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# Application Bulletin

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Of interest to: General Analysis, Environmental Protection, B 1, 2, 3, 4, 6, 7, 8, 10, 13, 14  
Organic Chemistry, Pharmacy, Film, Food,  
Biology, Electroplating, Textiles, Paint

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## Polarographic determination of formaldehyde

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### 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 derivated with hydrazine forming the hydrazone, which can be measured polarographically in acidic solution.

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### Apparatus and accessories

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

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### 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 appr. 20 min in a shaker with  $c(\text{LiOH}) = 0.05 \text{ mol/L}$ . The extract is then separated by filtration or centrifugation.
- Air samples are absorbed in  $c(\text{LiOH}) = 0.05 \text{ mol/L}$ : 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  $w(\text{H}_2\text{SO}_4) = 30 \%$  is added. The formaldehyde is then steam distilled and absorbed in  $c(\text{LiOH}) = 0.05 \text{ mol/L}$ .

**Literature**

- Absenger R., Schliefer K.  
Analysis of textile-finishing agents. XI. Polarographic determination of free formaldehyde in nitrogen-containing cross-linking agents.  
Textilveredlung 8(1973) 580-581
- Ardelt H.W., Opel P.H., Steindorf W.  
Polarographische Bestimmung des freien Formaldehyds in Kunststoffbedarfsgegenständen  
Pharmazie 16(1961) 128-131  
Ref.: Fresenius Z Anal Chem 186(1962) 457
- Barbolani-Piccardi E., Legittimo-Cellini P.  
Hydroxymethanesulphinate salts and related decomposition products in waste water.  
Water, Air, Soil Poll 9(1978)301-307
- Collet P.  
Polarographische Bestimmung von Formaldehyd in Fische, Fischerzeugnissen und Krustentieren.  
GIT 32(1988) 191-194
- Eskinja I., Grabaric Z., Tkalcec M., Merzel V.  
On determination of formaldehyde in air by differential pulse polarography and related techniques.  
Microchim Acta (1984) 215-227
- Linhart K.  
Bestimmung von freiem und gebundenem Formaldehyd in Textilhilfsmitteln durch Wechselstrompolarographie  
Melliand Textilber. 56(1975) 240-245
- Novak V.  
Die polarographische Bestimmung von Verunreinigungen in Monomeren. II. Formaldehyd- und Benzaldehydbestimmung in Styrol.  
Chem Prumysl. 19(1969) 25-26  
Ref.: Fresenius Z Anal Chem 250(1970) 280
- Sandler S., Chung Y.H.  
Polarographic determination of hydrogen peroxide, formaldehyde and acetaldehyde in mixtures  
Anal Chem 30(1958) 1252-1255
- Wild P.W.  
Einige polarographische Methoden in der Galvanotechnik. Formaldehyd in einem Reduktiv-Kupfer-Bad.  
Galvanotechnik 62(1971) 2-4
- Zaitseva Z.V., Prokhorova E.K.  
Polarographic determination of formaldehyde in production area air.  
Zh Anal Khim 40(1985) 1308-1311  
Ref.: Fresenius Z Anal Chem 324(1986) 80
- Metrohm Info 2/98, 22-23

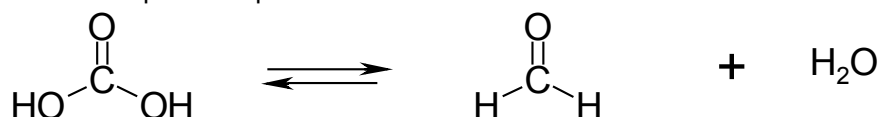
## **Method 1**

### **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 precedes the electrochemical reaction:



#### **Reagents**

- Lithium hydroxide monohydrate (LiOH · H<sub>2</sub>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(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 solution:  
β(HCHO) = 200 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:

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

Two standard additions are done to determine the concentration.

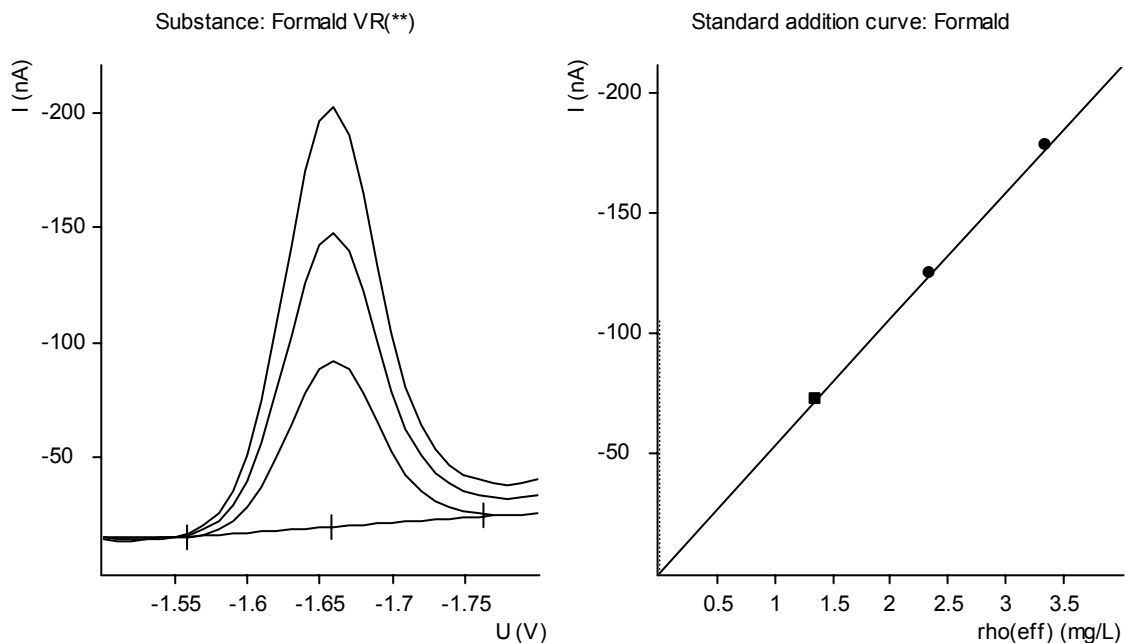
**Remarks**

- 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**

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===== 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
-----
Method : AB196_1a
Title  : Determination of Formaldehyde. AB196
Remark1: 5 mL electrolyte + 5 mL sample
Remark2:
-----
Substance : Formald
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
-----
Soln.name  Pos.  Std.subst.  Mass conc.  Remark
-----
Final results  +/- Res.dev.  %  Comments
-----
Formald = 2.7246 mg/L  0.050  1.83
    
```



**Fig. 1** Determination of formaldehyde acc. to Method 1 with the 746 VA Trace Analyzer

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===== 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	SAMPL/M		V.fraction	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	OPURGE			
2	OSTIR	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	OMEAS		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	Technique	Curve type	Coefficients
2000-12-01 16:38:17	std.add.	linear	Y.reg -7.171e-08
			Slope -5.264e-05
			Nonlin.
			Mean dev. 4.059e-10

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

```

Method: AB196_1a CALCULATION
                    max. 15 lines
    
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Quantity	Formula (R##, C##, A##)	Res.unit	Sig.dig.
Formald	R1000=MC:Formald	#g/L	5

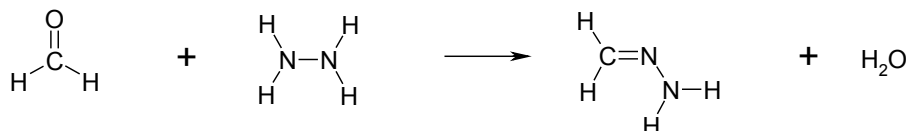
Fig. 2 Method for the determination of formaldehyde acc. to Method 1 with the 746 VA Trace Analyzer

## **Method 2**

### **Determination of formaldehyde as hydrazone**

#### **Theory**

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



#### **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  $\mu\text{L}$  sulphuric acid  
 + 1 mL hydrazine solution

The polarogram is registered with the following parameters:

Working electrode	DME
Stirrer	2000 rpm
Measurement mode	DP
Purge time	300 s
Pulse amplitude	50 mV
Start potential	-0.5 V
End potential	-1.2 V
Voltage step	6 mV
Voltage step time	0.3 s
Sweep rate	20 mV/s
Peak potential	-0.72 V

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**

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===== 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 Std	For	Ident.2/S2	Ident.3/S3	Method.call	Sample size/S0 100 uL
Method : AB196_2						
Title : Determination of Formaldehyde, AB196 method 2						
Remark1 : 10 ml Wasser + 50 µl H2SO4 + 1 ml Hydrazinsulfat						
Remark2 : + Probe						

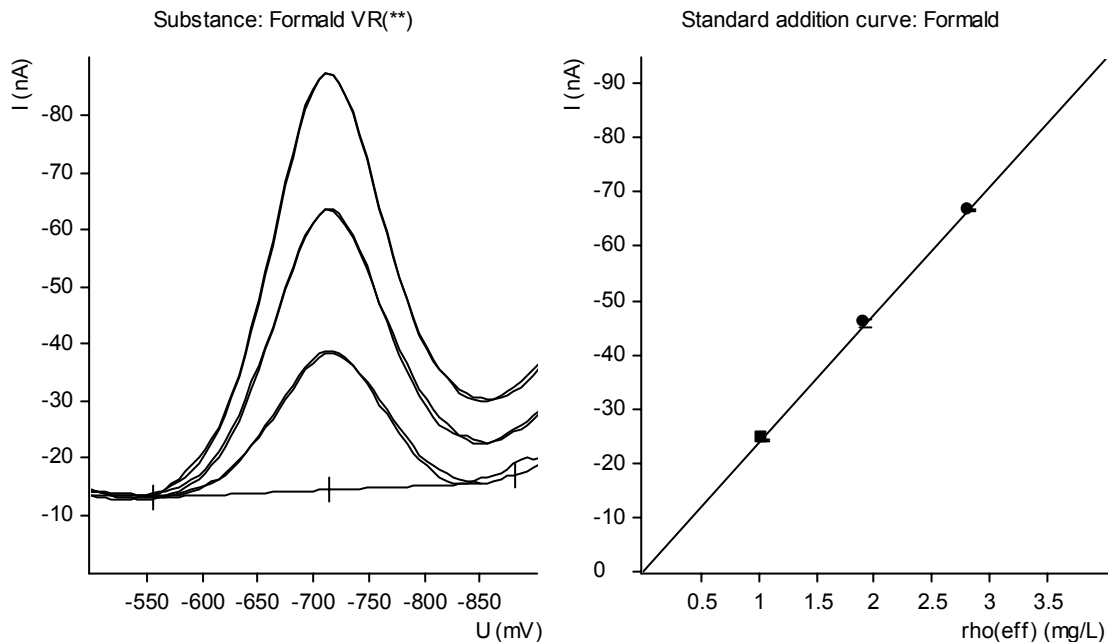
  

Substance	Techn.	Y.reg/offset	Slope	Nonlin.	Mean deviat.	Comments
Formald	std.add.	-2.434e-08	-2.362e-05		4.193e-10	

SOLUTIONS  
max. 40

Soln.name	Pos.	Std.subst.	Mass conc.	Remark
Final results			+/- Res.dev. %	Comments
Formald =	114.90 mg/L		2.58 2.25	



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

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===== 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	OPURGE			
2	OSTIR	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	OMEAS		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

 Technique std.add.  
Curve type linear

Coefficients
Y.reg -2.434e-08
Slope -2.362e-05
Nonlin.
Mean dev. 4.193e-10

Additions

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

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