO} \cdot 3 \text{H}_2\text{O}$, p.a.
- Glacial acetic acid, CH_3COOH , p.a.
- Sodium hydroxide, NaOH, p.a.
- Trisodium nitrilotriacetate monohydrate, $\text{N}(\text{CH}_2\text{COONa})_3 \cdot \text{H}_2\text{O}$, NTA, p.a.

Solutions

Titrant	$c(\text{NTA}) = 0.3 \text{ mol/L}$ 41 g NTA is weighed into a 500 mL volumetric flask and dissolved in deion. H_2O . The flask is then filled up to the mark with deion. H_2O .
$\text{Cu}(\text{NO}_3)_2$ solution	$c(\text{Cu}(\text{NO}_3)_2) = 0.1 \text{ mol/L}$ 24.1 g $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ is weighed into a 1 L volumetric flask and dissolved in deion. H_2O . 5 mL conc. HNO_3 is added and the flask is then filled up to the mark with deion. H_2O .
NaOH solution	$w(\text{NaOH}) = 20\%$ 240 g NaOH is weighed into a 1 L volumetric flask and dissolved in

deion. H_2O . After cooling down the flask is filled up to the mark with deion. H_2O .

Acetate buffer

68 g sodium acetate trihydrate is weighed into a 1 L volumetric flask and dissolved in deion. H_2O . 28.6 mL glacial acetic acid is added. The flask is then filled up to the mark with deion. H_2O .

Standard solution

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

An already standardized solution should be bought from a supplier. Otherwise standardize as described in Metrohm Application Bulletin AB-206

Sample preparation

10 g sample are weighed into a 500 mL volumetric flask. The flask is filled to the mark with deion. H_2O .

Note that the sample might not dissolve completely. In this case it is necessary that the sample is stirred, while an aliquot is taken for the analysis.

Analysis

Titer $\text{Cu}(\text{NO}_3)_2$

50 mL deion H_2O , 3 mL conc. HNO_3 and 25 mL $c(\text{Cu}(\text{NO}_3)_2) = 0.1 \text{ mol/L}$ are pipetted into a 250 mL beaker. The pH is then adjusted to 1.0–1.1 with $w(\text{NaOH}) = 20\%$. 25 mL acetate buffer is added and the pH is adjusted to 4.6–4.7 with $w(\text{NaOH}) = 20\%$. After cooling down to room temperature, the sample is titrated with $c(\text{EDTA}) = 0.1 \text{ mol/L}$ until after the equivalence point.

Titer NTA

50 mL deion H_2O , 3 mL conc. HNO_3 and 25 mL $c(\text{Cu}(\text{NO}_3)_2) = 0.1 \text{ mol/L}$ are pipetted into a 250 mL beaker. The pH is then adjusted to 1.0–1.1 with $w(\text{NaOH}) = 20\%$. 25 mL acetate buffer is added and the pH is adjusted to 4.6–4.7 with $w(\text{NaOH}) = 20\%$. After cooling down to room temperature, the sample is titrated with $c(\text{NTA}) = 0.3 \text{ mol/L}$ until after the equivalence point.

Sample

A 100 mL aliquot of the prepared sample is pipetted into a 250 mL beaker. 3 mL conc. HNO_3 are added while stirring and the sample is then left to settle for 5 min. The addition of conc. HNO_3 is then continued until a pH of 0 is reached. 25 mL $c(\text{Cu}(\text{NO}_3)_2) = 0.1 \text{ mol/L}$ are added while stirring. The pH

is then adjusted to 1.0–1.1 with $w(\text{NaOH}) = 20\%$. Afterwards 25 mL acetate buffer is added and the pH is adjusted to 4.6–4.7 with $w(\text{NaOH}) = 20\%$. After cooling down to room temperature, the sample is titrated with $c(\text{NTA}) = 0.3 \text{ mol/L}$ until after the equivalence point.

Parameters

Titer $\text{Cu}(\text{NO}_3)_2$ and NTA

Mode	MET U
Pause	30 s
Stirring rate	8
Signal drift	30 mV/min
Min. waiting time	5 s
Max. waiting time	32 s
Volume increment	0.05 mL
Stop volume	10 mL
EP criterion	30 mV
EP recognition	greatest

SET pH

Mode	SET pH
Stirring rate	8
EP at pH	1.05 or 4.65
Dynamics	2
Max. rate	10 mL/min
Min. rate	25 $\mu\text{L}/\text{min}$
Stop criterion	Drift
Stop drift	20 $\mu\text{L}/\text{min}$

MET U

Mode	MET U
Pause	30 s
Stirring rate	8
Signal drift	30 mV/min
Min. waiting time	5 s
Max. waiting time	32 s
Volume increment	0.05 mL
Stop volume	10 mL
EP criterion	5 mV
EP recognition	greatest

Calculation

Titer $\text{Cu}(\text{NO}_3)_2$

$$f_{(\text{CuNO}_3)_2} = \frac{V_{\text{EP1}} \times c_{\text{EDTA}} \times f_{\text{EDTA}}}{V_{(\text{CuNO}_3)_2} \times c_{(\text{CuNO}_3)_2}}$$

- $f_{(\text{CuNO}_3)_2}$: Titer of the cupric nitrate solution
 V_{EP1} : Titrant consumption until the equivalence point in mL
 c_{EDTA} : Concentration of the EDTA standard solution; $c(\text{EDTA}) = 0.1 \text{ mol/L}$
 f_{EDTA} : Titer of the EDTA standard solution
 $V_{(\text{CuNO}_3)_2}$: Volume of cupric nitrate solution in mL; 25 mL
 $c_{(\text{CuNO}_3)_2}$: Concentration of the cupric nitrate solution; $c(\text{Cu}(\text{NO}_3)_2) = 0.1 \text{ mol/L}$

Titer NTA

$$f_{\text{NTA}} = \frac{V_{(\text{CuNO}_3)_2} \times c_{(\text{CuNO}_3)_2} \times f_{(\text{CuNO}_3)_2}}{V_{\text{EP1}} \times c_{\text{NTA}}}$$

- f_{NTA} : Titer of the NTA solution
 $V_{(\text{CuNO}_3)_2}$: Volume of cupric nitrate solution in mL; 25 mL
 $c_{(\text{CuNO}_3)_2}$: Concentration of the cupric nitrate solution; $c(\text{Cu}(\text{NO}_3)_2) = 0.1 \text{ mol/L}$
 $f_{(\text{CuNO}_3)_2}$: Titer of the cupric nitrate solution
 V_{EP1} : Titrant consumption until the equivalence point in mL
 c_{NTA} : Concentration of the NTA solution; $c(\text{NTA}) = 0.3 \text{ mol/L}$

Sample

$$w_{\text{NTA}} = \frac{(V_{(\text{CuNO}_3)_2} \times c_{(\text{CuNO}_3)_2} \times f_{(\text{CuNO}_3)_2} - V_{\text{EP1}} \times c_{\text{NTA}} \times f_{\text{NTA}}) \times M_{\text{NTA}}}{m_{\text{S}} \times 10}$$

- w_{NTA} : Content of NTA in %
 $V_{(\text{CuNO}_3)_2}$: Volume of cupric nitrate solution in mL; 25 mL
 $c_{(\text{CuNO}_3)_2}$: Concentration of the cupric nitrate solution; $c(\text{Cu}(\text{NO}_3)_2) = 0.1 \text{ mol/L}$
 $f_{(\text{CuNO}_3)_2}$: Titer of the cupric nitrate solution
 V_{EP1} : Titrant consumption until the equivalence point in mL
 c_{NTA} : Concentration of the NTA solution; $c(\text{NTA}) = 0.3 \text{ mol/L}$
 f_{NTA} : Titer of the NTA solution
 M_{NTA} : Molecular weight of the NTA; 275.10 g/mol
 m_{S} : Sample size in g present in the aliquot.
 10: Conversion factor

Example determination

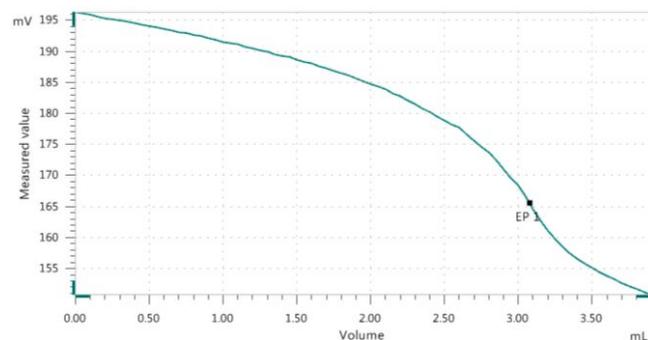


Fig. 2: Titration curve of the determination of NTA in detergents.

Comments

- For Titrandos, the internal reference electrode of the Unitrode can be used for the Cu ISE with the strand 6.2106.020.
- For the OMNIS Titrators, the internal reference of the Unitrode is automatically used for the Cu ISE when both electrodes are connected to the same analog measuring module.
- Other chelating agents which react with copper (e.g., citrate, formate, EDTA and phosphate) interfere with this determination.
- For a separate determination of NTA apart from other chelating agents, please refer to AB-076 - Polarographic determination of nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA) according to DIN 38413 part 5
- Detergents which strongly foam upon the addition of the nitric acid should be dissolved in approx. 100 mL deion. H₂O. The pH of this solution is then adjusted to 7 using conc. nitric acid (strong foam formation). The neutralized solution is then quantitatively transferred into a 500 mL volumetric flask and made up the mark with deion. H₂O. This stock solution should then be used for the titration.

References

- ASTM D4954-89(2009)
Standard Test Method for Determination of Nitrilotriacetates in Detergents
- AB-206
Titer determination in potentiometry

Determination of citrate

Summary

The citrate determination is based on the ASTM D4608 using copper sulfate as titrant.

Instruments

- Titrator with SET and MET mode
- 10 mL buret, 2x
- Stirrer

Electrode

Cu ISE	6.0502.140
Unitrode with Pt1000 (Head U)	6.0258.600

Reagents

- Copper sulfate pentahydrate, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, p.a.
- Hydrochloric acid, HCl, conc.
- Sodium hydroxide, NaOH, p.a.
- Ethylenediaminetetraacetic acid disodium salt dehydrate, EDTA, p.a.
- Sodium borate pentahydrate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$
- Boric acid, H_3BO_3

Solutions

Titant	$c(\text{CuSO}_4) = 0.05 \text{ mol/L}$ 12.48 g $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ is weighed into a 1 L volumetric flask and dissolved in deion. H_2O . The flask is then filled up to the mark with deion. H_2O .
$\Phi(\text{HCl}) = 50\% \text{ (v/v)}$	250 mL conc. HCl and 250 mL deion. H_2O are mixed.
$w(\text{NaOH}) = 20\% \text{ (w/w)}$	240 g NaOH is weighed into a 1 L volumetric flask and dissolved in approx. 800 mL deion. H_2O . After cooling down the flask is filled up to the mark with deion. H_2O .
Borate buffer	12.8 g Sodium borate pentahydrate and 16.6 g boric acid are dissolved in 900 mL deion. H_2O . The pH is adjusted to 8.5 with $w(\text{NaOH}) = 20\%$ and the solution is quantitatively transferred into a 1 L volumetric

flask. The flask is then filled up to the mark with deion. H_2O .

$c(\text{NaOH}) = 0.1 \text{ mol/L}$	If possible this solution should be bought from a supplier.
$c(\text{HCl}) = 0.1 \text{ mol/L}$	If possible this solution should be bought from a supplier.

Standard solution

$c(\text{EDTA}) = 0.05 \text{ mol/L}$	EDTA is dried over night in a drying oven at $105 \text{ }^\circ\text{C}$ and allowed to cool down in a desiccator for at least 1 h. 1.86 g EDTA is weighed into a 100 mL volumetric flask and dissolved in deion. H_2O . The flask is then filled up to the mark with deion. H_2O .
---------------------------------------	---

Sample preparation

No sample preparation is required.

Analysis

Titer

5 mL of the EDTA standard solution is pipetted into a titration vessel. About 75 mL deion. H_2O and 5 mL borate buffer are added. The sample is then titrated with $c(\text{CuSO}_4) = 0.05 \text{ mol/L}$ until after the equivalence point

Sample

An appropriate amount of sample (containing about 150 mg citrate or 100 mg citric acid) is weighed into a titration vessel. About 150 mL deion. H_2O is added and the pH is adjusted between 8 and 9 with $\Phi(\text{HCl}) = 50\% \text{ (v/v)}$ or $\beta(\text{NaOH}) = 20\% \text{ (w/v)}$. 25 mL borate buffer is added and if necessary, the pH is adjusted to 8.5 with $c(\text{HCl}) = 0.1 \text{ mol/L}$ or $c(\text{NaOH}) = 0.1 \text{ mol/L}$. The solution is then titrated with $c(\text{CuSO}_4) = 0.05 \text{ mol/L}$ until after the equivalence point.

Parameters

Titer

Mode	MET U
Pause	30 s
Stirring rate	8
Signal drift	30 mV/min
Min. waiting time	5 s
Max. waiting time	32 s
Volume increment	0.05 mL
Stop volume	10 mL
EP criterion	30 mV
EP recognition	greatest

SET pH

Mode	SET pH
Pause	30 s
Stirring rate	8
EP at pH	8.5
Dynamics	2
Max. rate	10 mL/min
Min. rate	100 µL/min
Stop criterion	Drift
Stop drift	20 µL/min

DET U

Mode	DET U
Pause	30 s
Stirring rate	8
Signal drift	30 mV/min
Min. waiting time	5 s
Max. waiting time	32 s
Stop volume	10 mL
EP criterion	10
EP recognition	greatest

Calculation

Titer

$$f = \frac{V_{\text{EDTA}} \times c_{\text{EDTA}}}{V_{\text{EP1}} \times c_{\text{CuSO}_4}}$$

f: Titer of the copper sulfate solution; $c(\text{CuSO}_4) = 0.05 \text{ mol/L}$

V_{EDTA} : Volume of EDTA standard solution in mL

c_{EDTA} : Exact concentration of the EDTA standard solution in mol/L

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

c_{CuSO_4} : Concentration of the titrant in mol/L; here $c(\text{CuSO}_4) = 0.05 \text{ mol/L}$

Sample

$$w_{\text{Citric acid}} = \frac{V_{\text{EP1}} \times c_{\text{CuSO}_4} \times f \times M_A \times 0.1}{m_s}$$

$w_{\text{Citric acid}}$: Content of citric acid in %

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

c_{CuSO_4} : Concentration of the titrant in mol/L; here $c(\text{CuSO}_4) = 0.05 \text{ mol/L}$

f: Titer of CuSO_4

M_A : Molecular weight of the analyte (citric acid); 192.13 g/mol

m_s : Sample size in g

0.1: Conversion factor

Example determination

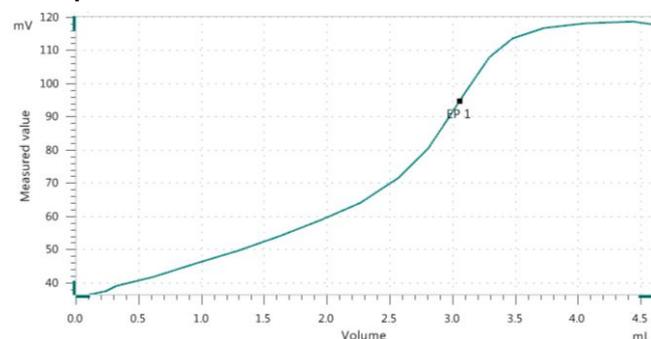


Fig. 3: Titration curve of the determination of the citric acid in detergents.

Comments

- For Titrandos, the internal reference electrode of the Unitrode can be used for the Cu ISE with the strand 6.2106.020.
- For the OMNIS Titrators, the internal reference of the Unitrode is automatically used for the Cu ISE when

both electrodes are connected to the same analog measuring module.

- Other chelating agents which react with copper (e.g., EDTA, formate, NTA and phosphate) interfere with this determination.
- The ASTM D4608 specifies the use of sodium thiosulfate solution standardized against potassium dichromate for the titer determination. Due to the easier handling, a standard EDTA solution is suggested as an alternative.

References

- ASTM D4608-89(2009)
Standard Test Method for Citrate in Detergents