Diethyl Ketone

Method number:	PV2136
Matrix:	Air
Target concentration:	200 ppm (705 mg/m^3)
OSHA PEL:	none
ACGIH TLV-TWA:	200 ppm (705 mg/m^3)
ACGIH TWA-STEL	300 ppm (1057 mg/m^3)
Procedure:	Samples are collected by drawing a known volume of air through a Carbosieve S-III tube. Samples are desorbed with carbon disulfide and analyzed by GC using a flame ionization detector.
Recommended sampling time and sampling rate:	100 min at 0.1 L/min (10 L)
Status of method:	Partially Evaluated Method. This method has been has been subjected to established evaluation procedures of the Methods Development Team and is presented for information and trial use.

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1 General Discussion

1.1 Background

1.1.1 History of procedure

This work was performed because there was no OSHA or NIOSH method for diethyl ketone.

1.1.2 Toxic Effects (This section is for information only and should not be taken as the basis for OSHA policy.) (Ref. 5.1)

A 4-hour exposure to 8000 ppm was fatal to four of six rats. LD_{50} orally in rats: 2.1 g/kg. Diethyl ketone may be poisonous if inhaled or absorbed through skin; vapors may cause dizziness or suffocation; contact causes irritation of the eyes and skin. Burning diethyl ketone may produce irritating or poisonous gases. Diethyl ketone is a narcotic and causes irritation of the upper respiratory tract.

1.1.3 Potential workplace exposure

No potential workplace exposure data could be found. However, the major uses of diethyl ketone are organic synthesis and medicine.

1.1.4 Properties: (Ref. 5.2)

Synonyms:	metacetone; propione; 3-pentanone; ethyl propionyl
Molecular weight:	86.13
Density:	0.816 (19/4 °C)
Melting point:	-42 °C
Boiling point:	101 °C
Odor:	acetone-like odor
Color:	colorless, mobile liquid
Solubility:	soluble in alcohol, carbon disulfide and ether; slightly soluble in water
Molecular formula:	C_5-H_{10}-0
Flash point:	55 °F (12.78 °C) (open cup)
CAS:	96-22-0
IMIS:	D707
RTECS:	SA8050000; 54791

1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 32.6 pg/injection. (1.0-µL injection with 12.5:1 split) This is the amount of analyte that produced a peak 5 times the baseline noise. (Figure 1)

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

There are no known disadvantages to this method.

2 Sampling procedure

2.1 Apparatus

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

2.1.2 Samples are collected with solid sorbent sampling tubes containing 60/80 mesh Carbosieve S-III. Each tube consists of two sections of adsorbent separated by a glass wool plug. The front section contains 130 mg of adsorbent and the back section, 65 mg. The sections are held in place with glass wool plugs in a glass tube 4-mm i.d. x 6 mm o.d. x 70 mm length. For this evaluation, Supelco's ORBO-91 (Carbosieve S-III) tubes were used, (catalog no. 20360)

2.2 Sampling technique

2.2.1 The ends of the absorbent tube are opened immediately before sampling.

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

2.2.3 Tubes should be placed 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 sampling tube.

2.2.5 Seal the tubes with plastic caps immediately after sampling. Seal each sample lengthwise with OSHA Form-21 sealing tape.

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 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 container from the samples.

2.3 Desorption efficiency

The average desorption efficiency for diethyl ketone from Carbosieve S-III is 95.9% over the range of 0.1 to 1 times the target concentration. (Table 1)

Table 1
Desorption Efficiency

sample number	1x 7.0176 mg	0.5x 3.5088 mg	0.1x 0.70176 mg
		desorption (%)	
1	101.13	98.88	87.51
2	98.47	100.29	94.39
3	99.25	96.71	91.27
4	98.51	98.70	91.54
5	96.55	96.68	92.56
6	97.78	95.84	89.59
average	98.62	97.85	91.14
std dev	1.53	1.70	2.38

2.4 Retention efficiency

Three liters of humid air (about 75% relative humidity) were drawn through six adsorbent tubes. The front glass wool plug of the tubes were then spiked at two times the target concentration and an additional ten liters of humid air was drawn through the tubes at 0.1 L/min. The adsorbent tubes were stored in a refrigerator overnight before analysis. The tubes were desorbed with 1 mL of carbon disulfide with 0.25 µL/mL *p*-cymene internal standard and analyzed by gas chromatography with a flame ionization detector. (Table 2)

Table 2
Retention Efficiency

sample number	air volume (L)	amount spiked (mg)	retained (%)
1	10	14.0352	98.88
2	10	14.0352	97.18
3	10	14.0352	98.52
4	10	14.0352	99.82
5	10	14.0352	98.22
6	10	14.0352	98.50
average			98.52

2.5 Storage

Storage samples were prepared by drawing three liters of humid air (about *75%* relative humidity) through the adsorbent tubes. The front glass wool plug of each tube was spiked with diethyl ketone at the target concentration. An additional ten liters of humid air was drawn through the tubes at 0.1 L/min. The tubes were stored at ambient temperature (about 23 °C) and three samples were analyzed approximately every three days. The average recovery was 89.4% over the 12 days studied. (Table 3)

Table 3
Storage Test

storage time (days)	ambient recovery (%)		
0	98.32	95.50	96.95
5	89.68	88.66	89.40
8	86.24	88.41	86.82
12	84.22	82.23	85.90

2.6 Precision (Analytical Procedure)

2.6.1 The precision of the analytical procedure for diethyl ketone is measured by the pooled coefficient of variation determined from replicate injection of standards. The pooled coefficient of variation is 0.0064. (Table 4)

Table 4
Precision

injection number	2x 14035 µg/mL	1x 7018 µg/mL	0.5x 3509 µg/mL
1	14389.0	6936.1	3522.9
2	14431.0	7020.4	3529.9
3	14323.0	6938.4	3517.9
4	14224.0	6983.7	3516.1
5	14216.0	6962.3	3503.7
6	14216.0	7020.0	3541.1
7	14148.0	7005.0	3536.8
8	14032.0	7013.1	3510.4
average	14247.4	6984.88	3522.4
std dev	129.98	35.35	12.91
CV	0.00912	0.00506	0.00367
pooled CV=	0.00638		

$$\text{CV (Coefficient of Variation)} = \frac{\text{standard deviation}}{\text{average}}$$

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

where: A1, A2, A3, A4 = number of injections at each level
CV1, CV2, CV3, CV4 = coefficients at each level

2.7 Air volume and sampling rate

2.7.1 The air volume studied was 10 liters.

2.7.2 The sampling rate studied was 0.1 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 Sampling Method

3.1 Technique

3.1.1 Immediately before sampling, break off the ends of the adsorbent tube. All tubes should be from the same lot.

3.1.2 Connect the sampling tube to the sampling pump with flexible tubing. Position the tube so that sampled air first passes through the 130-mg section.

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

3.1.4 Place the sampling tube vertically (to avoid channeling) in the employee's breathing zone.

3.1.5 After sampling, seal the tubes immediately with plastic caps and wrap lengthwise with OSHA Form 21.

3.1.6 Submit at least one blank sampling tube with each sample set. Blanks should be handled in the same manner as samples, except no air is drawn through them.

3.1.7 Record sample volumes (in liters of air) for each sample, along with any potential interference.

3.1.8 Ship any bulk sample(s) in a container separate from the air samples.

4 Analytical Method

4.1 Apparatus

4.1.1 Gas chromatograph equipped with a flame ionization detector.

4.1.2 GC column capable of separating the analyte and an internal standard from any interference. A 60-m x 0.32-mm i.d. fused silica RTX-1 capillary column with a 1.5 µrn film thickness was used in this evaluation.

4.1.3 An electronic integrator or other suitable method of measuring peak areas. A Hewlett-Packard 3392A integrator was used in this evaluation.

4.1.4 Two-milliliter vials with Teflon-lined caps.

4.1.5 A 10-µL syringe or other convenient size for sample injection.

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

4.1.7 Volumetric flasks – 5-mL and other convenient sizes for preparing standards.

4.3 Sample preparation

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

4.3.2 Each section is desorbed with 1 mL of carbon disulfide.

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

4.4 Standard preparation

4.4.1 Standards are prepared by diluting known quantities of diethyl ketone with carbon disulfide.

4.4.2 At least two separate standards should be made.

4.5 Analysis.

4.5.1 Gas chromatograph conditions.

Flow rates (mL/min)		Temperature (°C)	
Nitrogen (make-up):	11	Injector:	225
Hydrogen (carrier):	1.6	Detector:	250
Hydrogen (flame):	32	Column:	80-150
Air:	360		

Injection size: 1.0 µL (with a 12.5:1 split)
Elution time: 6.5 min
Chromatogram: (Figure 2)
Column: 60-m x 0.32-mm i.d. fused silica, RTX-1, 1.5 µm film thickness

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

4.6 Interferences (analytical)

4.6.1 Any compound having the general retention time of the analyte or the internal standard is an 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.

4.6.2 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.

4.7 Calculations

The analyte concentration for samples is obtained from the following formula. If any analyte is found on the back section, it is added to the amount found on the front section. This total amount is then corrected by subtracting the total amount found on the blank.

$$mg/m^3 = \frac{\mu g\ analyte\ per\ sample}{(liters\ of\ air\ sampled)(desorption\ efficiency)}$$

$$ppm = \frac{(mg/m^3)\ (24.46)}{molecular\ weight}$$

where, 24.46 = molar volume (liters) at 760 mmHg and 25 °C
molecular weight = 86.13 for diethyl ketone.

4.8 Safety precautions

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

4.8.2 Avoid skin contact with all solvents.

4.8.3 Wear safety glasses at all times.

4.9 Recommendations for further study

Further work should be done to fully validate the method.

5 References

5.1 *Documentation of the Threshold Limit Values and Biological Exposure Indices*; 7th ed., American Conference of Governmental Industrial Hygienists, Inc.: Cincinnati, OH, 2001.

5.2 “Hawley's Condensed Chemical Dictionary"; 11th edition; Sax, N.I.; Lewis, R.J., Ed; Van Norstrand Reinhold Company; New York; 1987; p.394.

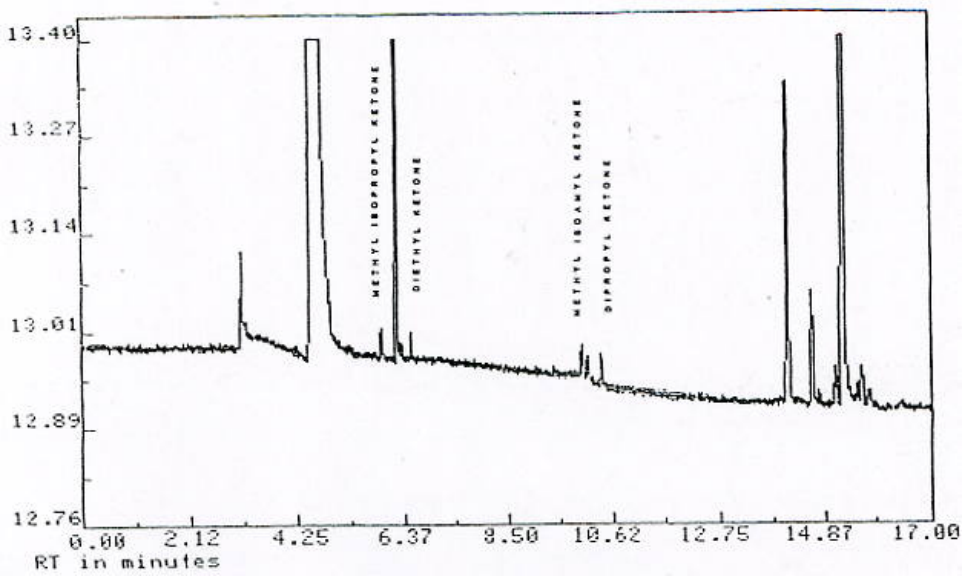

Figure 1: Chromatogram of Detection Limit

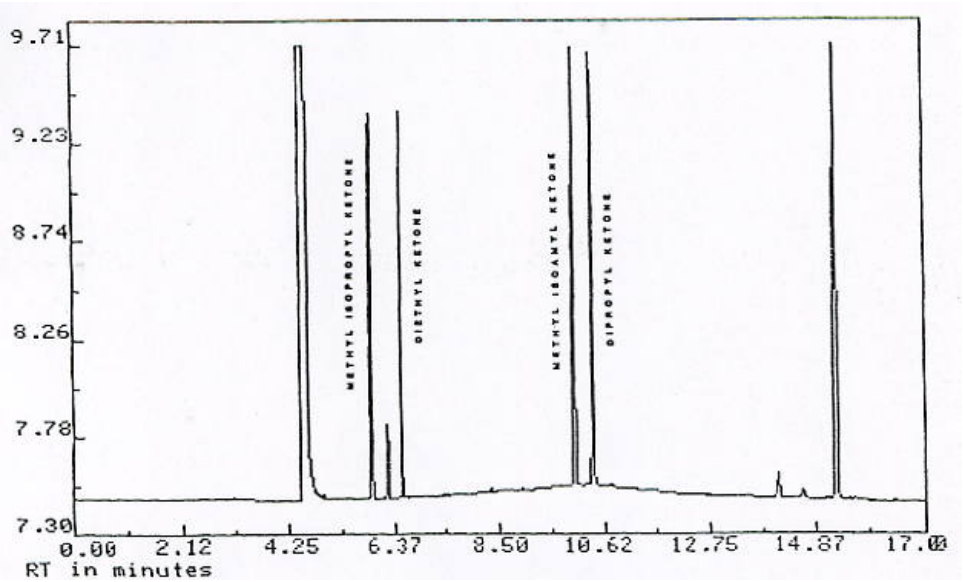

Figure 2: Chromatogram of Analytical Standard