Metrohm

Application Bulletin AB-042/2 e

Determination of carbonyl compounds by potentiometric titration

Branch

General analytical chemistry; organic chemistry; petrochemistry, biofuels; food, stimulants, beverages, flavors; paints, lacquers, solvents

Keywords

Titration; potentiometric titration; non-aqueous titration; water-soluble carbonyl compounds; carbonyl compounds; dUnitrode with Pt 1000; dSolvotrode; petroleum products; pyrolysis bio-oil; pyrolysis oil; mineral-oil; OMNIS Titrator Advanced; branch 1; branch 3; branch 5; branch 7; branch 14; 6.00200.300; 6.00203.300

Summary

Carbonyl compounds (CC) occur in many products, such as bio-oils and fuels, cyclic and acyclic solvents, flavors and mineral oils.

Carbonyl compounds can be responsible for the instability of these products during storage or processing. Especially pyrolysis bio-oils are known to cause issues during storage, handling and upgrading.

This bulletin describes an aqueous and a non-aqueous analytical titration method for the determination of carbonyl compounds by potentiometric titration.

Method 1 – Water soluble carbonyl compounds

Instruments

- Titrator with DET U and MET U mode
- 10 mL buret
- Stirrer
- Thermostat
- Titration vessel with thermostat jacket

Electrodes

dUnitrode*[1] with Pt 1000	6.00200.300
iUnitrode*[2] with Pt 1000	6.0278.300
Unitrode with Pt 1000 (head U)	6.0258.600
Unitrode easyClean*[2] with Pt 1000	6.0260.010

*[1]Can only be used with OMNIS, *[2]Can only be used with Titrando

Reagents

- Hydroxylamine hydrochloride, $H_2NOH \cdot HCl$, puriss. p.a., ≥ 99.0%
- Potassium phthalate monobasic, KHP, puriss. p.a., ≥ 99.5%

Solution

Reaction solution	c($H_2NOH \cdot HCl$) = 1.0 mol/L 70 g $H_2NOH \cdot HCl$, is weighed into a 1000 mL volumetric flask and dissolved in approximately 500 mL deionized water. The flask is then filled up to the mark with deionized water.
Titrant	c(NaOH) = 1.0 mol/L in H_2O If possible this solution should be bought from a supplier.

Standard

KHP	KHP is dried for 2 h in a drying oven at 105 °C and allowed to cool down overnight in a desiccator.

Sample preparation

Dissolve a specific (or definite) amount of water-soluble sample in deionized water so that 10 mL of the sample solution contains approximately 5 mmol carbonyl compounds.

Analysis

Titer

1000 mg KHP is weighed into a titration vessel. Afterwards 50 mL deionized water is added and while stirring the solution is titrated with c(NaOH) = 1.0 mol/L until after the equivalence point. After each titration, the titration vessel and the buret tips as well as the electrode are rinsed with deionized water.

Sample blank

1 mL sample is dosed into a titration vessel with thermostat jacket and the vessel is filled up to 100 mL with deionized water. While stirring, the solution is heated up for 5 min to 50 °C. Afterwards the solution is titrated with c(NaOH) = 1.0 mol/L until after the equivalence point. After each titration, the titration vessel and the buret tips as well as the electrode are rinsed with deionized water.

Reaction solution blank

50 mL water and 50 mL c($H_2NOH \cdot HCl$) = 1.0 mol/L are dosed into a titration vessel with thermostat jacket. While stirring, the solution is heated up for 5 min to 50 °C. Afterwards the solution is titrated with c(NaOH) = 1.0 mol/L until after the equivalence point. After each titration the titration vessel and the buret tips as well as the electrode are rinsed with deionized water.

Sample

1 mL sample solution is pipetted into a titration vessel with thermostat jacket containing 50 mL c($H_2NOH \cdot HCl$) = 1.0mol/L. The titration vessel is then filled up to 100 mL with deionized water. While stirring, the solution is heated up for 5 min to 50 °C. The solution is titrated with (NaOH) = 1.0 mol/L until after the equivalence point. After each titration, the titration vessel and the buret tips as well as the electrode are rinsed with deionized water.

Parameters

Titer and sample

Mode	DET U
Signal drift	30 mV/min
Min. waiting time	0 s
Max. waiting time	32 s
Meas. point density	4
Min. increment	10 µL
Max. increment	Off
Stop EP	1
EP criterion	5
EP recognition	Greatest

Sample blank and reaction solution blank

Mode	MET U
Volume increment	0.01 mL
Signal drift	30 mV/min
Min. waiting time	0 s
Max. waiting time	32 s
Stop EP	1
EP criterion	1 mV
EP recognition	Greatest

Calculation

Titer

$$f = \frac{m_S}{V_{EP1} \times c_{NaOH} \times M_{KHP}}$$

f:	Titer of titrant
m_S:	Sample size in mg
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c_{NaOH}:	Concentration of titrant, c(NaOH) = 1.0 mol/L
M_{KHP}:	Molecular weight of potassium phthalate monobasic, M(KHP) = 204.22 g/mol

Blanks

$B_{SA} = V_{EP1}$
$B_{RS} = V_{EP1}$

B_{SA}:	Blank of the sample in mL
B_{RS}:	Blank of the reaction solution in mL
V_{EP1}:	Titrant consumption until the first equivalence point in mL

Sample

$$CC = \frac{(V_{EP1} - B_{SA} - B_{RS}) \times c_{NaOH} \times f}{V_S \times \beta_S}$$

CC:	Carbonyl compound in mmol/g sample
V_{EP1}:	Titrant consumption until the first equivalence point in mL
B_{SA}:	Blank of the sample in mL
B_{RS}:	Blank of the reaction solution in mL
c_{NaOH}:	Concentration of titrant, c(NaOH) = 1.0 mol/L
f:	Titer of titrant
V_S:	Sample size in mL
β_S:	Mass concentration in g/mL

Examples

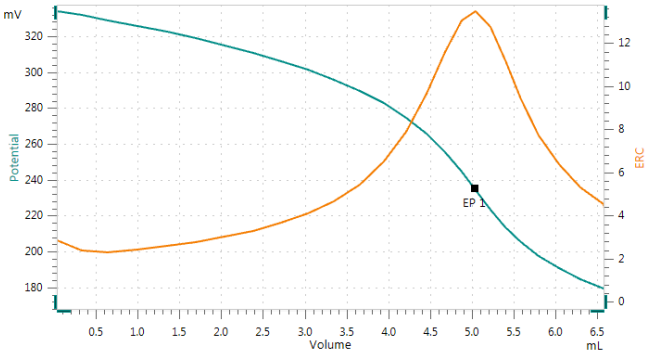

Fig. 1: Potentiometric determination of water-soluble carbonyl compound

Comments

- For the analysis of the blanks and the samples the thermostat is set the entire time to 50 °C.
- Cyclohexanone can be used as a validation standard. The theoretical carbonyl compound value is 10.14 mmol/g.

References

- Faix, O.; Andersons, B.; Zakis, G. Determination of carbonyl groups of six round robin lignins. Holzforschung 1998, 52; pp. 268−272.
- Nicolaides, G. M. The chemical characterization of pyrolytic oils. MASc Thesis, Dept. of Chemical Engineering; University of Waterloo, Waterloo, Ontario, Canada, 1984; pp. 27−42.

Method 2 – Water insoluble carbonyl compounds

Instruments

- Titrator with DET U mode
- 10 mL buret
- Stirrer
- Thermostat
- Titration vessel with thermostat jacket

Electrodes

dSolvotrode*[1], reference electrolyte c(TEABr) = 0.4 mol/L in ethylene glycol	6.00203.300
iSolvotrode*[2], reference electrolyte c(TEABr) = 0.4 mol/L in ethylene glycol	6.0279.300
Solvotrode easyClean*[2], reference electrolyte c(TEABr) = 0.4 mol/L in ethylene glycol	6.0229.010
Solvotrode*[2], reference electrolyte c(TEABr) = 0.4 mol/L in ethylene glycol	6.0229.100

*[1]Can only be used with OMNIS, *[2]Can only be used with Titrando

Reagents

- Hydroxylamine hydrochloride, $H_2NOH \cdot HCl$, puriss. p.a., ≥ 99.0%
- Benzoic acid, C_6H_5COOH, ACS reagent, ≥ 99.5%
- 2-Propanol, $(CH_3)_2CHOH$, ACS reagent, ≥ 99.5%

Solution

Reaction solution	c($H_2NOH \cdot HCl$) = 0.2 mol/L 14 g $H_2NOH \cdot HCl$ is weighed into a 1000 mL volumetric flask and dissolved in 200 mL deionized water. The flask is then filled up to the mark with 2-propanol.
Titrant	c(TBAOH) = 0.1 mol/L in isopropanol/methanol. If possible this solution should be bought from a supplier.

Standard

Benzoic acid	Benzoic acid is dried overnight in a desiccator.

Sample preparation

Dissolve an appropriate amount of sample in 2-propanol so that 10 mL of the sample solution contains approximately 1 mmol carbonyl compounds.

Analysis

Titer

100 mg benzoic acid is weighed into a titration vessel. Afterwards 100 mL 2-propanol is added and while stirring the solution is titrated with c(TBAOH) = 0.1 mol/L until after the equivalence point. After each titration the titration vessel and the buret tips as well as the electrode are rinsed with 2-propanol.

The glass membrane of the Solvotrode is reconditioned for 5 min in deionized water before the next titration.

Sample blank

90 mL 2-propanol and 10 mL sample are pipetted into a titration vessel with thermostat jacket. While stirring the solution is heated for 5 min up to 50 °C. Afterwards the solution is titrated with c(TBAOH) = 0.1 mol/L until after the equivalence point. After each titration the titration vessel and the buret tips as well as the electrode are rinsed with 2-propanol.

The glass membrane of the Solvotrode is reconditioned for 5 min in deionized water before the next titration.

Reaction solution blank

50 mL 2-propanol and 50 mL c($H_2NOH \cdot HCl$) = 0.2 mol/L are pipetted into a titration vessel with thermostat jacket. While stirring, the solution is heated for 5 min up to 50 °C. Then the solution is titrated with c(TBAOH) = 0.1 mol/L until after the equivalence point. After each titration the titration vessel and the buret tips as well as the electrode are rinsed with 2-propanol.

The glass membrane of the Solvotrode is reconditioned for 5 min in deionized water before the next titration.

Sample

40 mL 2-propanol, 50 mL c($H_2NOH \cdot HCl$) = 0.2 mol/L and 10 mL sample are pipetted into a titration vessel with thermostat jacket. While stirring, the solution is heated for 5 min up to 50 °C. The solution is titrated with c(TBAOH) = 0.1 mol/L until after the equivalence point. After each titration the titration vessel and the buret tips as well as the electrode are rinsed with 2-propanol.

The glass membrane of the Solvotrode is reconditioned for 5 min in deionized water before the next titration.

Parameters

Titer, sample blank and reaction solution blank

Mode	DET U
Signal drift	30 mV/min
Min. waiting time	0 s
Max. waiting time	32 s
Meas. point density	4
Min. increment	10 µL
Max. increment	Off
Stop EP	1
EP criterion	5
EP recognition	Greatest

Sample

Mode	DET U
Signal drift	30 mV/min
Min. waiting time	0 s
Max. waiting time	32 s
Meas. point density	4
Min. increment	10 µL
Max. increment	Off
Stop EP	1
EP criterion	1
EP recognition	Greatest

Calculation

Titer

$$f = \frac{m_S}{V_{EP1} \times c_{TBAOH} \times M_{BA}}$$

f:	Titer of titrant
m_S:	Sample size in mg
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c_{TBAOH}:	Concentration of titrant, c(TBAOH) = 0.1 mol/L
M_{BA}:	Molecular weight of benzoic acid, M(Benzoic acid) = 122.12 g/mol

Blanks

$B_{SA} = V_{EP1}$

$B_{RS} = V_{EP1}$

B_{SA}:	Blank of the sample in mL
B_{RS}:	Blank of the reaction solution in mL
V_{EP1}:	Titrant consumption until the first equivalence point in mL

Sample

$$CC = \frac{(V_{EP1} - B_{SA} - B_{RS}) \times c_{TBAOH} \times f}{V_S \times \beta_S}$$

CC:	Carbonyl compound in mmol/g sample
V_{EP1}:	Titrant consumption until the first equivalence point in mL
B_{SA}:	Blank of the sample in mL
B_{RS}:	Blank of the reaction solution in mL
c_{TBAOH}:	Concentration of titrant, c(TBAOH) = 0.1 mol/L
f:	Titer of titrant
V_S:	Sample size in mL
β_S:	Mass concentration in g/mL

Examples

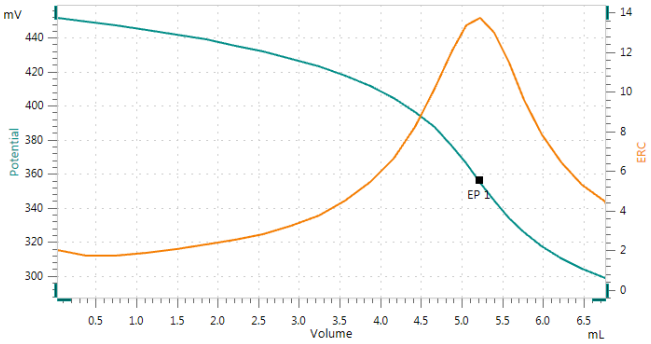

Fig. 2: Potentiometric determination of water-insoluble carbonyl compound

Comments

- For the analysis of the blanks and the samples the thermostat is set the entire time to 50 °C.
- Cyclohexanone can be used as a validation standard. The theoretical carbonyl compound value is 10.14 mmol/g.

References

- Faix, O.; Andersons, B.; Zakis, G. Determination of carbonyl groups of six round robin lignins. Holzforschung 1998, 52; pp. 268−272.
- Nicolaides, G. M. The chemical characterization of pyrolytic oils. MASc Thesis, Dept. of Chemical Engineering; University of Waterloo, Waterloo, Ontario, Canada, 1984; pp. 27−42.
- Ferrell, J. R. III; Olarte, M. V.; Christensen, E. D.; Padmaperuma, A. B.; Connatser, R. M.; Stankovikj, F.; Meier, D.; Paasikallio, V. Standardization of Analytical Techniques for Pyrolysis Bio-oil: History, Challenges, and Current Status of Methods. Biofuels, Bioproducts & Biorefining, 2016, 10; pp. 496-507.
- Black, S. and Ferrell, J.R. III, Determination of carbonyl groups in pyrolysis bio-oils using potentiometric titration: review and comparison of methods. Energ. Fuel, 2016, 30; pp. 1071–1077.
- ASTM D4423-10
  Standard Test Method for Determination of Carbonyls in C_4 Hydrocarbons
- ASTM E3146-18
  Standard Test Method for Determination of Carbonyls in Pyrolysis Bio-Oils by Potentiometric Titration
- Leaflet LL Solvotrode (8.109.8046)

Author

Competence Center Titration

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