# *N*-Methyl-2-pyrrolidone

| | |
|---|---|
| **Method number** | 2 |
| **Application** | Air analysis |
| **Analytical principle** | Gas chromatography |
| **Completed in** | November 2007 |

## Summary

This analytical method permits the determination of *N*-methyl-2-pyrrolidone (NMP) in a concentration range from 0.005 times to 2 times the currently valid limit value for workplace air (MAK value) proposed by the Deutsche Forschungsgemeinschaft (DFG). The ambient air is sampled using a suitable sampling pump that draws the air through an ADS-type silica gel tube; *N*-methyl-2-pyrrolidone is adsorbed onto the silica gel. After sampling, the collection layer and the control layer of the adsorber tube loaded with *N*-methyl-2-pyrrolidone are covered with a potassium hydroxide solution in methanol. When desorption of NMP has been achieved, the desorption solutions are analyzed by gas chromatography. The NMP is quantified with the aid of a nitrogen-selective detector (N-FID).

## Characteristics of the method

Precision:
Standard deviation (rel.): $s = 2.2–4.1\%$
Confidence interval: $u = 5.6–10.5\%$
Expanded uncertainty: $U = 11.6–15.8\%$
in the concentration range from 0.4 to 130 mg/m$^3$ and where $n = 6$ determinations

Limit of quantification:
Absolute: 6.77 ng *N*-methyl-2-pyrrolidone, which is equivalent to 0.42 mg/m$^3$ at an air sample volume of 40 L.

Recovery:
$\eta = 0.99$ (99%)

Sampling recommendation:
Sampling time: 2 h
Air sample volume: 40 L

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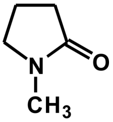

*N*-Methyl-2-pyrrolidone [CAS No. 872-50-4]

*N*-Methyl-2-pyrrolidone (NMP) is a colorless to slightly yellowish liquid with a weak amine-like odor (molecular weight 99.13 g/mol, melting point –24 °C, boiling point 203 °C) that is miscible with water, alcohol, benzene, acetone and chloroform. Due to its properties as a solubilizer, NMP is suitable for use with aqueous-organic mixed phases. According to the TRGS 900 as well as the List of MAK and BAT Values, the currently valid occupational exposure limit is 82 mg/m$^3$ (20 mL/m$^3$); the peak limit of *N*-methyl-2-pyrrolidone has been allocated an excursion factor of 2 in Category II [1, 2].

NMP is used to produce spinnable solutions of polyacrylnitrile, copolymerisates containing polyacrylnitrile, and polyesters from terephthalic acid. It dissolves polyvinyl chloride, polystyrene, polyamides, and polyurethanes in addition to many other plastics, resins, cellulose derivatives and colorants. NMP is used as a solvent for numerous inorganic substances such as sulfur, zinc chloride, sodium nitrite, sodium bromide, mercury chloride and some salts of iron, copper and lead. It is also used as a specific solvent for separating gas mixtures of hydrocarbons that are obtained by cracking processes. Furthermore, it can occur as a solvent in parquet floor adhesives or as a component of paint stripping agents. Please refer to the occupational medical justifications for MAK values for details on the toxicity of *N*-methyl-2-pyrrolidone [3].

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## Contents

## 1 General principles

This analytical method permits the determination of *N*-methyl-2-pyrrolidone (NMP) in a concentration range from 0.005 times to 2 times the limit value for workplace air (MAK value) proposed by the Deutsche Forschungsgemeinschaft (DFG). The ambient air is sampled using a suitable sampling pump that draws the air through an ADS-type silica gel tube; *N*-methyl-2-pyrrolidone is adsorbed onto the silica gel. After sampling, the collection layer and the control layer of the adsorber tube loaded

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with *N*-methyl-2-pyrrolidone are covered with a potassium hydroxide solution in methanol. When desorption of NMP has been achieved, the desorption solutions are analyzed by gas chromatography. The NMP is quantified with the aid of a nitrogen-selective detector (N-FID).

## 2 Equipment, chemicals and solutions

### 2.1 Equipment

- Pump for personal air sampling, flow rate 20 L/h
- Gas meter
- Tube holder, suitable for accommodating the tubes used
- Silica gel adsorber tube, type ADS, Dräger Safety AG & Co. KGaA, 23560 Lübeck, Germany
- Gas chromatograph with liquid injector, nitrogen-phosphorus detector and data evaluation unit
- Volumetric flasks, 2, 5, 10, 20 and 100 mL
- Glass pipette, 2.5 mL
- Microliter tips, 5, 10, 25, 50, 100, 250 and 500 µL
- Disposable PTFE filter, pore size 0.45 µm
- Screw-cap vials, sealable, nominal volume 7 mL
- Sample vials, sealable, nominal volume 1.5 mL
- Crimp-cap vials, sealable, nominal volume about 25 mL

### 2.2 Chemicals

- *N*-Methyl-2-pyrrolidone, p.a. (e.g. Fluka, Steinheim, Germany)
- Dibutylamine, 99%
- Methanol, >99.99%
- Potassium hydroxide pellets (KOH), p.a.
- Helium, 5.0 for gas chromatography

### 2.3 Solutions

Extraction solution: c (KOH) = 2% in methanol

2.0 g of potassium hydroxide pellets are weighed in a 100 mL volumetric flask and dissolved in approx. 30 mL of methanol while being stirred. When the KOH pellets have dissolved, the flask is filled to its nominal volume with methanol.

Internal standard (IS): c (dibutylamine) = 3.04 mg/mL

Approx. 10 mL of methanol are placed in a 20 mL volumetric flask and 80 µL of dibutylamine (60.8 mg) are added directly to the methanol. The flask is filled to its nominal volume with methanol and the solution is then transferred to a sealable crimp-cap vial and tightly sealed.

## 2.4 Calibration standards

It must be ensured that the volumetric flask remains open for as short a period as possible and that the *N*-methyl-2-pyrrolidone is directly dosed into the previously supplied methanol. The stock solution is then transferred to a sealable crimp-cap vial.

Stock solution: c (*N*-methyl-2-pyrrolidone) = 30.78 mg/mL

For the stock solution approx. 10 mL of methanol are placed in a 20 mL volumetric flask and 600 µL (615.6 mg) of *N*-methyl-2-pyrrolidone are added. The volumetric flask is then filled to its nominal volume with methanol.
This solution can be stored in the refrigerator at approx. 4 °C for up to four months.

Calibration solutions: c (*N*-methyl-2-pyrrolidone) = 18.47 to 307.80 µg/2.5 mL

Approx. 2.5 mL of methanol are placed in a 5 mL volumetric flask and the volume of the stock solution given in Table 1 is added in each case. The flasks are filled to their nominal values with methanol, 40 µL of the internal standard solution are added and they are shaken. A calibration standard of medium concentration is used for quality control each working day.
The calibration solutions must be freshly prepared before each calibration.

**Table 1.** Pipetting scheme for the calibration solutions in the concentration range from 18.5 to 307.8 µg/2.5 mL.

| Calibration solution No. | Volume of the stock solution [µL]] | Final volume of the calibration solution [mL] | Concentration of (*N*- methyl-2-pyrrolidone) [µg/2.5 mL] |
|---|---|---|---|
| 1 | 1.2 | 5.04 | 18.5 |
| 2 | 2.8 | 5.04 | 43.1 |
| 3 | 5.0 | 5.04 | 77.0 |
| 4 | 7.4 | 5.04 | 113.0 |
| 5 | 10.0 | 5.04 | 153.9 |
| 6 | 12.0 | 5.04 | 184.7 |
| 7 | 14.0 | 5.04 | 215.5 |
| 8 | 16.0 | 5.04 | 246.2 |
| 9 | 18.0 | 5.04 | 277.0 |
| 10 | 20.0 | 5.04 | 307.8 |

## 3 Sampling and sample preparation

Suitable pumps with a stabilized flow are used for sampling. The flow rate is set at 20°L/h with the help of a representative silica gel tube of the same manufacturing batch as the tube used for measurement. Immediately before sampling, the fused glass ends of the sampling tube are opened and the silica gel tube is connected to the pump. The recommended sampling time is 2 h. Immediately after sampling, the silica gel tube is tightly sealed with the caps designated for this purpose and the loaded tube is transferred as rapidly as possible to the analytical laboratory.

The tubes are opened in the laboratory and the contents are transferred completely into a 7 mL screw-cap vial. Then the silica gel is covered with 2.5 mL of the extraction solution and the vial is sealed. After 2 hours, 20 µL of the IS solution are added, the vial is briefly shaken, the solution is filtered through a disposable filter into a test vial and analyzed.

## 4 Operating conditions for chromatography

| | | |
|---|---|---|
| Apparatus: | Gas chromatograph with a nitrogen phosphorus detector, e.g. Clarus 1, PerkinElmer, Rodgau, Germany | |
| Precolumn: | FS Methyl-Sil 2.5 m CS fused silica, ID 0.25 mm | |
| Separation column: | Material: | Fused silica |
| | Stationary phase: | Rtx®-5 amine (from Restek) |
| | Length: | 30 m |
| | Internal diameter: | 0.25 mm |
| | Film thickness: | 1 µm |
| Detector: | Nitrogen-selective detector (N-FID) | |
| Temperatures: | Column: | 80 °C (5 min isothermal), heating rate 5 °C/min to 160 °C, analysis time 21 minutes |
| | Injector: | 180 °C, split 15 mL/min |
| Carrier gas: | Helium 5.0 | |
| Flow rate: | 1.5 mL/min (constant flow) | |
| Injection volume: | 1 µL | |

## 5 Analytical determination

To analyze the samples processed as described in Section 3, in each case 1 µL of the sample solution is injected into the gas chromatograph and analyzed under the conditions stated in Section 4.

If the measured concentrations are above the calibration range, then a suitable dilution must be prepared and the analysis must be carried out again.

## 6 Calibration

The calibration solutions described in Section 2.4 are used to obtain a calibration function. In each case 1 µL of the calibration solutions is injected into the gas chromatograph and analyzed in the same manner as the sample solutions. The peak areas obtained are plotted as a function of the corresponding concentration. The calibration curve is linear in the investigated concentration range. A control sample must be analyzed each working day to check the calibration function.

The calibration must be performed anew if the analytical conditions change or the quality control results indicate that this is necessary.

## 7 Calculation of the analytical result

The concentration of *N*-methyl-2-pyrrolidone in workplace air is obtained using the concentration of the substance in the test solution calculated by the data evaluation unit.

The following equations apply to the concentration of *N*-methyl-2-pyrrolidone in the workplace air:

$$\rho = \frac{(Fl - a)}{b \times V_{\mathrm{Air}} \times \eta} \times F \times \frac{273 + t_g}{273 + t_a} \; [\mathrm{mg/m^3}] \tag{1}$$

The following equation serves to calculate the value at 20 °C and 1013 hPa:

$$\rho_o = \rho \frac{273 + t_a}{293} \times \frac{1013}{p_a} \; [\mathrm{mg/m^3}] \tag{2}$$

The corresponding volume concentration $\sigma$ – independent of the pressure and temperature – is:

$$\sigma = \rho_o \times \frac{V_m}{M} \tag{3}$$

$$\sigma = \rho \frac{273 + t_a}{p_a} \times \frac{1013}{293} \times \frac{V_m}{M} \tag{4}$$

The following applies to *N*-methyl-2-pyrrolidone at $t_a = 20\,^{\circ}\mathrm{C}$ and $p_a = 1013$ hPa:

$$\sigma(\mathrm{NMP}) = \rho \times 0.243 \; \frac{\mathrm{mL}}{\mathrm{m^3}} \tag{5}$$

Where:

$\rho$ is the mass concentration of NMP in the ambient air at $t_a$ and $p_a$ in mg/m$^3$
$\rho_o$ is the mass concentration of NMP in the ambient air at 20 °C and 1013 hPa in mg/m$^3$
$a$ is the intercept of the calibration function with the y axis
$b$ is the gradient of the calibration function
$\eta$ is the recovery (to be taken into consideration if necessary)
$Fl$ is the peak area of the sample signal
$F$ is the conversion factor for the volume of the measured sample (in this case 0.0025 L)
$V_{Air}$ is the air sample volume in m$^3$
$t_g$ is the temperature in the gas meter in °C
$t_a$ is the temperature during sampling in °C
$p_a$ is the air pressure at the sampling location in hPa
$\sigma$ is the volume concentration of *N*-methyl-2-pyrrolidone in the ambient air in mL/m$^3$
$V_m$ is the molar volume of NMP in L/mol
$M$ is the molar mass of NMP in g/mol

## 8 Evaluation of the method

The characteristics of the method were calculated as stipulated in EN 482 [4] and DIN 32645 [5].

### 8.1 Precision

Five solutions in a concentration range from approx. 0.005 times to 1.5 times the MAK value for *N*-methyl-2-pyrrolidone were evaporated in a dynamic test gas facility at a relative air humidity of 36 to 83%. Six silica gel tubes per concentration were loaded as described in Section 3, processed under the working conditions stated in Section 4 and then analyzed. The results are shown in Table 2.

**Table 2.** Standard deviation (rel.) and expanded uncertainty $U$ for $n=6$ determinations [3].

| Concentration [mg/m$^3$] | Standard deviation (rel.) [%] | Expanded uncertainty $U$ [%] |
|---|---|---|
| 0.4 | 4.1 | 16 |
| 1.0 | 3.5 | 14 |
| 8.6 | 2.5 | 12 |
| 31 | 2.6 | 12 |
| 130 | 2.2 | 12 |

## 8.2 Recovery

The recovery of *N*-methyl-2-pyrrolidone was evaluated in the course of the determination of the precision in the lowest measurement range. A mean recovery of $\overline{\eta}=0.99$ (99%) was calculated from the individual recovery rates.
No influence due to higher air humidity was ascertained.

## 8.3 Limit of quantification

The limit of quantification was determined from a ten-point calibration in the concentration range from 7.0 to 70 µg/mL as stipulated in DIN 32645 [4]. The limit of quantification for *N*-methyl-2-pyrrolidone was 6.77 µg/mL (absolute 6.77 ng), which is equivalent to a relative limit of quantification of 0.42 mg/m$^3$ based on an air sample volume of 40 L.

## 8.4 Storage stability

A low concentration ($c = 1.4$ mg/m$^3$) and a high concentration ($c = 35$ mg/m$^3$) of *N*-methyl-2-pyrrolidone were evaporated in the dynamic test gas facility in order to determine the storage stability of the loaded samples. After sampling, the silica gel tubes were initially stored for seven days at room temperature and then in the refrigerator at +4 °C. A duplicate determination was carried out on the 1st, 3rd, 7th, 14th and 21st day.
No changes in the concentrations of *N*-methyl-2-pyrrolidone were found in the given time intervals.

## 8.5 Interference

The gas chromatographic analytical procedure is specific for *N*-methyl-2-pyrrolidone under the working conditions given here. A good separation from interfering signals generated by other amines is achieved with the selected separation column and under the working conditions stated in Section 4 (cf. Section 9).

## 8.6 Blank values

No blank values were detected.

## 9 Discussion

The concentration of *N*-methyl-2-pyrrolidone in workplace air can be selectively and exactly determined using the method presented here. The procedure is suitable for monitoring the currently valid MAK value of NMP.

The method described here (NMP, Method No. 2) was checked as part of a comparative measurement (NMP, Method No. 3) [6] in a dynamic test gas facility. The results show good agreement (cf. Table 3).

**Table 3.** Results of the comparison of the methods.

Determination of *N*-methyl-2-pyrrolidone, Method 2: GC/PND

| Design | 1 | 2 | 3 | per 6 samples |
|---|---|---|---|---|
| Number of analyses n= | 6 | 6 | 6 | |
| Theoretical value | 9.33 | 62.2 | 157 | mg/m$^3$ |
| **Measured value** | **9.5** | **68.1** | **165** | **mg/m$^3$** |
| **Standard deviation** | **0.4** | **4.4** | **5.7** | **mg/m$^3$** |
| **Standard deviation (rel.)** | **4.1** | **6.4** | **3.4** | **%** |
| Deviation from the | 0.2 | 5.9 | 8.0 | mg/m$^3$ |
| theoretical value | 1.8 | 9.5 | 5.1 | % |

Determination of *N*-methyl-2-pyrrolidone, Method 3: GC/MS

| Design | 1 | 2 | 3 | per 8 samples |
|---|---|---|---|---|
| Number of analyses n = | 8 | 8 | 8 | |
| Theoretical value | 9.33 | 62.2 | 157 | mg/m$^3$ |
| **Measured value** | **10.4** | **65.2** | **173** | **mg/m$^3$** |
| **Standard deviation** | **0.6** | **1.4** | **6.2** | **mg/m$^3$** |
| **Standard deviation (rel.)** | **5.5** | **2.2** | **3.6** | **%** |
| Deviation from the | 1.1 | 3.1 | 16.1 | mg/m$^3$ |
| theoretical value | 11.7 | 4.9 | 10.2 | % |

The analytical conditions given here are also suitable for determination of amines such as diethylamine, diethylmethylamine, triethylamine, ethyldimethylamine or cyclohexylamine [7].

It should be noted that the 2.5 m precolumn is indispensable for the gas chromatographic analysis. The precolumn prevents potassium hydroxide from being deposited in the separation column, which would lead to immediate lost of separation power.

## 10 References

[1] TRGS 900 (2009) Arbeitsplatzgrenzwerte. www.baua.de

[2] DFG (Deutsche Forschungsgemeinschaft) (2010) List of MAK and BAT Values 2010. Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Report No. 46. Wiley-VCH, Weinheim.

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[7] Messung von Gefahrstoffen – BGIA-Arbeitsmappe (2007) Aliphatische Amine. Kennzahl 6072, 39th issue. Erich Schmidt Verlag, Bielefeld.

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