Metrohm

Application Bulletin 441/1 e

Assay of pyrithione complexes

Reliable determination by potentiometric titration

Branch

Chemical; Pharmaceuticals; Personal care & cosmetics

Keywords

Titration; potentiometric titration; pyrithione; pyridinethione; zinc pyrithione; ZnPT; copper pyrithione; CuPT; sodium pyrithione; NaPT; Pt Titrode; 6.0431.100; S01; S010; S013; S04; S040; S12; S120; S122

Summary

Pyrithione complexes, such as zinc pyrithione (ZnPT), copper pyrithione (CuPT), and sodium pyrithione (NaPT), are used as fungicides and bactericides. ZnPT is used in the treatment of skin conditions such as seborrheic dermatitis or dandruff. Furthermore, ZnPT is sometimes used as an antibacterial agent in paints to prevent algae and mildew growth. CuPT is primarily in use as a biocide to prevent biofouling of surfaces submerged in water. Meanwhile, NaPT is used as antifungal agent for treatment of mycosis, such as athlete's foot.

The different pyrithione complexes are determined by iodometric titration using a maintenance-free Pt Titrode for the indication.

Zinc pyrithione

Summary

ZnPT is dissolved in water, acidified with HCl, and then titrated with iodine. During the titration, iodine is consumed by the thiol groups present in ZnPT.

Instruments

- Titrator with DET mode
- Autosampler (optional)
- Magnetic stirrer
- 50 mL buret

Electrode

Pt Titrode	6.0431.100

Reagents

- Hydrochloric acid, w(HCl) = 37%
- Ultrapure water
- Iodine, $c(I_2)$ = 0.05 mol/L
- Sodium thiosulfate, $Na_2S_2O_3$, p.a.
- Glacial acetic acid, CH_3COOH, p.a.

Solutions

Titrant	$c(I_2)$ = 0.05 mol/L Should be bought from a supplier.
Acetic acid solution	$c(CH_3COOH)$ = 2 mol/L 114.8 mL glacial acetic acid is pipetted into a clean 1000 mL volumetric flask containing 500 mL ultrapure water. The flask is then filled up to the mark with ultrapure water.

Standard

Sodium thiosulfate	$Na_2S_2O_3$ was dried for 3 h in a drying oven at 120 °C and allowed to cool down in a desiccator overnight.

Sample preparation

An appropriate amount of sample is weighed into a 250 mL sample beaker and the exact weight is recorded. 10 mL ultrapure water is added, and the beaker is swirled to disperse the sample. In a fume hood, 20 mL of concentrated HCl is added, and the beaker is swirled until the sample is fully dissolved.

Analysis

Titer

60–80 mg of dry sodium thiosulfate is weighed into a 120 mL beaker and dissolved in approximately 50 mL of ultrapure water. After the addition of 5 mL c(CH_3COOH) = 2 mol/L, the solution is titrated with c(I_2) = 0.05 mol/L until after the equivalence point.

Sample

125 mL ultrapure water is added to the prepared sample in order to submerge electrode and dosing tips. Then the solution is titrated with c(I_2) = 0.05 mol/L until after the first equivalence point.

Parameters

The same parameters are used for the titer and sample determination.

Mode	DET U
Stirring rate	10
Start volume	1 mL
Pause	10 s
Signal drift	25 mV/min
Measuring point density	4
Min. increment	20 µL
Max. increment	Off
Dosing rate	10 mL/min
Stop volume	40 mL
Stop EP	1
Volume after stop	3 mL
EP criterion	30
EP recognition	greatest

Calculations

Titer

$$f = \frac{m_S}{V_{EP1} \times 2 \times c_{I2} \times M_{Std}}$$

f:	Correction factor («titer») without unit
m_s:	Sample size in mg
V_{EP1}:	Titrant consumption until the first equivalence point in mL
2:	Stoichiometric factor
c_{I2}:	Concentration of the selected titrant in mol/L; here c(I_2) = 0.05 mol/L
M_{Std}:	Molecular weight of $Na_2S_2O_3$; 158.11 g/mol

Sample

$$ZnPT = \frac{V_{EP1} \times f \times c_{I2} \times M_A}{m_S \times 10}$$

ZnPT:	ZnPT content in percent
V_{EP1}:	Titrant consumption until the first equivalence point in mL
f:	Correction factor («titer») without unit
c_{I2}:	Concentration of the selected titrant in mol/L; here c(I_2) = 0.05 mol/L
M_A:	Molecular weight of ZnPT; 317.72 g/mol
m_s:	Sample size in g
10:	Conversion factor for %

Example determination

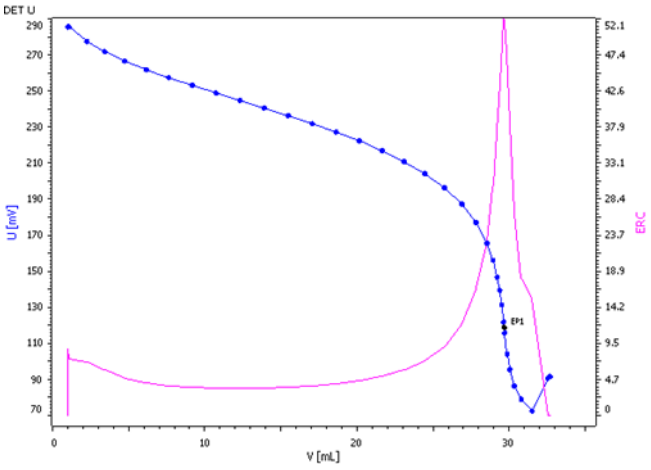

Fig. 1: Determination of ZnPT (blue = titration curve, pink = ERC)

Comments

- Any thiol-containing impurities can interfere with this analysis.
- Anti-diffusion dosing tips can be fouled by the iodine titrant, therefore capillary tips are recommended.

Sodium pyrithione

Summary

NaPT is dissolved in water, acidified with HCl, and then titrated with iodine. During the titration, iodine is consumed by the thiol group present in NaPT.

Instruments

- Titrator with DET mode
- Autosampler (optional)
- Magnetic stirrer
- 50 mL buret

Electrodes

Pt Titrode	6.0431.100

Reagents

- Hydrochloric acid, w(HCl) = 37%
- Ultrapure water
- Iodine, c(I_2) = 0.05 mol/L
- Sodium thiosulfate, $Na_2S_2O_3$, p.a.
- Glacial acetic acid, CH_3COOH, p.a.

Solutions

Titrant	c(I_2) = 0.05 mol/L Should be bought from a supplier.
Acetic acid solution	c(CH_3COOH) = 2 mol/L 114.8 mL glacial acetic acid is pipetted into a clean 1000 mL volumetric flask containing 500 mL ultrapure water. The flask is then filled up to the mark with ultrapure water.

Standard

Sodium thiosulfate	$Na_2S_2O_3$ was dried for 3 h in a drying oven at 120 °C and allowed to cool down in a desiccator overnight.

Sample preparation

An appropriate amount of sample is weighed into a 250 mL sample beaker and the exact weight is recorded. 10 mL of ultrapure water is added, and the beaker is swirled to disperse the sample. In a fume hood, 20 mL concentrated HCl are added and the beaker is swirled until the sample is fully dissolved.

Analysis

Titer

60–80 mg of dry sodium thiosulfate is weighed into a 120 mL beaker and dissolved in approximately 50 mL of ultrapure water. After the addition of 5 mL c(CH_3COOH) = 2 mol/L, the solution is titrated with c(I_2) = 0.05 mol/L until after the equivalence point.

Sample

125 mL ultrapure water is added to the prepared sample in order to submerge electrode and dosing tips. Then, the solution is titrated with c(I_2) = 0.05 mol/L until after the first equivalence point.

Parameters

The same parameters are used for the titer and sample determination.

Mode	DET U
Stirring rate	10
Start volume	1 mL
Pause	10 s
Signal drift	25 mV/min
Measuring point density	4
Min. increment	20 µL
Max. increment	Off
Dosing rate	10 mL/min
Stop Volume	40 mL
Stop EP	1
Volume after stop	3 mL
EP criterion	30
EP recognition	greatest

Calculations

Titer

$$f = \frac{m_S}{V_{EP1} \times 2 \times c_{I2} \times M_{Std}}$$

f: Correction factor («titer») without unit
m_S: Sample size in mg
V_{EP1}: Titrant consumption until the first equivalence point in mL
2: Stoichiometric factor

c_{I2}: Concentration of the selected titrant in mol/L; here $c(I_2)$ = 0.05 mol/L

M_{Std}: Molecular weight of $Na_2S_2O_3$; 158.11 g/mol

Sample

$$NaPT = \frac{V_{EP1} \times f \times c_{I2} \times M_A}{m_S \times 2 \times 10}$$

NaPT: NaPT content in percent

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

f: Correction factor («titer») without unit

c_{I2}: Concentration of the selected titrant in mol/L; here $c(I_2)$ = 0.05 mol/L

M_A: Molecular weight of NaPT; 149.15 g/mol

m_s: Sample size in g

2: Stoichiometric factor

10: Conversion factor to obtain %

Example determination

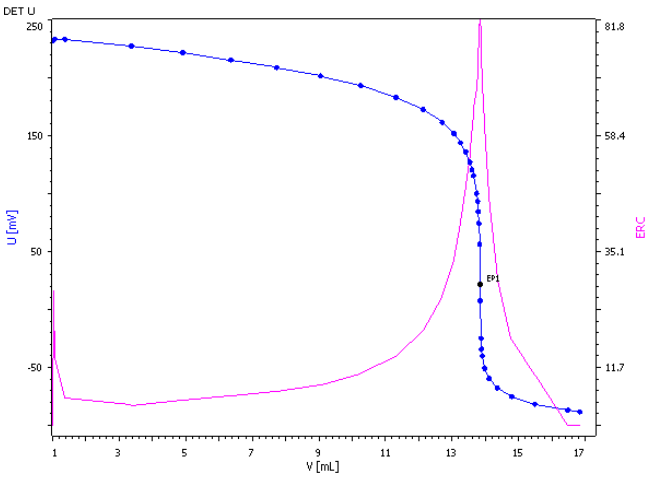

Fig. 2: Determination of the NaPT (blue = titration curve, pink = ERC)

Comments

- This method is applicable to all in-process and final samples that contain from 0.1% to 100% sodium pyrithione by weight.
- This method does not apply to sodium pyrithione formulations where other oxidizable species are present, or where other ingredients interfere with equivalence point detection.
- Glacial acetic acid can be used instead of concentrated HCl for a more defined equivalence point in samples with low concentrations of sodium pyrithione.

Copper pyrithione

Summary

Assay of copper pyrithione (CuPT) is determined by iodometric titration with sodium thiosulfate as titrant using Pt Titrode.

Instruments

- Titrator with DET mode
- Autosampler (optional)
- Magnetic stirrer
- 20 mL buret

Electrodes

Pt Titrode	6.0431.100

Reagents

- Sodium thiosulfate, $Na_2S_2O_3$, p.a.
- Glacial acetic acid, CH_3COOH, p.a.
- Potassium iodide, KI, p.a.
- Potassium iodate, KIO_3, p.a.
- Sulfuric acid, $w(H_2SO_4)$ = 98%
- Nitric acid, $w(HNO_3)$ = 65%
- Ammonia solution, $w(NH_3) \approx 25\%$
- Urea, CH_4N_2O, p.a.
- Sodium thiocyanate, NaSCN, p.a.
- Ultrapure water

Solutions

Titrant	$c(Na_2S_2O_3)$ = 0.1 mol/L Should be bought from a supplier.
Urea solution	$w(CH_4N_2O)$ = 5% 5 g urea is weighed accurately and transferred into a clean 100 mL volumetric flask. After dissolution, the flask is filled up to the mark with ultrapure water.
Sodium thiocyanate solution	w(NaSCN) = 20% 20 g NaSCN is weighed accurately and transferred into a clean 100 mL volumetric flask. The flask is then made up to the mark with ultrapure water.

Potassium iodide solution	w(KI) = 20% 20 g KI is weighed accurately and transferred into a clean 100 mL volumetric flask. Then the flask is made up to the mark with ultrapure water.
Sulfuric acid solution	$w(H_2SO_4)$ = 10% 10 mL concentrated sulfuric acid is taken in a clean 100 mL volumetric flask containing already 50 mL ultrapure water. The flask is then made up to the mark with ultrapure water.

Standard solution

Potassium iodate	Potassium iodate is dried in a drying oven for 2 h at 110 °C and allowed to cool down in a desiccator for at least 1 h.

Sample preparation

Approximately 0.1 g sample is weighed accurately and transferred into 150 mL beaker. 15 mL of ultrapure water and 6 mL concentrated nitric acid are added. The content is heated and kept boiling for 1 min. The solution is then taken from the hot plate and allowed to cool slowly to room temperature. 40 mL of ultrapure water and 5 mL of urea solution are added to the mixture, and it is heated again and kept boiling for 2 min. The solution is again allowed to cool to room temperature. Ammonia solution is then added dropwise with stirring until a permanent pale blue precipitation occurs. Immediately, 6 mL glacial acetic acid is added to the solution and the solution is then allowed to cool down thoroughly.

Analysis

Titer

Approximately 50 mg of dry potassium iodate is weighed into a 120 mL beaker, and dissolved in approximately 50 mL of ultrapure water. Approximately 1 g KI and 25 mL $w(H_2SO_4)$ = 10% are added. Then, the solution is immediately titrated with $c(Na_2S_2O_3)$ = 0.1 mol/L until after the equivalence point.

Sample

To the cooled solution, 20 mL KI solution and 10 mL sodium thiocyanate solution are added. The beaker is then covered with a watch glass and kept in the dark for 15 min. It is then titrated with $c(Na_2S_2O_3)$ = 0.1 mol/L until after the equivalence point.

Parameters

Mode	DET U
Stirring rate	8
Pause	30 s
Signal drift	50 mV/min
Min. waiting time	0 s
Max. waiting time	26 s
Min increment	10 µL
Dosing rate	max mL/min
Stop volume	10 mL
EP criterion	30
EP recognition	greatest

Calculations

Titer

$$f = \frac{m_S \times 6}{V_{EP1} \times c_{Na2S2O3} \times M_{Std}}$$

f: Correction factor («titer») without unit
m_S: Sample size in mg
6: Stoichiometric factor
V_{EP1}: Titrant consumption until the first equivalence point in mL
$c_{Na2S2O3}$: Concentration of the selected titrant in mol/L; here $c(Na_2S_2O_3)$ = 0.1 mol/L
M_{Std}: Molecular weight of KIO_3; 214.001 g/mol

Sample

$$CuPT = \frac{V_{EP1} \times f \times c_{Na2S2O3} \times M_A}{m_S \times 2 \times 10}$$

CuPT: CuPT content in percent
V_{EP1}: Titrant consumption until the first equivalence point in mL
f: Correction factor («titer») without unit
$c_{Na2S2O3}$: Concentration of the selected titrant in mol/L; here $c(Na_2S_2O_3)$ = 0.1 mol/L
M_A: Molecular weight of CuPT; 315.86 g/mol
m_S: Sample size in g
2: Stoichiometric factor
10: Conversion factor to obtain %

Example determination

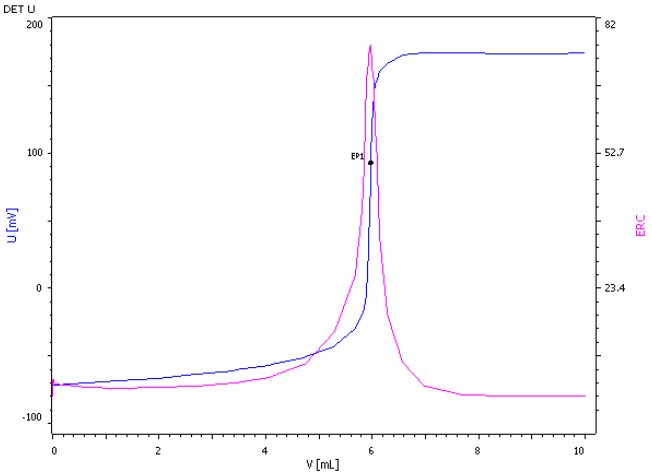

Fig. 3: Determination of the CuPT (blue = titration curve, pink = ERC)

Comments

- Before every reagent addition, the content should be cooled to room temperature.
- Urea solution is added and boiled to remove excess of nitric acid in solution.
- During the ammonia addition, Cu(II) ammonia complex will be formed, giving a light blue color. When the precipitation occurs, heat the solution again to remove excess ammonia and continue the analysis.
- Liberated iodine will be adsorbed onto the surface of the CuI precipitate. To negate that interaction, enough sodium thiocyanate should be added to the solution.

Date

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Competence Center Titration

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