Metrohm

Application Bulletin 190/3 e

Determination of 4-carboxybenzaldehyde in terephthalic acid by polarography

Summary

4-Carboxybenzaldehyde, in the following referred to as 4-CBA, can be reduced directly on the dropping mercury electrode (DME) in an ammoniacal solution. After a very simple sample preparation, it is thus possible to determine the concentration of 4-CBA in terephthalic acid quickly and precisely by polarography down to the lower ppm range.

Instruments

VA instrument capable of operating a Multi-Mode Electrode and supporting differential pulse (DP) measuring mode

Electrodes

WE	Multi-Mode Electrode pro Mercury drop capillary	6.1246.120 6.1226.030
RE	Ag/AgCl reference electrode Ag/AgCl/KCl (3 mol/L) Electrolyte vessel Filled with c(KCl) = 3 mol/L	6.0728.x20 6.1245.010
AE	Pt rod electrode	6.0343.x00

Reagents

All of the used reagents must be of analysis quality (for analysis).

- Ammonia solution, w(NH_3) = 25%, for analysis, CAS 1336-21-6
- Hydrochloric acid, w(HCl) = 32%, for analysis, CAS 7647-01-0
- 4-Carboxybenzaldehyde, 4-CBA, for analysis, CAS 619-66-9
- Sodium hydroxide solution, w(NaOH) = 32%, for analysis, CAS 1310-73-2
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

Solutions

Ammonia buffer (pH = 9.6)	c(NH_4Cl) = 1 mol/L c(NH_3) = 2 mol/L Make up 112 mL w(NH_3) = 25% and 49 mL w(HCl) = 32% to 500 mL with ultrapure water.

Standard solutions

4-Carboxy-benzaldehyde standard solution	β(4-CBA) = 1 g/L Dissolve 100 mg 4-CBA in 10 mL ammonium buffer and make up to 100 mL with ultrapure water

Sample preparation

Weigh 5 g sample into a beaker and mix to a slurry with 40 mL ultrapure water. While adding 15 mL w(NH_3) = 25%, heat up the solution. If the sample does not dissolve completely, add w(NaOH) = 32% (approx. 1 mL) until a clear solution is obtained.

After cooling down, transfer the solution to a 100 mL volumetric flask, add 3 mL ammonium buffer and fill to the mark with ultrapure water.

Analysis

Pipet 10 mL sample solution into the polarographic vessel and record the polarogram.

The concentration is determined by standard addition.

Measuring solution

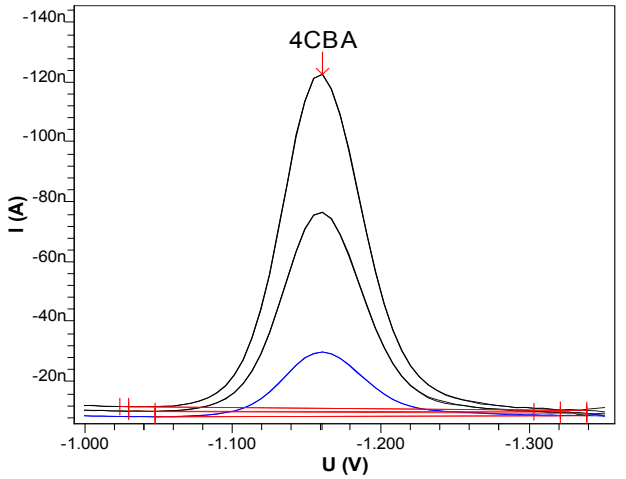
10 mL dissolved sample solution (equals 0.5 g sample)

Parameters

Voltammetric	
Electrode operating mode	DME
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Equilibration time	10 s

Sweep	
Start potential	-1.05 V
End potential	-1.35 V
Potential step	0.006 V
Potential step time	0.4 s
Sweep rate	0.015 V/s
Pulse amplitude	0.05 V
Substance	
Name	4-CBA
Characteristic potential	-1.2 V

Example




```
4CBA
c =     9.530 ug/g
+/-     0.010 ug/g (0.11%)
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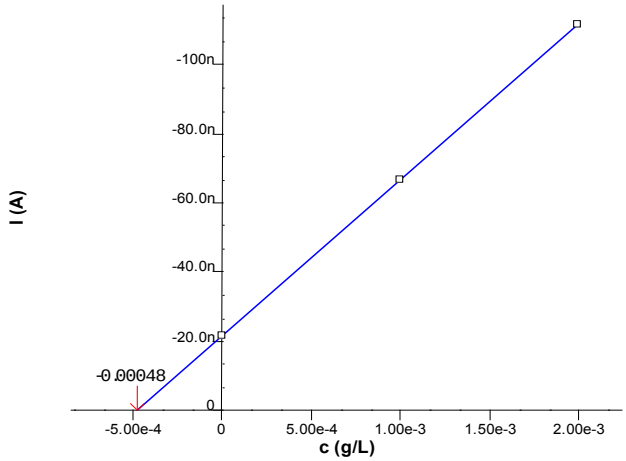

Result

Sample	Terephthalic acid
Sample size	5.0 g
β(4-CBA)	9.5 µg/g

Appendix

Report for the example determination of 4-carboxybenzaldehyde in terephthalic acid

```
========== METROHM 797 VA COMPUTRACE (Version 1.0.0.1) (Serial No. 0) ==========
 Determination  : 10211126_Terephthalsäure.dth
 Sample ID      : Terephthalsäure
 Creator method :                   Date :                     Time:
 Creator determ.:                   Date : 1999-10-21          Time:  11:26:50
 Modified by    : ---               Date :                     Time:
--------------------------------------------------------------------------------
 Method         : AB190_4CBA in Terephthalic acid.mth
 Title          : 4-Carboxybenzaldehyde in Terephthalic acid
 Remark1        : 10 mL dissolved sample
 Remark2        : sample preparation according to AB 190
--------------------------------------------------------------------------------
 Sample amount  :  10.000 mL
 Cell volume    :  10.000 mL
--------------------------------------------------------------------------------
 Substance      : 4CBA
 Conc.          : 476.501 ug/L
 Conc.dev.      :   0.507 ug/L     ( 0.11%)
 Amount         :   4.765 ug
 Add.amount     :  10.000 ug

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -1.161   -21.5   -21.5     0.007       0.0
 1 - 2  -1.161   -21.5
 2 - 1  -1.161   -66.8   -66.7     0.087     -45.2
 2 - 2  -1.161   -66.6
 3 - 1  -1.161  -111.7  -111.7     0.022     -45.0
 3 - 2  -1.161  -111.6


 Substance    Calibr.      Y.reg/offset        Slope Mean deviat. Corr.Coeff.
 ------------ ------------ ------------ ------------ ------------ ------------
 4CBA         std.add.      -2.153e-008  -4.519e-005   3.994e-011      1.00000


 Final results                         +/- Res. dev.   %     Comments
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 4CBA:
 default           =    9.530  ug/g    0.010        0.106
```

Method print for the determination of 4-carboxybenzaldehyde

```
--------------------------------------------------------------------------------
 Method parameters
--------------------------------------------------------------------------------
Method          : AB190_Det of 4Carboxybenzaldehyd.mth
Title           : Determination of 4-carboxybenzaldehyde in terephthalic acid
Remark1         : 5g terephthalic acid dissolved in 15mL ammonia --> 100mL
Remark2         : 10 mL dissolved sample

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       : Terephthalsäure
Sample amount (mL): 10.000
Cell volume (mL): 10.000

Voltammetric parameters
--------------------------------------------------------------------------------
Mode                              : DP - Differential Pulse

Highest current range             : 10  mA
Lowest current range              : 100 nA

Electrode                         : DME
Stirrer speed (rpm)               : 2000

Initial electr. conditioning      : No

No. of additions                  : 2
No. of replications               : 2
```

```
Measure blank                     : No
Addition purge time (s)           : 10

Initial purge time (s)            :      300

Sweep
Equilibration time (s)            :    5.000
Start potential (V)               :   -1.050
End potential (V)                 :   -1.350
Voltage step (V)                  :    0.006
Voltage step time (s)             :    0.600
Sweep rate (V/s)                  :    0.010
Pulse amplitude (V)               :    0.050
Pulse time (s)                    :    0.040

Cell off after measurement        :      Yes

Peak evaluation
-------------------------------------------------------------------------------
Regression technique              : Linear Regression
Peak evaluation                   : Height
Minimum peak width (V.steps)      : 5
Minimum peak height (A)           : 1.000e-010
Reverse peaks                     : No
Smooth factor                     : 4
Eliminate spikes                  : Yes

Substances
-------------------------------------------------------------------------------
4CBA                    : -1.200 V   +/- 0.050 V

Standard solution       : 1   1.000 g/L
Addition volume (mL)    : 0.010

default                 : Final result (4CBA) =
                          Conc * (10 / 10) * (1e+006 / 50) + 0 - 0

Baseline
-------------------------------------------------------------------------------
Substance Addition    automatic start (V) end (V) type        scope
-------------------------------------------------------------------------------
4CBA      Sample      yes       ---       ---     linear      wholePeak
          Addition 1  yes       ---       ---     linear      wholePeak
          Addition 2  yes       ---       ---     linear      wholePeak
-------------------------------------------------------------------------------
```