N-Methyl-2-pyrrolidone

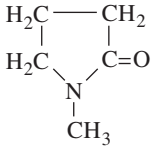
Application	Air analysis
Analytical principle	Gas chromatography
Completed in	May 1984

Summary

A sampling pump is used to draw air containing N-methyl-2-pyrrolidone vapour through acetone in wash bottles. Acetone absorbs the N-methyl-2-pyrrolidone and the concentration is subsequently determined by gas chromatography with a thermionic nitrogen detector or a flame ionization detector.
The quantitative evaluation makes use of a calibration curve in which the N-methyl-2-pyrrolidine concentrations of the calibration standards are plotted versus the peak areas.

Precision (N-FID):	Standard deviation (rel.)	s = 4.0–3.7 %
	Mean variation:	u = 8.4–7.7 %
	in a concentration range of 0.22–4.76 mL/m^3 of N-methyl-2-pyrrolidone in air	
	where	n = 20 determinations
Precision (FID):	Standard deviation (rel.)	s = 6.1 %
	Mean variation:	u = 13.2 %
	at a concentration of 3.38 mL/m^3 of N-methyl-2-pyrrolidone in air	
	where	n = 14 determinations
Detection limit (N-FID):	0.036 mL/m^3 N-methyl-2-pyrrolidone in air (equivalent to 0.15 mg/m^3) for a sample volume of 1 L	
Detection limit (FID):	0.15 mL/m^3 N-methyl-2-pyrrolidone in air (equivalent to 0.6 mg/m^3) for a sample volume of 1 L	
Recovery rate:		η = 0.87–0.96 (87–96 %)
Recommended sampling time:		> 5 min
Recommended sample volume:		1 L

N-Methyl-2-pyrrolidone



The compound N-methyl-2-pyrrolidone is a colourless liquid (molar mass 99.13 g/mole, boiling point 202 °C at 1013 hPa, vapour pressure 1.33 hPa at 40 °C) which is used as an additive in the agricultural pesticides. The MAK value (1983) is 100 mL/m^3 (400 mg/m^3).
For information about the toxic effects and modes of action of this substance see reference [1].

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Contents

1 General principles of the method

A sampling pump is used to draw air containing N-methyl-2-pyrrolidone vapour through acetone in wash bottles. Acetone absorbs the N-methyl-2-pyrrolidone and the concentration is subsequently determined by gas chromatography with a thermionic nitrogen detector or a flame ionization detector.
The quantitative evaluation makes use of a calibration curve in which the N-methyl-2-pyrrolidone concentrations of the calibration standards are plotted versus the peak areas.

2 Equipment, chemicals and solutions

2.1 Equipment (see Fig. 1)

Gas chromatograph equipped with a thermoionic nitrogen detector (N-FID) or flame ionization detector (FID), integrator or 1 mV recorder
2 Wash bottles (25 mL volume) with frits (A_1, A_2)
Thermos flasks (B_1, B_2)
Suction pump with a pumping capacity of at least 1 L/min (P)
Throttle valve (V)
Calibrated gas meter for volume measurements, suitable for measuring a flow rate of 1 L/min (G)
Thermometer (T_g, T_a)
Barometer (Ba)
10, 20, 50 and 100 mL Volumetric flasks
0.1, 0.5, 1, 2, 5 and 6 mL Automatic pipettes

2.2 Chemicals

Acetone, analytical grade
N-Methyl-2-pyrrolidone, for synthesis (about 99 %)

2.3 Calibration standards

Initial solution:
The initial solution is prepared by weighing a mass of about 20 mg N-methyl-2-pyrrolidone into a 100 mL volumetric flask containing about 20 mL acetone. The flask is filled up to the mark with acetone (200 µg/mL).

Stock solution:
The stock solution is prepared by pipetting 5 mL of the initial solution into a 100 mL volumetric flask and diluting it to the mark with acetone (10 µg/mL).

The stock solutions are diluted to give the calibration standards which contain 0.02–2.0 µg/mL of N-methyl-2-pyrrolidone.

Volume of the stock solution	Final volume of the calibration standards	Concentration of the calibration standards
mL	mL	µg/mL
0.1	50	0.02
0.1	20	0.05
0.1	10	0.10
0.5	10	0.50
1.0	10	1.00
2.0	10	2.00

3 Sample collection and preparation

Two wash bottles, each containing 6 mL of acetone, are connected in series and cooled by immersion in ice-water in thermos flasks. After the bottles have been connected with the sampling device (cf. Fig. 1), the air to be sampled is drawn through the wash bottles by a flow-stabilized pump or a pump fitted with a gas meter at a flow rate of 0.5 L/min (throttle valve).
Parameters influencing the measured concentration, such as sample volume (V_z), the temperature in the gas meter (t_g), the ambient temperature (t_a) and the ambient pressure (p_a), are noted.
After sampling is completed, the contents of wash bottles A_1 and A_2 are each transferred into a 10 mL volumetric flask, the wash bottles are rinsed out with acetone and the flasks are filled up to the mark. The concentration is determined by means of gas chromatography.

4 Operating conditions for gas chromatography

Column:	Material:	steel	
	Length:	2.4 m	
	Inner diameter:	2.36 mm (1/8 inch)	
Column packing:	10% Carbowax 20 M on Chromosorb W AW/DMCS 60–80 mesh		
Detector:	Thermoionic nitrogen detector (N-FID) or flame ionization detector (FID)		
Temperatures:		N-FID	FID
	Column:	200 °C	170 °C
	Injection block:	200 °C	200 °C
	Detector:	300 °C	300 °C
Carrier gas:	Helium:	(30 mL/min)	(30 mL/min)
Detector gases:	Hydrogen:	(3 mL/min)	(5 mL/min)
	Synthetic air:	(60 mL/min)	(50 mL/min)
Injected volume:		1 µL	1–5 µL

Examples of gas chromatograms of several concentrations of N-methyl-2-pyrrolidone are shown in Fig. 2.

5 Analytical determination

The instrument parameters are set up on the gas chromatograph. Volumes of 1 µL (N-FID) or 1–5 µL (FID) of the solutions from A_1 and A_2 are injected into the injection

block several times. The peak areas of the signals are determined. Analytical samples and calibration standards of comparable concentration are alternately injected to check the calibration factor.

6 Calibration

Volumes of 1 or 1–5 µL (N-FID or FID, respectively) of at least three calibration standards containing different concentrations of N-methyl-2-pyrrolidone are taken and analyzed by means of gas chromatography. The calibration curve is obtained by plotting the peak areas versus the concentrations of N-methyl-2-pyrrolidone. Computerized integrators automatically determine the calibration factor. A typical calibration curve is shown in Fig. 3.
The linearity of the calibration function for each detector was tested up to 20 µg of N-methyl-2-pyrrolidone in 10 mL of acetone. This is equivalent to 1/20 of the current MAK value with a sample volume of 1 L.

7 Calculation of the analytical results

The concentrations of N-methyl-2-pyrrolidone are read from the calibration curve. The mass of N-methyl-2-pyrrolidone (µg) in each sample solution is obtained by multiplying these values by the volume of the solution (mL). The sum of the masses contained in the two wash bottles corresponds to the total mass of N-methyl-2-pyrrolidone X (µg) in the sample.
The corresponding concentration ρ (mg/m^3) is calculated as follows:

$$\rho = \frac{X}{V_z \cdot \eta} \cdot \frac{273 + t_g}{273 + t_a}$$

At 20°C and 1013 hPa:

$$\rho_0 = \rho \cdot \frac{273 + t_a}{293} \cdot \frac{1013\ \text{hPa}}{p_a}$$

The corresponding concentration σ in mL/m^3 – independent of pressure and temperature – is calculated as follows:

$$\sigma = \rho_0 \cdot \frac{24.1\ \text{L} \cdot \text{mole}^{-1}}{99.13\ \text{g} \cdot \text{mole}^{-1}} =$$

$$\rho \cdot \frac{273 + t_a}{p_a} \cdot \frac{1013\ \text{hPa}}{293} \cdot \frac{24.1\ \text{L} \cdot \text{mole}^{-1}}{99.13\ \text{g} \cdot \text{mole}^{-1}}$$

$$\sigma = \rho \cdot \frac{273 + t_a}{p_a} \cdot 0.814 \cdot \frac{\text{hPa} \cdot \text{mL}}{\text{mg}}$$

At t_a = 20 °C and p_a = 1013 hPa:

$$\sigma = \rho \cdot 0.243 \frac{\text{mL}}{\text{mg}}$$

Legend:

X Sum of the masses of N-methyl-2-pyrrolidone in µg in the sample solutions
V_z Measured sample volume in L
η Recovery rate
t_g Temperature in the gas flow meter in °C
t_a Temperature of the ambient air in °C
p_a Pressure of the ambient air in hPa
ρ Concentration of N-methyl-2-pyrrolidone in the ambient air in mg/m^3 at t_a and p_a (see above)
ρ_0 Concentration of N-methyl-2-pyrrolidone in the ambient air in mg/m^3 at 20°C and 1013 hPa
σ Concentration of N-methyl-2-pyrrolidone in the ambient air in mL/m^3

8 Reliability of the method

8.1 Precision

In order to determine the precision of the gas chromatographic method with the N-FID, 20 separate analyses of two solutions containing average concentrations of 0.089 µg/mL and 1.96 µL of N-methyl-2-pyrrolidone in acetone were carried out. The standard deviation (rel.) was s = 3.7 and 4 %. The mean variation was 7.7 and 8.4 %. In the case of the FID the standard deviation (rel.) was s = 6.1 % and the mean variation u = 13.2 % for a concentration of 1.39 µg/mL.

8.2 Recovery rate

The extent to which N-methyl-2-pyrrolidone vapour is absorbed in acetone was tested with the experimental apparatus shown in Fig. 4. A defined mass of the component (dissolved in 0.5 L of acetone) was pipetted into wash bottle D which was warmed in a water bath to 35 °C. The vapour was drawn through two consecutive wash bottles with frits (W_1 and W_2) with a stream of dry air (flow rate 0.5 L/min). The recovery rate was 78–100 % (cf. Tab. 1). The entire amount of recovered N-methyl-2-pyrrolidone was in the first wash bottle.

8.3 Detection limit

Under the conditions described here, the detection limit for N-methyl-2-pyrrolidone was 0.036 mL/m^3 (equivalent to 0.15 mg/m^3) for a sample volume of 1 L with the N-FID and 0.15 mL/m^3 (equivalent to 0.6 mg/m^3) with the FID.

8.4 Specificity

With the N-FID and under these conditions, the following compounds do not interfere with the determination at concentrations of 10 mg per 10 mL of acetone: benzene, trichloromethane, diethyl ether, dichloromethane, N,N-dimethyl formamide, 1,4-dioxane, ethyl acetate, methanol, n-hexane, n-heptane, methyl isobutyl ketone, xylene, tetrachloromethane, acetonitrile, 1-butanol, ethanol, cyclohexane, pyridine, carbon disulfide and tetrachloroethene.

9 Discussion of the method

The method described here permits an accurate and rapid determination of N-methyl-2-pyrrolidone in air.
Although the sensitivity of a normal FID is sufficient to detect about 1 % of the current MAK value of N-methyl-2-pyrrolidone, the thermoionic detector is to be recommended, especially when components which cannot be detected by means of the N-FID cause interference in the FID chromatogram.

Apparatus:
Gas chromatograph 5710 equipped with a thermoionic nitrogen detector made by Hewlett Packard, or gas chromatograph 5880 equipped with a flame ionization detector from Hewlett Packard.

10 References

[1] *D. Henschler* (Ed.): Gesundheitsschädliche Arbeitsstoffe, toxikologisch-arbeitsmedizinische Begründung von MAK-Werten. Deutsche Forschungsgemeinschaft, Verlag Chemie, Weinheim, 6th issue 1978.

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Table 1. Recovery rate for N-methyl-2-pyrrolidone.

Mass of N-methyl-2-pyrrolidone	Receiver	Recovered in the 1st Wash bottle	2nd Wash bottle	Total	Total
µg	µg	µg	µg	µg	%
19.840	10.135	6.295	–	16.430	82.8
1.984	0.620	1.365	–	1.985	100.1
0.198	–	0.155	–	0.155	78.3

$$M = \frac{M\,(\%)}{n} = 87.1\%$$

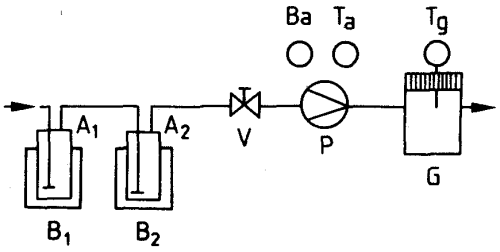

Fig. 1. Sampling apparatus.
A_1, A_2 Wash bottles with frits
B_1, B_2 Thermos flasks filled with ice-water
V Throttle valve
P Pump
G Gas meter
T_g Thermometer for the sample air
T_a Thermometer for the ambient air
Ba Barometer

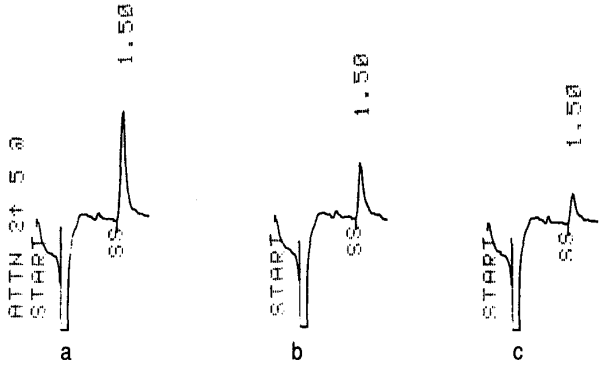

Fig. 2. Gas chromatograms of three solutions of N-methyl-2-pyrrolidone in acetone (N-FID)
a) 0.245 µg/mL
b) 0.123 µg/mL
c) 0.061 µg/mL
Attenuation: 32
Retention time for N-methyl-2-pyrrolidone: 1.5 min
Operating conditions for gas chromatography see Section 4.

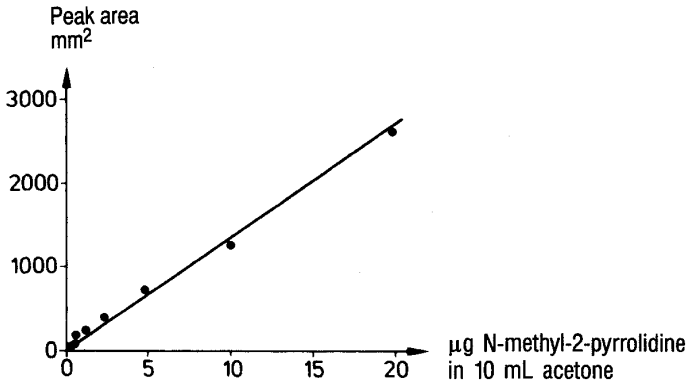

Fig. 3. Example of a calibration curve for the gas chromatographic analysis of N-methyl-2-pyrrolidone in air with the N-FID.

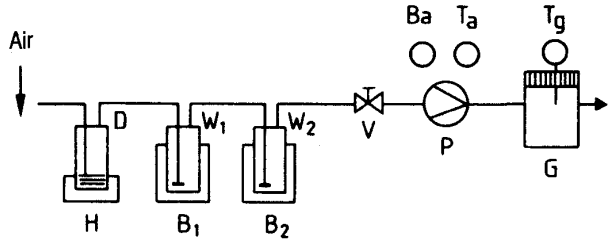

Fig. 4. Apparatus to determine the recovery rate.

D	50 mL Wash bottle (N-methyl-2-pyrrolidone)
H	Water bath, 35 °C
W_1, W_2	Wash bottles with frits
B_1, B_2	Thermos flasks filled with ice-water
V	Throttle valve
P	Pump
G	Gas meter
T_g, T_a	Thermometers
Ba	Barometer