Polarographic determination of formaldehyde

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.

Apparatus and accessories

- 746 VA Trace Analyzer with 747 VA Stand or
- 757 VA Computrace

Sample preparation

- Waste water, solutions, and plating baths (e.g. electroless copper baths) can be analysed directly.
- Plastics and textiles are ground and extracted for aprr. 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(H₂SO₄) = 30 % is added. The formaldehyde is then steam distilled and absorbed in c(LiOH) = 0.05 mol/L.
Literature

- Linhart K. Bestimmung von freiem und gebundenem Formaldehyd in Textilhilfsmitteln durch Wechselstrompolarographie Melliand Textilber. 56(1975) 240-245
- Metrohm Info 2/98, 22-23
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:

\[
\text{HO-C-OH} \rightleftharpoons \text{H-O-C-H} + \text{H}_2\text{O}
\]

Reagents

- Lithium hydroxide monohydrate (LiOH·H$_2$O), CAS 1310-65-2
- Ethylenediaminetetraacetic acid (EDTA, Titriplex II®, Komplexon II®, Idranal II®), p.a., CAS 60-00-4
- Formaldehyde solution, w(HCHO) = 37%

Ready to use solutions

- Absorption solution:
  \[c(\text{LiOH}) = 0.05 \text{ mol/L}\]
  2.1 g LiOH are dissolved in 1000 mL water.
- Supporting electrolyte:
  \[c(\text{LiOH}) = 0.22 \text{ mol/L}, c(\text{EDTA}) = 0.02 \text{ mol/L}\]
  9.23 g LiOH and 5.85 g EDTA are dissolved in 1000 mL water.
- Standard solution:
  \[\beta(\text{HCHO}) = 200 \text{ mg/L}\]
  The standard solutions are prepared from a concentrated formaldehyde solution, which is diluted with water. The exact concentration is determined by titration.

Analysis

Measurement solution:

5 mL supporting electrolyte
+ 5 mL sample or absorption solution

The polarogram is registered with the following parameters:

<table>
<thead>
<tr>
<th>Working electrode</th>
<th>DME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stirrer</td>
<td>2000 rpm</td>
</tr>
<tr>
<td>Measurement mode</td>
<td>DP</td>
</tr>
<tr>
<td>Purge time</td>
<td>600 s</td>
</tr>
<tr>
<td>Pulse amplitude</td>
<td>50 mV</td>
</tr>
<tr>
<td>Start potential</td>
<td>-1.4 V</td>
</tr>
<tr>
<td>End potential</td>
<td>-1.8 V</td>
</tr>
<tr>
<td>Voltage step</td>
<td>10 mV</td>
</tr>
<tr>
<td>Voltage step time</td>
<td>0.4 s</td>
</tr>
<tr>
<td>Sweep rate</td>
<td>25 mV/s</td>
</tr>
<tr>
<td>Peak potential</td>
<td>-1.65 V</td>
</tr>
</tbody>
</table>

Two standard additions are done to determine the concentration.
Remarks

- 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.
- On the 746 VA Trace Analyzer SQW mode can be used instead of DP. The modulation frequency should be 25 Hz.

Figures

--- METROHM 746 VA TRACE ANALYZER (5.746.0101) ---

<table>
<thead>
<tr>
<th>Substance</th>
<th>Mass conc.</th>
<th>Mass</th>
<th>Cal.dev.</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formald</td>
<td>2.725 mg/L</td>
<td>13.62 ug</td>
<td>0.050 mg/L</td>
<td>1.83%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance</th>
<th>Techn.</th>
<th>Y.reg/offset</th>
<th>Slope</th>
<th>Nonlin.</th>
<th>Mean deviat.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formald</td>
<td>std.add.</td>
<td>-7.17e-08</td>
<td>-5.264e-05</td>
<td>4.059e-10</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Soln.name</th>
<th>Pos.</th>
<th>Std.subst.</th>
<th>Mass conc.</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formald</td>
<td>0.050</td>
<td>1.83</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance: Formald VR(**)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sub.</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>Forma 0.050 1.83</td>
</tr>
</tbody>
</table>

Standard addition curve: Formald

Fig. 1 Determination of formaldehyde acc. to Method 1 with the 746 VA Trace Analyzer
Fig. 2  Method for the determination of formaldehyde acc. to Method 1 with the 746 VA Trace Analyzer
Method 2

Determination of formaldehyde as hydrazone

Theory

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

\[
\begin{align*}
\text{HC} & \quad \text{H} \quad \text{N} \\
\text{C} & \quad \text{H} \quad \text{N} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

Reagents

- Sulphuric acid, \( w(\text{H}_2\text{SO}_4) = 96 \% \)
- Hydrazinium sulphate, p.a., CAS 10034-93-2
- Formaldehyde solution, \( w(\text{HCHO}) = 37 \% \)

Ready to use solutions

- Hydrazine solution:
  \[ \beta(\text{hydrazinium sulphate}) = 20 \text{ g/L} \]
  2 g hydrazinium sulphate are dissolved in 100 mL water.
- Standard solution:
  \[ \beta(\text{HCHO}) = 100 \text{ mg/L} \]
  The standard solutions are prepared from a concentrated formaldehyde solution, which is diluted with water. The exact concentration is determined by titration.

Analysis

Measurement solution:

- 10 mL (diluted) sample or absorption solution
- + 50 \( \mu \)L sulphuric acid
- + 1 mL hydrazine solution

The polarogram is registered with the following parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working electrode</td>
<td>DME</td>
</tr>
<tr>
<td>Stirrer</td>
<td>2000 rpm</td>
</tr>
<tr>
<td>Measurement mode</td>
<td>DP</td>
</tr>
<tr>
<td>Purge time</td>
<td>300 s</td>
</tr>
<tr>
<td>Pulse amplitude</td>
<td>50 mV</td>
</tr>
<tr>
<td>Start potential</td>
<td>-0.5 V</td>
</tr>
<tr>
<td>End potential</td>
<td>-1.2 V</td>
</tr>
<tr>
<td>Voltage step</td>
<td>6 mV</td>
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<tr>
<td>Voltage step time</td>
<td>0.3 s</td>
</tr>
<tr>
<td>Sweep rate</td>
<td>20 mV/s</td>
</tr>
<tr>
<td>Peak potential</td>
<td>-0.72 V</td>
</tr>
</tbody>
</table>

Two standard additions are done to determine the concentration.
Remarks

- The linear range is between appr. 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.

Figures

--- METROHM 746 VA TRACE ANALYZER (5.746.0101) ---

Determin. : AB196_2  
Title : Determination of Formaldehyde, AB196 method 2  
Remark1 : 10 ml Wasser + 50 µl H2SO4 + 1 ml Hydrazinsulfat  
Remark2 : + Probe

<table>
<thead>
<tr>
<th>Substance</th>
<th>Mass conc.</th>
<th>Add.mass</th>
<th>Comments</th>
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</thead>
<tbody>
<tr>
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<td>114.9 mg/L</td>
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<table>
<thead>
<tr>
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<th>I/nA</th>
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<th>Std.dev.</th>
<th>I.delta</th>
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<td>-24.37</td>
<td>-24.20</td>
<td>0.2360</td>
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<tr>
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<td>-24.04</td>
<td>-24.20</td>
<td>0.2360</td>
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<tr>
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<td>-65.39</td>
<td>0.1461</td>
<td>-20.00 rear overlapping</td>
<td></td>
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<tr>
<td>21</td>
<td>-711</td>
<td>-65.29</td>
<td>-65.39</td>
<td>0.1461</td>
<td>-20.00 rear overlapping</td>
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<thead>
<tr>
<th>Substance</th>
<th>Techn. Y.reg/offset</th>
<th>Slope</th>
<th>Nonlin. Mean deviat.</th>
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</thead>
<tbody>
<tr>
<td>Formald</td>
<td>-2.434e-08</td>
<td>-2.362e-05</td>
<td>4.193e-10</td>
</tr>
</tbody>
</table>

SOLUTIONS

<table>
<thead>
<tr>
<th>Soln.name</th>
<th>Pos.</th>
<th>Std.subst.</th>
<th>Mass conc.</th>
<th>Remark</th>
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<table>
<thead>
<tr>
<th>Substance: Formald</th>
<th>VR(**)</th>
<th>I (nA)</th>
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<tbody>
<tr>
<td></td>
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<td>-600</td>
</tr>
<tr>
<td></td>
<td>-650</td>
<td>-700</td>
</tr>
<tr>
<td></td>
<td>-750</td>
<td>-800</td>
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</table>

<table>
<thead>
<tr>
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<th>I (nA)</th>
<th>Standard addition curve: Formald</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>-550</td>
<td>-600</td>
</tr>
<tr>
<td></td>
<td>-650</td>
<td>-700</td>
</tr>
<tr>
<td></td>
<td>-750</td>
<td>-800</td>
</tr>
</tbody>
</table>

Fig. 3 Determination of formaldehyde acc. to Method 2 with the 746 VA Trace Analyzer
Method: AB196_2

--- OPERATING SEQUENCE ---

<table>
<thead>
<tr>
<th>Instructions</th>
<th>t/s</th>
<th>Main parameters</th>
<th>Auxiliary parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOS/M</td>
<td></td>
<td>V.added</td>
<td>11.050 mL</td>
</tr>
<tr>
<td>REM</td>
<td></td>
<td>Wasser/Hydr./Puffer</td>
<td></td>
</tr>
<tr>
<td>STIR</td>
<td>300.0</td>
<td>Rot.speed</td>
<td>2000 /min</td>
</tr>
<tr>
<td>SMPL&gt;M</td>
<td></td>
<td>V.fraction</td>
<td>mL</td>
</tr>
<tr>
<td>(ADD)</td>
<td>10.0</td>
<td>V.total</td>
<td>L</td>
</tr>
<tr>
<td>SEGMENT</td>
<td></td>
<td>Segm.name</td>
<td>pol</td>
</tr>
<tr>
<td>(ADD)</td>
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<td>Soln.name</td>
<td>For-Std</td>
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<tr>
<td>END</td>
<td></td>
<td>V.add</td>
<td>0.100 mL</td>
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</tbody>
</table>

Method: AB196_2

--- SEGMENT ---

<table>
<thead>
<tr>
<th>Instructions</th>
<th>t/s</th>
<th>Main parameters</th>
<th>Auxiliary parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>PURGE</td>
<td>10.0</td>
<td>U.ampl</td>
<td>-500 mV</td>
</tr>
<tr>
<td>STIR</td>
<td></td>
<td>t.step</td>
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<tr>
<td>REP</td>
<td></td>
<td>U.end</td>
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<tr>
<td>DME</td>
<td></td>
<td>U.standby</td>
<td>mV</td>
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<tr>
<td>SWEEP</td>
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<td>U.start</td>
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</tr>
<tr>
<td>MEAS</td>
<td></td>
<td>U.end</td>
<td>-1200 mV</td>
</tr>
<tr>
<td>REP</td>
<td></td>
<td>Sweep rate</td>
<td>20 mV/s</td>
</tr>
<tr>
<td>PURGE</td>
<td></td>
<td>U.begin</td>
<td>-500 mV</td>
</tr>
<tr>
<td>STIR</td>
<td></td>
<td>U.end</td>
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</tr>
<tr>
<td>END</td>
<td></td>
<td>Rot.speed</td>
<td>2000 /min</td>
</tr>
</tbody>
</table>

Method: AB196_2

--- SUBSTANCES ---

<table>
<thead>
<tr>
<th>Formald</th>
<th>pol</th>
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</thead>
<tbody>
<tr>
<td>U.verify</td>
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<td>U.tol.(+/-)</td>
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</tr>
<tr>
<td>U.width min</td>
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<td>U.meas</td>
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<tr>
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<tr>
<td>U.end</td>
<td>20 mV/s</td>
</tr>
<tr>
<td>I.peakd</td>
<td>4</td>
</tr>
<tr>
<td>I.front</td>
<td>auto</td>
</tr>
<tr>
<td>S.front</td>
<td>auto</td>
</tr>
<tr>
<td>I.rear</td>
<td>auto</td>
</tr>
<tr>
<td>S.rear</td>
<td>auto</td>
</tr>
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</table>

Coefficients:

Technique std.add.

<table>
<thead>
<tr>
<th>Curve Type</th>
<th>linear</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y.reg</td>
<td>-2.434e-08</td>
</tr>
<tr>
<td>Slope</td>
<td>-2.362e-05</td>
</tr>
<tr>
<td>Nonlin. Mean dev.</td>
<td>4.193e-10</td>
</tr>
</tbody>
</table>

Method: AB196_2

--- CALCULATION ---

| Formald | R1000=MC:Formald | #g/L | 5 |

Fig. 4 Method for the determination of formaldehyde acc. to Method 2 with the 746 VA Trace Analyzer