Method number:	PV2043
Target concentration:	51 ppm (103 mg/m^3)
Procedure:	Samples are collected by drawing a known volume of air through a charcoal tube. Samples are desorbed with 95:5 methylene chloride:methanol and analyzed by gas chromatography with a flame ionization detector (GC-FID).
Air volume and sampling rate studied:	50 minutes at 0.2 Lpm. (10 L)
Status of method:	Partially Validated method. This method has been only partially evaluated and is presented for information and trial use.

June 1991

Mary E. Eide

Organic Service Branch I
OSHA Salt Lake Technical Center
Salt Lake City UT 84115-1802

1 General Discussion

1.1 Background

1.1.1 History of procedure

The OSHA Technical Center has received many requests for a sampling and analytical procedure for methyl pyrrolidinone. Charcoal tube sampling and desorption with 1 mL carbon disulfide was tried initially, but the desorption efficiency averaged 32.7%. Desorption with 1 mL 99:1 carbon disulfide:DMF had concentration dependent desorption ranging from 73.2% to 84.4% for concentrations ranging from 2.066 to 16.528 mg. Desorption with 1 mL 95:5 methylene chloride:methanol averaged 99.4% for concentrations from 0.1033 to 2.066 mg. Charcoal tubes had good storage and retention efficiencies. A target level of 51 ppm was chosen, as it is half the recommended TWA TLV listed on the MSDS from several manufacturers.

1.1.2 Potential workplace exposure (Ref. 5.1)

Methyl pyrrolidinone is used as a solvent in many applications. It is used to facilitate the formation of many chemicals. It is also used as a solvent for various extractions in cracking oils and in further petrochemical reactions. It is used as a medium for polymerization, and as a solvent for finished polymers. In addition, it is used in stripping potting resins and epoxides.

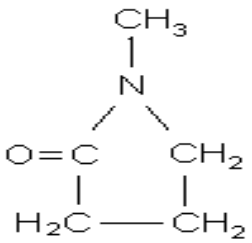
1.1.3 Toxic Effects (This section is for information purposes and should not be taken as the basis for OSHA policy.) (Ref. 5.2)

Methyl pyrrolidinone in rats had a TD_{LO} of 7500 mg/kg for skin exposure and a LD_{50} of 3564 mg/kg, with weight loss and body temperature decreases noted in the survivors. In humans, methyl pyrrolidinone is an irritant to eyes, skin, and mucous membranes. Prolonged exposure may cause headache, nausea, vomiting, and dizziness.

1.1.4 Physical properties (Ref. 5.3):

CAS:	872-50-4
IMIS:	M139
RTECS:	74457 (UY5790000)
Synonyms:	1-Methyl-2-pyrrolidinone; 1-Methyl-5-pyrrolidinone; NMP; Methyl pyrrolidone; M-Pyrol
Molecular weight:	99.13
Density:	1.033
Freezing point:	- 24 °C
Boiling point:	202 °C
Flash point:	95 °C (204 °F) (open cup)
Color:	colorless liquid
Odor:	mild amine-like
Molecular formula:	C_5H_9NO

Compound:



1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 4 ng with a 1-µL injection volume. This is the smallest amount which could be detected under normal operating conditions.

1.2.2 The overall detection limit is 0.1 ppm based on a 10-liter air volume. (All ppm amounts in this study are based on a 10 L air volume.)

1.3 Advantages

1.3.1 The sampling procedure is convenient.

1.3.2 The analytical method is reproducible and sensitive.

1.3.3 Reanalysis of samples is possible.

1.3.4 It may be possible to analyze other compounds at the same time.

1.3.5 Interferences may be avoided by proper selection of column and GC parameters.

1.4 Disadvantages

Due to the volatility of the methylene chloride in the desorbing solvent, it may be necessary to have a fan blowing on the instrument, in order to have consistent injections, when using an autosampler.

2 Sampling procedure

2.1 Apparatus

2.1.1 A calibrated personal sampling pump, the flow of which can be determined within ±5% at the recommended flow.

2.1.2 Charcoal tubes, lot 120, containing 100 mg adsorbing section with a 50 mg backup section separated by a 2-mm portion of urethane foam, with a silanized glass wool plug before the adsorbing section and a 3-mm plug of urethane foam at the back of the backup section. The ends are flame sealed and the glass tube containing the adsorbent is 7-cm x 6-mm o.d. x 4-mm i.d., SKC tubes, or equivalent.

2.2 Sampling technique

2.2.1 Open the ends of the charcoal tubes immediately before sampling.

2.2.2 Connect the charcoal tube to the sampling pump with flexible tubing.

2.2.3 Place the tubes in a vertical position to minimize channeling, with the smaller section towards the pump.

2.2.4 Air being sampled should not pass through any hose or tubing before entering the charcoal tube.

2.2.5 Seal the charcoal tube with plastic caps immediately after sampling. Seal each sample lengthwise with Form OSHA-21 seal.

2.2.6 With each batch of samples, submit at least one blank tube from the same lot used for samples. This tube should be subjected to exactly the same handling as the samples (break ends, seal, & transport) except that no air is drawn through it.

2.2.7 Transport the samples (and corresponding paperwork) to the lab for analysis.

2.2.8 Bulks submitted for analysis must be shipped in a separate mailing container from other samples.

2.3 Desorption efficiency

Six tubes were liquid spiked at each loading of 0.103, 0.517, 1.03, and 2.07 mg/mL methyl pyrrolidinone. They were allowed to equilibrate overnight at room temperature. They were then opened; each section placed into a separate 2-mL vial and desorbed with 1 mL of the desorbing solution for 30 minutes with occasional shaking. They were then analyzed by GC-FID. The overall average was 99.4 %.(Table 1)

Table 1
Desorption Efficiency

tube #	% recovered			
	0.103 mg	0.517 mg	1.03 mg	2.07 mg
1	99.9	99.5	100	100
2	98.8	100	96.9	99.6
3	98.5	99.8	100	99.6
4	99.1	100	100	99.7
5	98.2	99.5	99.0	100
6	99.0	99.8	99.3	99.7
average	99.0	99.8	99.3	99.7

overall average = 99.4%
standard deviation ±0.735

2.4 Retention efficiency

Six tubes were liquid spiked with 2.07 mg (51.0 ppm) methyl pyrrolidinone, allowed to equilibrate overnight, and had 10 liters humid air (91% RH) pulled through them. They were then opened, desorbed, and analyzed by GC-FID. The retention efficiency averaged 99.6%. There was no methyl pyrrolidinone found on the backup portions of the tubes. (Table 2)

Table 2
Retention Efficiency

tube #	% recovered		total
	'A'	'B'	
1	99.9	0.0	99.9
2	97.7	0.0	97.7
3	98.9	0.0	98.9
4	99.9	0.0	99.9
5	101	0.0	101
6	100	0.0	100

average = 99.6%

2.5 Storage

Six tubes were spiked with 2.07 mg (51.0 ppm) methyl pyrrolidinone and stored at room temperature until opened and analyzed. Three tubes were opened and analyzed at seven days and the other three were analyzed after 15 days. The recoveries averaged 99.3 % over the 15 days stored. (Table 3)

Table 3
Storage Study

days	% recovered
7	101
7	97.0
7	95.9
15	100
15	101
15	101
average	99.3%

2.6 Precision

The precision was calculated using the area counts from six injections of each standard at concentrations of 0.103, 0.517, 1.03, and 2.07 mg/mL methyl pyrrolidinone in the desorbing solvent. The pooled coefficient of variation was 0.00731. (Table 4)

Table 4
Precision Study

injection number	0.103 mg/mL	0.517 mg/mL	1.03 mg/mL	2.07 mg/mL
1	31014	147390	286310	568130
2	31413	147880	283730	566190
3	31606	146470	286010	571550
4	31033	147830	288630	572980
5	31339	147000	288270	565930
6	31196	145030	282800	574330
average	31267	146933	285958	569852
standard deviation –	±230	±1072	±2347	±3591
CV -	0.00736	0.00730	0.00821	0.00630

pooled CV = 0.00731

Where:

$$CV\ \left(Coefficient\ of\ Variation\right) = \frac{\left(s\,tan\,dard\ \ deviation\right)}{\left(average\right)}$$

$$Pooled\ \ CV\ = \sqrt{\frac{A1\left(CV1\right)^{2}\ +\ A2\left(CV2\right)^{2}\ +\ A3\left(CV3\right)^{2}\ +\ A4\left(CV4\right)^{2}}{A1\ +\ A2\ +\ A3\ +\ A4}}$$

A1, A2, A3, A4 = number of injections at each level
CV1, CV2, CV3, CV4 = Coefficients of variation at each level

2.7 Air volume and sampling rate studied

2.7.1 The air volume studied was 10 liters.

2.7.2 The sampling rate studied was 0.2 liters per minute.

2.8 Interferences

Suspected interferences should be listed on sample data sheets.

2.9 Safety precautions

2.9.1 Sampling equipment should be placed on an employee in a manner that does not interfere with work performance or safety.

2.9.2 Safety glasses should be worn at all times.

2.9.3 Follow all safety practices that apply to the workplace being sampled.

3 Analytical method

3.1 Apparatus

3.1.1 Gas chromatograph equipped with a flame ionization detector. An HP 5890 was used in this study.

3.1.2 GC column capable of separating the analyte and an internal standard from any interference. The column used in this study was a 60-m x 0.32-mm i.d. (0.5 µm d_f DB-Wax) capillary.

3.1.3 An electronic integrator or some other suitable method of measuring peak areas.

3.1.4 Two milliliter vials with PTFE-lined caps.

3.1.5 A 1.0-µL syringe or other convenient size for sample injection.

3.1.6 Pipets for dispensing the desorbing solution. The Glenco 1-mL dispenser was used in this method.

3.1.7 Volumetric flasks, 5-mL, and other convenient sizes for preparing standards.

3.2 Reagents

3.2.1 Purified GC grade nitrogen, hydrogen, and air.

3.2.2 Methyl pyrrolidinone, Reagent grade

3.2.3 Methylene chloride, HPLC grade

3.2.4 Methanol, HPLC grade

3.2.5 n-Hexanol, Reagent grade, used as the internal standard

3.2.6 The desorbing solution is 95:5 methylene chloride:methanol with 0.25 µL/mL n-hexanol internal standard.

3.3 Sample preparation

3.3.1 Sample tubes are opened and the front and back section of each tube are placed in separate 2-mL vials.

3.3.2 Each section is desorbed with 1 mL of the desorbing solution of 95:5 methylene chloride:methanol with 0.25 µL/mL n-hexanol internal standard.

3.3.3 The vials are sealed immediately and allowed to desorb for 30 minutes with occasional shaking.

3.4 Standard preparation

3.4.1 Standards are prepared by diluting a known quantity of methyl pyrrolidinone with the desorbing solution. A standard of 1 µL/mL methyl pyrrolidinone in the desorbing solution is 1033 µg/mL.

3.4.2 At least two separate standards at the calibration level should be made.

3.4.3 A third analytical standard should be prepared at a higher concentration to check the linearity of the detection. For this study, two standards at 1 µL/mL (1.033 mg/mL) and one standard at 4 µL/mL (4.132 mg/mL) methyl pyrrolidinone were used.

3.5 Analysis

3.5.1 Gas chromatograph conditions.

Flow rates	**(mL/min.)**	**Temperature**	**(°C)**
Nitrogen (make-up):	30	Injector:	200
Hydrogen (carrier):	2	Detector:	225
Hydrogen (detector):	30	Column:	80 °C 1min then heat at
Air:	350		10 °C/min to 160 °C

Chromatogram: see Figure 1
Injection size: 1 µL

3.5.2 Peak areas are measured by an integrator or other suitable means.

3.6 Interferences (analytical)

3.6.1 Any compound having the general retention time of the analyte or the internal standard used is interference. Possible interferences should be listed on the sample data sheet. GC parameters should be adjusted if necessary so these interferences will pose no problems.

3.6.2 Retention time data on a single column is not considered proof of chemical identity. Samples over the target concentration should be confirmed by GC/Mass Spec or other suitable means.

3.7 Calculations

3.7.1 The instrument is calibrated with a standard of 1.033 mg/mL (1 µL/mL) methyl pyrrolidinone in the desorbing solution. The linearity of the calibration is checked with a standard of 4.132 mg/mL (4 µL/mL) methyl pyrrolidinone in the desorbing solution.

3.7.2 If the calibration is non-linear, two more standards must be analyzed so a calibration curve can be plotted and sample values obtained.

3.7.3 To calculate the concentration of analyte in the air sample the following formulas are used:

$$mass\ of\ analyte,\ \mu g = \frac{(\mu g\ /\ mL)(desorption\ volume,\ mL)}{(desorption\ efficiency,\ decimal)}$$

$$moles\ of\ analyte = \frac{(mass\ of\ analyte,\ \mu g)(1\ g)}{(molecular\ weight)(10^6\ \mu g)}$$

$$volume\ of\ analyte = (moles\ of\ analyte)(molar\ volume)$$

$$ppm = \frac{(volume\ of\ analyte)(10^6)^*}{(air\ volume,\ L)}$$

* All units must cancel.

3.7.4 The above equations can be consolidated to form the following formula. To calculate the ppm of analyte in the sample based on a 10-liter air sample:

$$ppm = \frac{(\mu g\ /\ mL)(DV)(24.46)}{(10\ L)(DE)(MW)}$$

Where:

μg/mL = concentration of analyte in sample
24.46 = Molar volume (liters/mole) at 25 °C and 760 mmHg
MW = Molecular weight (g/mole)
DV = Desorption volume, mL
10 L = Air volume sampled, L
DE = Desorption efficiency, decimal

3.7.5 This calculation is done for each section of the sampling tube and the results added together.

3.8 Safety precautions

3.8.1 All handling of solvents should be done in a hood.

3.8.2 Avoid skin contact with all solvents.

3.8.3 Wear safety glasses at all times.

4 Recommendations for further study

Collection studies need to be performed.

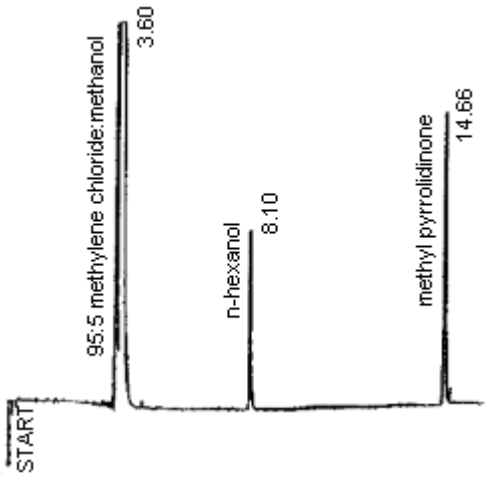


Figure 1. An analytical standard of 1.033 mg/mL
Methyl pyrrolidinone in the desorbing solvent of 95:5
methylene chloride:methanol with n-hexanol internal standard.

5 References

5.1 Grayson, M., "Kirk Othmer Encyclopedia of Chemical Technology," Third Edition, John Wiley & Son, N.Y., 1981, Vol. 19, p. 514.

5.2 Sweet, D., "Registry of Toxic Effects of Chemical Substances," 1985-86 Edition, U.S. Department of Health and Human Services, Public Health Service, Center for Disease Control, NIOSH, 1987, Vol. 5, p. 4221.

5.3 Sax, N., "Dangerous Properties of Industrial Materials," Fifth Edition, Van Nostrand Reinhold Co., New York, 1979, p. 831.