Metrohm

Application Bulletin 196/4 e

Determination of formaldehyde by polarography

Summary

Formaldehyde can be determined reductively at the DME. Depending on the sample composition it can be possible to determine the formaldehyde directly in the sample. If interferences occur, a sample preparation may be necessary, i.e. absorption, extraction, or distillation.

Two methods are described. In the first method formaldehyde is reduced directly in alkaline solution. Higher concentrations of alkaline or alkaline earth metals interfere. In those cases the second method can be applied. Formaldehyde will be derivatized with hydrazine forming the hydrazone, which can be measured polarographically in acidic solution.

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

Sample preparation

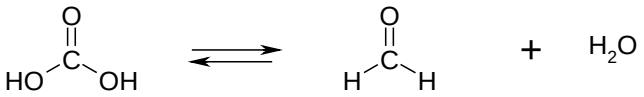
- Waste water, solutions, and plating baths (e.g. electroless copper baths) can be analyzed directly.
- Plastics and textiles are ground and extracted for approximately 20 min in a shaker with c(LiOH) = 0.05 mol/L. The extract is then separated by filtration or centrifugation.
- Air samples are absorbed in c(LiOH) = 0.05 mol/L: 2 to 10 L air with a flow rate of 500 mL/min.
- Fish, crustacean, and film material are ground. 1 to 5 g of the sample are suspended in 20 mL distilled water, 1 mL w(H_2SO_4) = 30 % is added. The formaldehyde is then steam distilled and absorbed in c(LiOH) = 0.05 mol/L.

Method 1: Determination of formaldehyde in alkaline solution

Theory

Formaldehyde can be reduced directly to methanol in alkaline solution. This reaction is used to determine formaldehyde polarographically. The method is suitable for samples, which do not contain a too high content of alkaline or earth alkaline metal ions.

A chemical equilibrium proceeds the electrochemical reaction:



Reagents

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

- Lithium hydroxide monohydrate (LiOH · H_2O), for analysis, CAS 1310-66-3
- Ethylenediaminetetraacetic acid (EDTA, Titriplex II®, Komplexon II®, Idranal II®), for analysis, CAS 60-00-4
- Formaldehyde solution, w(HCHO) = 37%, for analysis, CAS 50-00-0
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

Solutions

Absorption solution	c(LiOH) = 0.05 mol/L 2.1 g LiOH are dissolved in 1000 mL water.
Supporting electrolyte	c(LiOH) = 0.22 mol/L, c(EDTA) = 0.02 mol/L 9.23 g LiOH and 5.85 g EDTA are dissolved in 1000 mL water.

Standard solutions

Formaldehyde standard solution	β(HCHO) = 200 mg/L The standard solution is prepared from a concentrated formaldehyde solution, which is diluted with water. The exact concentration is determined by titration.

Analysis

5 mL sample or absorption solution are pipetted into the measuring vessel and 5 mL supporting electrolyte are added. The measuring solution is purged for 600 s.

Measuring solution

5 mL supporting electrolyte

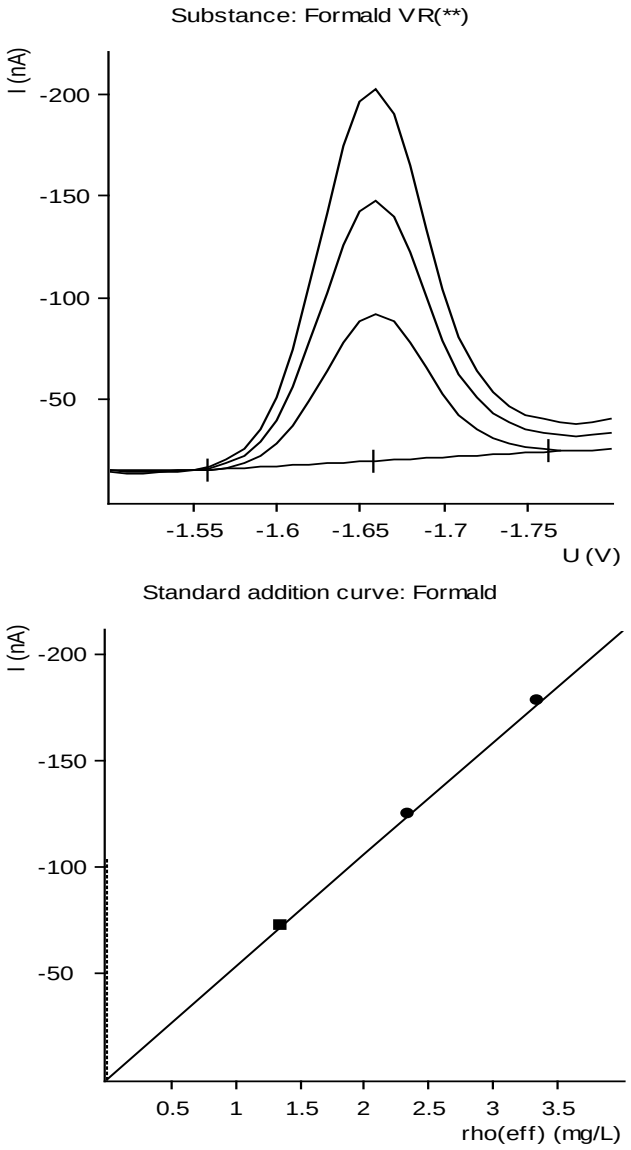
5 mL sample or absorption solution

The concentration of formaldehyde is determined by standard addition technique.

Parameters

Voltammetric	
Electrode operating mode	DME
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Equilibration time	5 s
Sweep	
Start potential	-1.4 V
End potential	-1.8 V
Potential step	0.01 V
Potential step time	0.4 s
Sweep rate	0.025 V/s
Pulse amplitude	0.05 V
Substance	
Name	Formaldehyde
Characteristic potential	-1.65 V

Example



Result

Sample size	5.0 mL
β(Formaldehyde)	2.7 mg/L

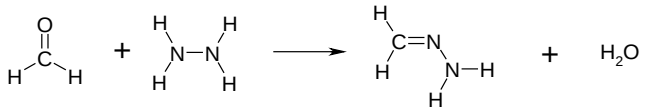
Comments

- The linear range is between 300 µg/L and 300 mg/L formaldehyde in the sample. Higher concentrations have to be diluted.
- The formaldehyde peak is very close to the sodium peak. It is important to avoid high concentrations of sodium ions in the measurement solution.
- If the formaldehyde peak is not separated from the rising background current (sodium peak), we recommend to use method 2.

Method 2: Determination of formaldehyde as hydrazone

Theory

In acidic solutions formaldehyde and hydrazine condense to a hydrazone. This can be determined polarographically.



Reagents

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

- Sulfuric acid, w(H_2SO_4) = 96 %, for analysis, CAS 7664-93-9
- Hydrazine sulfate, for analysis, CAS 10034-93-2
- Formaldehyde solution, w(HCHO) = 37 %, for analysis, CAS 50-00-0
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

Solutions

The standard solutions are prepared from a concentrated formaldehyde solution, which is diluted with water. The exact concentration is determined by titration.

Hydrazine solution	β(hydrazine sulfate) = 20 g/L 2 g hydrazine sulfate are dissolved in 100 mL water

Standard solutions

Formaldehyde standard solution	β(HCHO) = 100 mg/L The standard solution is prepared from a concentrated formaldehyde solution, which is diluted with water. The exact concentration is determined by titration.

Analysis

10 mL (diluted) sample or adsorption solution are pipetted into the measuring vessel. 50 µL sulfuric acid and 1 mL hydrazine solution are added. The measuring solution is purged for 300 s.

Measuring solution

10 mL (diluted) sample or absorption solution

50 µL sulfuric acid

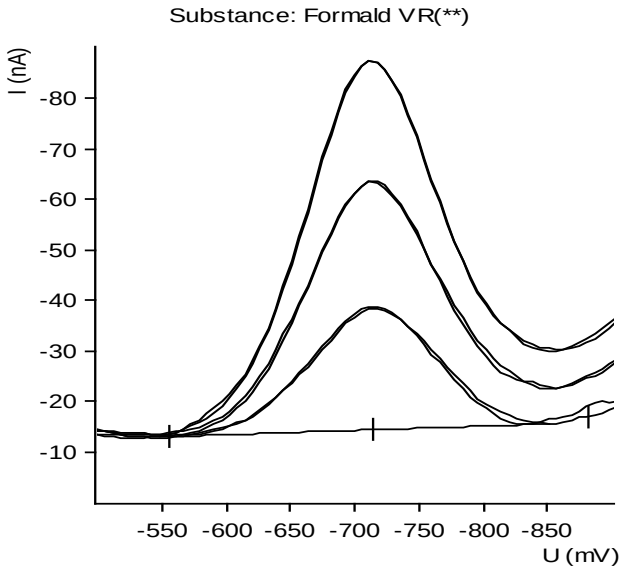
1 mL hydrazine solution

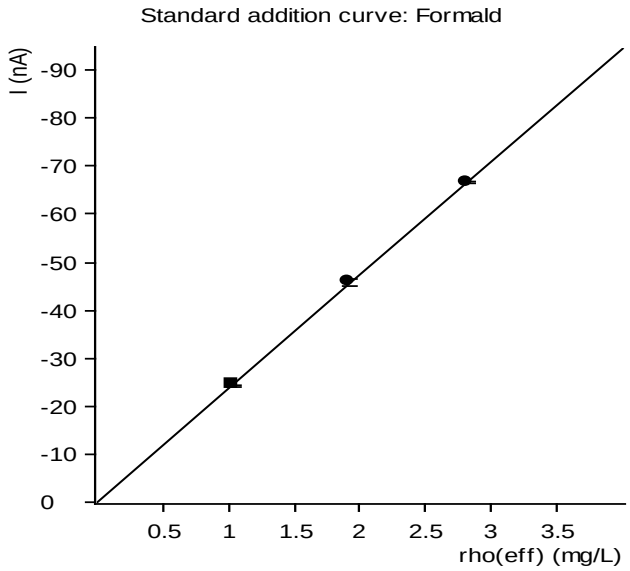
The concentration of formaldehyde is determined by standard addition technique.

Parameters

Voltammetric	
Electrode operating mode	DME
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Equilibration time	10 s
Sweep	
Start potential	-0.5 V
End potential	-1.2 V
Potential step	0.006 V
Potential step time	0.3 s
Sweep rate	0.02 V/s
Pulse amplitude	0.05 V
Substance	
Name	Formaldehyde
Characteristic potential	-0.72 V

Example





Result

Sample size	0.1 mL
β(Formaldehyde)	114.9 mg/L

Comments

- The linear range is between approximately 50 µg/L and 30 mg/L. Higher concentrations have to be diluted.
- This method is recommended, if interferences by higher contents of sodium ions occur when using method 1 in alkaline solutions.

References

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- Metrohm Info 2/98, 22-23

Appendix

Report for the example determination of formaldehyde according to method 1

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Determ.     : 05071509             User:                      Date: 1999-05-07
 Modified    : 2000-12-01 16:35:19  Run :  0                   Time: 15:09:05
 Sample table: -
--------------------------------------------------------------------------------
  Pos.  Ident.1/S1    Ident.2/S2    Ident.3/S3    Method.call   Sample size/S0
        sample                                                        5 mL
--------------------------------------------------------------------------------
 Method  :  AB196_1a
 Title   :  Determination of Formaldehyde. AB196
 Remark1 :  5 mL electrolyte + 5 mL sample
 Remark2 :
--------------------------------------------------------------------------------

  Substance : Formald                                          Comments
  Mass conc.:    2.725 mg/L            Mass     : 13.62 ug   ------------------
  MC.dev.   :    0.050 mg/L (1.83%)    Add.mass :    10 ug
  Cal.dev.  :    -                     V0.sample:     5 mL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ------------------
              00   -1658  -71.87  -71.87
              10   -1657  -123.4  -123.4            -51.52
              20   -1656  -175.4  -175.4            -52.00

 Substance    Techn.     Y.reg/offset   Slope        Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------   ----------   ------------
 Formald      std.add.     -7.171e-08   -5.264e-05                 4.059e-10


Final results                        +/- Res.dev.   %      Comments
 ---------------------------------     -----------------     ------------------
    Formald =   2.7246 mg/L               0.050    1.83
```

Method print for the determination of formaldehyde according to method 1

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB196_1a.mth         OPERATION SEQUENCE
 Title : Determination of Formaldehyde. AB196
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  ------------------------  ------------------------
 1    DOS/M                V.added       5.000 mL
 2    REM                  electrolyte
 3    SMPL/M               V.fraction          mL     V.total              L
 4    STIR                 Rot.speed      2000 /min
 5    PURGE          600.0
 6    (ADD
 7      NOP          10.0
 8      SEGMENT            Segm.name   pol
 9      ADD>M              Soln.name   For-Std        V.add         0.050 mL
10    ADD)2
11    END

 Method: AB196_1a              SEGMENT
                                    pol
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  ------------------------  ------------------------
 1    0PURGE
 2    0STIR           5.0
 3    (REP
 4      DME
 5      DPMODE             U.ampl          -50 mV     t.meas         30.0 ms
                           t.step         0.40 s      t.pulse        40.0 ms
 6      SWEEP       17.6   U.start       -1400 mV     U.step           10 mV
                           U.end         -1800 mV     Sweep rate       25 mV/s
 7    REP)0
 8    PURGE
 9    STIR                 Rot.speed      2000 /min
10    0MEAS                U.standby           mV
11    END

  Method: AB196_1a                SUBSTANCES
                              Formald  - pol
```

```
--------------------------------------------------------------------------------

      Recognition                              Display / Plot
      -------------------------                --------------------------
      U.verify         -1650 mV                I.scale       auto
      U.tol (+/-)         50 mV                U.div          50.00 mV/cm
      U.width min         10 mV                U.begin        -1500 mV
      U.width max        400 mV                U.end          -1800 mV
      I.threshold        200 pA


      Baseline                                 Evaluation
      -------------------------                --------------------------
      Type           linear                    Mode          VA
      Scope          whole                     Quantity      I.peak
      dU.front       auto                      Sign. digits     4
       S.front       auto
      dU.rear        auto
       S.rear        auto

  Calibration   2000-12-01 16:38:17            Coefficients
  ---------------------------------            -------------------------
  Technique     std.add.                       Y.reg        -7.171e-08
  Curve type    linear                         Slope        -5.264e-05
                                               Nonlin.
                                               Mean dev.     4.059e-10

               Additions
               ------------------------------------------------------------
  Soln.name      For-Std
  ----------
  Mass conc.        200 mg/L            g/L             g/L             g/L
  Range min            0 g/L            g/L             g/L             g/L
  Range max              g/L            g/L             g/L             g/L
  M.conc./cm             g/L            g/L             g/L             g/L

 Method: AB196_1a              CALCULATION
                              max. 15 lines
--------------------------------------------------------------------------------

 Quantity        Formula (R##, C##, A##)                   Res.unit   Sig.dig.
 ------------    ----------------------------------------  --------   --------
 Formald         R1000=MC:Formald                          #g/L          5
```

Report for the example determination of formaldehyde according to method 2

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Determ.     : 06211516             User:                      Date: 1994-06-21
 Modified    : 2000-12-01 17:00:42  Run :  0                   Time: 15:16:55
 Sample table: -
--------------------------------------------------------------------------------
  Pos.  Ident.1/S1    Ident.2/S2    Ident.3/S3    Method.call   Sample size/S0
        Std           For                                       100 uL
--------------------------------------------------------------------------------
 Method  :  AB196_2
 Title   :  Determination of Formaldehyde. AB196 method 2
 Remark1 :  10 ml Wasser + 50 µl H2SO4 + 1 ml Hydrazinsulfat
 Remark2 :  + Probe
--------------------------------------------------------------------------------

  Substance : Formald                                          Comments
  Mass conc.:    114.9 mg/L            Mass     : 11.49 ug    ----------------
  MC.dev.   :     2.58 mg/L (2.25%)    Add.mass :    10 ug
  Cal.dev.  :    -                     V0.sample:   100 uL

              VR   U/mV    I/nA   I.mean  Std.dev. I.delta   Comments
              ---  -----  ------  ------  -------  -------   ----------------
              00   -715   -24.37  -24.20   0.2360            rear overlapping
              01   -717   -24.04
              10   -714   -45.83  -45.39   0.6269   -21.18   rear overlapping
              11   -712   -44.95
              20   -711   -65.50  -65.39   0.1461   -20.00   rear overlapping
              21   -711   -65.29

 Substance    Techn.     Y.reg/offset   Slope        Nonlin.      Mean deviat.
 ---------    --------   ------------   ----------   ----------   ------------
 Formald      std.add.     -2.434e-08   -2.362e-05                 4.193e-10


Final results                        +/- Res.dev.   %      Comments
 ---------------------------------     -----------------     ----------------
    Formald =   114.90 mg/L               2.58    2.25
```

Method print for the determination of formaldehyde according to method 2

```
================== METROHM 746 VA TRACE ANALYZER (5.746.0101) ==================
 Method: AB196_2 .mth         OPERATION SEQUENCE
 Title : Determination of Formaldehyde. AB196 method 2
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  ------------------------  ------------------------
 1    DOS/M                V.added      11.050 mL
 2    REM                  Wasser/Hydr./Puffer
 3    STIR                 Rot.speed      2000 /min
 4    PURGE         300.0
 5    SMPL>M               V.fraction          mL     V.total              L
 6    (ADD
 7      NOP         10.0
 8      SEGMENT            Segm.name   pol
 9      ADD>M              Soln.name   For-Std        V.add         0.100 mL
10    ADD)2
11    END

 Method: AB196_2               SEGMENT
                                    pol
--------------------------------------------------------------------------------

      Instructions   t/s   Main parameters            Auxiliary parameters
      ------------- -----  ------------------------  ------------------------
 1    0PURGE
 2    0STIR         10.0
 3    (REP
 4      DME
 5      DPMODE             U.ampl          -50 mV     t.meas         20.0 ms
                           t.step         0.30 s      t.pulse        40.0 ms
 6      SWEEP       36.0   U.start        -500 mV     U.step            6 mV
                           U.end         -1200 mV     Sweep rate       20 mV/s
 7      0MEAS              U.standby           mV
 8    REP)1
 9    PURGE
10    STIR               Rot.speed      2000 /min
11    END

  Method: AB196_2                SUBSTANCES
                              Formald  - pol
--------------------------------------------------------------------------------

      Recognition                              Display / Plot
      -------------------------                ---------------------------
      U.verify          -720 mV                I.scale       auto
      U.tol (+/-)         30 mV                U.div          50.00 mV/cm
      U.width min         10 mV                U.begin         -500 mV
      U.width max        200 mV                U.end           -900 mV
      I.threshold        250 pA

      Baseline                                 Evaluation
      -------------------------                ---------------------------
      Type           linear                    Mode          VA
      Scope          whole                     Quantity      I.peak
      dU.front       auto                      Sign. digits     4
       S.front       auto
      dU.rear        auto
       S.rear        auto

  Calibration   2000-12-01 17:01:39            Coefficients
  ---------------------------------            -------------------------
  Technique     std.add.                       Y.reg        -2.434e-08
  Curve type    linear                         Slope        -2.362e-05
                                               Nonlin.
                                               Mean dev.     4.193e-10

               Additions
               ------------------------------------------------------------
  Soln.name     For-Std
  ----------
  Mass conc.       100 mg/L            g/L            g/L            g/L
  Range min             g/L            g/L            g/L            g/L
  Range max             g/L            g/L            g/L            g/L
  M.conc./cm            g/L            g/L            g/L            g/L

 Method: AB196_2              CALCULATION
                             max. 15 lines

--------------------------------------------------------------------------------
 Quantity        Formula (R##, C##, A##)                  Res.unit   Sig.dig.
 ------------    ---------------------------------------  --------   --------
 Formald         R1000=MC:Formald                         #g/L          5
```