



Methyl Isoamyl ketone (MIAK)

Method number:	PV2042
Target Concentration:	50-ppm (234 mg/m ³) OSHA permissible exposure limit (PEL).
Procedure:	Samples are collected by drawing known volumes of air through glass sampling tubes containing charcoal adsorbent. Samples are desorbed with a 99:1 (v/v) carbon disulfide/dimethyl formamide solution and analyzed by gas chromatography (GC) using a flame ionization detector (FID).
Recommended air volume and sampling rate:	50 minutes at 0.2 L/min (10 L)
Detection limit of the overall procedure:	0.21 ppm (0.985 mg/m ³) (based on the recommended air volume and the analytical detection limit)
Special requirement:	Ship the samples to the laboratory for analysis immediately after sampling. If delay is unavoidable, store the samples at reduced temperature. Store samples in a refrigerator upon receipt at the laboratory.
Status of method:	Partially Validated method. This method has been partially evaluated and is presented for information and trial use only.

January 1992 (Final)

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1 General Discussion

1.1 Background

1.1.1 History of procedure

This evaluation was undertaken to develop a sampling and analytical procedure for MIAK at 50 ppm OSHA PEL (Ref. 5.1).

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

Eye and nose irritation are encountered at low levels. Narcosis and death can result at high concentrations. The toxic behavior would be expected to closely resemble methyl isobutyl ketone (Ref. 5.2).

1.1.3 Potential workplace exposure

MIAK is used as a solvent for cellulose esters, acrylics, and vinyl copolymers (Ref. 5.2 and 5.3). No data is available on the extent of work place exposure.

1.1.4 Physical properties (Ref. 5.2, 5.3, and 5.4)

CAS number:	110-12-3
IMIS number:	1776
Molecular weight:	114.19
Molecular formula:	C ₇ H ₁₄ O
Density:	0.888 at 20 °C
Boiling point:	144 °C at 101.3 kPa (760 mmHg)
Solubility:	slightly soluble in water, soluble in alcohol and ether
Chemical name:	MIAK (methyl isoamyl ketone)
Synonyms:	5-Methyl-2-hexanone; 2-Methyl-5-hexanone; Methyl isopentyl ketone
Appearance:	colorless, clear liquid with a pleasant odor
Structure:	(CH ₃) ₂ CHCH ₂ CH ₂ COCH ₃

1.2 Limit defining parameters

The detection limit of the analytical procedure, including a 9:1 split ratio, is 1.09 ng per injection. This is the amount of analyte which will give a peak whose height is approximately five times the baseline noise.

2 Sampling Procedure

2.1 Apparatus

2.1.1 Samples are collected by using a personal sampling pump that can be calibrated to within ±5% of the recommended flow rate with the sampling device in line.

2.1.2 Samples are collected with 7.0-cm x 4-mm i.d. x 6-mm o.d. glass sampling tubes packed with two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 °C prior to packing. The sampling section contains 100 mg and the back section contains 50 mg of charcoal. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of Silane treated glass wool is placed in front of the sampling section.

2.2 Reagents

No sampling reagents are required.

2.3 Sampling technique

- 2.3.1 Immediately before sampling, break off the ends of the charcoal tube. All tubes should be from the same lot.
- 2.3.2 Attach the sampling tube to the sampling pump with flexible tubing. Position the tube so that sampled air first passes through the 100-mg section.
- 2.3.3 Attach the tube vertically in the employee's breathing zone in such a manner that it does not impede work performance.
- 2.3.4 After sampling for the appropriate time, remove the sampling tube and seal it with plastic caps.
- 2.3.5 Wrap each sample end-to-end with a Form OSHA-21 seal.
- 2.3.6 Record the air volume for each sample, and list any possible interference.
- 2.3.7 Submit at least one blank for each set of samples. Handle the blank in the same manner as the samples, except no air is drawn through it.
- 2.3.8 Ship the samples to the laboratory for analysis immediately after sampling. If delay is unavoidable, store the samples at reduced temperature.
- 2.3.9 Submit bulk samples for analysis in a separate container. Do not ship them with air samples.

2.4 Desorption efficiency

Sixteen vials, each containing a 100-mg portion of charcoal, were divided into four groups of four vials each. Vials of the first group were liquid spiked with 2.6 μL of 10% MIAK in carbon disulfide. Vials of the other three groups were liquid spiked with 1.4, 2.6 and 5.2 μL of neat MIAK ($d = 0.888$), respectively. These amounts represent 0.1 \times , 0.5 \times , 1.0 \times , and 2.0 \times the target concentration. The vials were stored overnight in a refrigerator (0°C), desorbed with 1.0 mL of the desorbing solution, and analyzed as in Section 3. The overall average desorption efficiency was 96.3%. The results are listed in Table 2.4.

Table 2.4
Desorption Efficiency

sample #	µg spiked	µg found	% recovered
1	229	214	93.6
2	229	214	93.6
3	229	222	97.0
4	229	218	95.3
average of 0.1x PEL = 94.9%			
5	1231	1145	92.5
6	1231	1193	96.9
7	1231	1180	95.9
8	1231	1198	97.4
average of 0.5x PEL = 95.7%			
9	2286	2232	97.6
10	2286	2235	97.8
11	2286	2226	97.4
12	2286	2221	97.1
average of 1.0x PEL = 97.5%			
13	4571	4453	97.4
14	4571	4429	96.9
15	4571	4392	96.1
16	4571	4438	97.1
17	blank	0	blank
average of 2.0x PEL = 96.9%			

2.5 Retention efficiency

Five charcoal tubes were each liquid spiked with 2.6 µL (1× PEL) of neat MIAK. These were allowed to equilibrate for 2 hours and then 10 L of humid air (~80% relative humidity) were drawn through each tube at 0.2 L/min. The tubes were then desorbed with 1.0 mL of desorbing solution, and analyzed as in Section 3. The results are listed in Table 2.5.

Table 2.5
Retention Efficiency

sample #	µg spiked	µg found	% recovered
1	2286	2131	93.2
2	2286	2111	92.4
3	2286	2137	93.5
4	2286	2146	93.9
5	2286	2133	93.3
average = 93.3%			

2.6 Sample storage

Twelve charcoal tubes were each liquid spiked with 2.6 µL (1× PEL) of neat MIAK. These were allowed to equilibrate for 2 hours and then 10 L of humid air (~80% relative humidity) were drawn through each tube at 0.2 L/min. Half of the tubes were stored in a drawer at ambient temperature, and the other half were stored in a refrigerator (0 °C). After ten days, they were extracted and analyzed as in Section 3. The results are given in Tables 2.6.1 and 2.6.2.

Table 2.6.1
Ambient Storage

days stored	µg spiked	µg found	% recovered
10	2286	1299	56.8
10	2286	1460	63.9
10	2286	1356	59.3
10	2286	1526	66.8
10	2286	1231	53.8
10	2286	1291	56.5

average = 59.5%

Table 2.6.
Refrigerator Storage

days stored	µg spiked	µg found	% recovered
10	2286	2183	95.5
10	2286	2207	96.6
10	2286	2166	94.7
10	2286	2175	95.1
10	2286	2178	95.3
10	2286	2178	95.3

average = 95.4%

2.7 Recommended air volume and sampling rate

2.7.1 The recommended air volume is 10 L.

2.7.2 The recommended flow rate is 0.2 L/min.

2.8 Interferences (sampling)

It is not known if any compounds will interfere with the collection of MIAK. Any suspected interferences should be reported to the laboratory with submitted samples.

2.9 Safety precautions (sampling)

2.9.1 Attach the sampling equipment in such a manner that it will not interfere with work performance or employee safety.

2.9.2 Follow all safety practices that apply to the work area being sampled.

3 Analytical Procedure

3.1 Apparatus

3.1.1 A GC equipped with an FID. A Hewlett-Packard 5890 Gas Chromatograph equipped with a 7673A Autosampler and an FID was used in this evaluation.

3.1.2 A GC column capable of separating MIAK and the internal standard from any interference. A 60-m × 0.32-mm i.d. (0.5 µm d_r DB-WAX) capillary column was used in this evaluation.

- 3.1.3 An electronic integrator or some other suitable means to measure detector response. A Waters 860 Networking Computer System was used in this evaluation.
- 3.1.4 Volumetric flasks, pipettes, and syringes for preparing standards, making dilutions and performing injections.
- 3.1.5 Vials, 2-mL and 4-mL with PTFE-lined caps.

3.2 Reagents

- 3.2.1 MIAK. 5-Methyl-2-hexanone, 99%, was obtained from Aldrich Chemical Company.
- 3.2.2 Reagent grade solvent or better should be used.
- 3.2.3 Carbon disulfide. The carbon disulfide used in this evaluation was purchased from EM Science.
- 3.2.4 Dimethyl formamide (DMF). The DMF was purchased from Burdick and Jackson.
- 3.2.5 p-Cymene. The p-cymene used as internal standard was purchased from Aldrich Chemical Company.
- 3.2.6 Desorbing solution. The desorbing solution is prepared by adding 250 μ L of p-cymene to 1 L of carbon disulfide/DMF (99:1, v/v).

3.3 Standard preparation

Prepare standards at concentrations of 1 μ L and 4 μ L of methyl isoamyl ketone per milliliter of desorbing solution. At least two standards at 1 μ L/mL are prepared. Standards must be used the day they are prepared.

3.4 Sample preparation

- 3.4.1 Transfer the 100 mg section of the sampling tube to a 2-mL vial. Place the 50 mg backup section in a separate 2-mL vial.
- 3.4.2 Add 1.0 mL of desorbing solution to each vial and seal with a PTFE-lined cap.
- 3.4.3 Shake the vials vigorously several times during the next 30 min.

3.5 Analysis

3.5.1 Instrument conditions

<u>Column</u>	60-m \times 0.32-mm i.d., (0.5 μ m dr DB-WAX) capillary
<u>Temperature</u>	($^{\circ}$C)
Injector temperature:	180 $^{\circ}$ C
Detector temperature:	200 $^{\circ}$ C
Column temperature:	90 $^{\circ}$ C (initial temp)
Temperature program:	hold initial temp 3 min, increase temp at 10 $^{\circ}$ C/min to 160 $^{\circ}$ C, hold final temp 1 min
<u>Gas flow rates</u>	mL/min
column:	2.0 (hydrogen)
septum purge:	1.2 (hydrogen)
FID:	34 (hydrogen)

FID makeup: 30 (nitrogen)
FID: 480 (air)

Injection volume 1 µL
Split ratio 9:1
Retention time 6.48 min (MIAK), 8.60 min (p-cymene)

3.5.2 Chromatogram (Figure 1.)

3.5.3 Measure detector response using a suitable method such as electronic integration.

3.6 Interferences (analytical)

3.6.1 Any collected compound which produces an FID response and has a similar retention time as MIAK or the internal standard is a potential interference.

3.6.2 GC conditions may generally be varied to circumvent interferences.

3.6.3 Retention time on a single column is not proof of chemical identity. Analysis by an alternate GC column, high performance liquid chromatography (HPLC) and confirmation by mass spectrometry are additional means of identification.

3.7 Calculations

3.7.1 An internal standard (ISTD) calibration method is used. The linear nature of FID allows the use of a point calibration, but the bracketing of samples with analytical standards is a good practice.

3.7.2 Determine the µg/mL of MIAK in both sections of each sample and blank from the calibration curve. If MIAK is found on the backup section, it is added to the amount found on the front section. Blank corrections should be performed before adding the results together.

3.7.3 Determine the air concentration by using the following formula.

$$\text{mg} / \text{m}^3 = \frac{(\mu\text{g} / \text{mL, blank corrected})(\text{desorption volume, mL})}{(\text{air volume, L})(\text{desorption efficiency, decimal})}$$

$$(\text{ppm})(\text{MW}) = (\text{mg} / \text{m}^3)(24.46)$$

$$\text{ppm} = \frac{(\text{mg} / \text{m}^3)(24.46)}{(114.19)}$$

Where:

24.46 = molar volume (liters/mole) at 25 °C and 101.3 kPa (760 mmHg)

114.19 = molecular weight of MIAK

3.8 Safety precautions (analytical)

3.8.1 Avoid skin contact and air exposure to MIAK.

3.8.2 Avoid skin contact with all solvents.

3.8.3 Wear safety glasses at all times.

4 Recommendation for Further Study

This method should be fully validated.

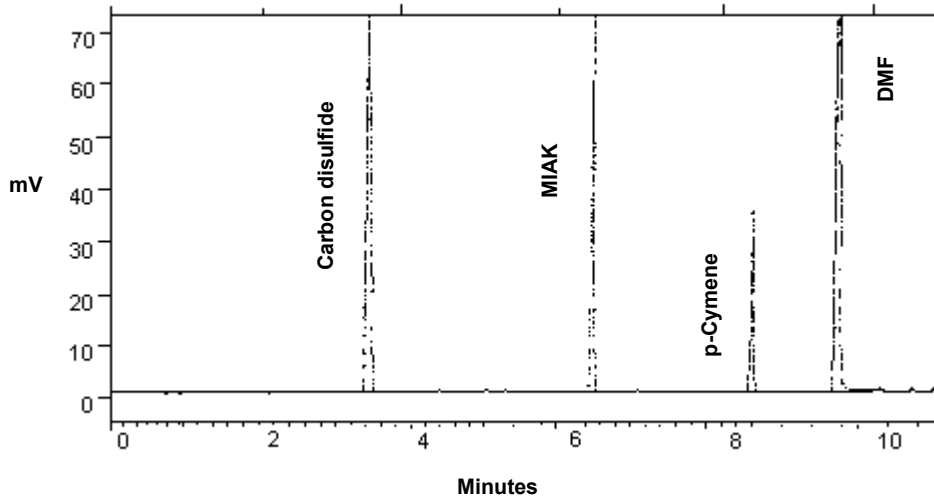


Figure 1. Chromatogram of MIAK at 0.5x target level

5 References

- 5.1 "Code of Federal Regulations," 29 CFR 1910.1000, Table Z-1-A. Limits for Air Contaminants, U.S. Government Printing Office, Washington, D.C., 1990.
- 5.2 Sitting, M., Handbook of Toxic and Hazardous Chemicals, Noyes Publications, Park Ridge, N.J., 1981; p 456.
- 5.3 Documentation of the Threshold Limit Values and Biological Exposure Indices, American Conference of Governmental Industrial Hygienist INC., 5th ed., 1986; p 400.
- 5.4 Weast, R.C., Astle, M.J., and Beyer, W.H., Handbook of Chemistry and Physics, 68th ed., CRC Press Inca, Boca Raton, Florida, 1987-88.