n –Hexane

Method number:	PV2248
Control number:	T-PV2248-01-9508-CH
Matrix:	Air
Target concentration:	500 ppm (1800 mg/m^3) (OSHA PEL) 50 ppm (180 mg/m^3) (OSHA proposed)
Procedure:	Samples are collected by drawing a known volume of air through a coconut shell charcoal tube. Samples are desorbed with 1 mL of carbon disulfide for 15 minutes with occasional shaking and analyzed by gas chromatography (GC) using a flame ionization detector (FID).
Recommended air volume and sampling rate:	20 minutes at 0.2 L/min (4 L)
Reliable quantitation limit:	0.19 ppm (0.68 mg/m^3)
Status of method:	Partially Evaluated Method. This method has been partially evaluated and is presented for information and trial use only.

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Note: OSHA no longer uses or supports this method (March 2021).

1 General discussion

1.1 Background

1.1.1 History

OSHA is proposing to lower the PEL from 500 ppm to 50 ppm which is the ACGIH TLV level. This forces a need to have a detailed study of the sampling and analytical technique. NIOSH has method 1500 which is a general method for lower boiling hydrocarbons. Traditionally, coconut shell charcoal tubes were used for hydrocarbons therefore charcoal tubes were the first choice. There are several isomers of hexane but n-Hexane is the one most commonly found and used. (Ref 5.1, 5.2)

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)

Hexane is three times as acutely toxic to mice as is pentane; concentrations of 30,000 ppm produced narcosis within 30 to 60 minutes, and convulsions and death resulted from 35,000 to 40,000 ppm. In man, inhalation of 2000 ppm for 10 minutes resulted in no effects, but 5000 ppm caused dizziness and a sense of giddiness. Drinkers et al found slight nausea, headache, eye, and throat irritation at 1400 to 1500 ppm. Occupational polyneuropathy has apparently resulted from hexane exposures as low as 500 ppm, and probably lower. Nearly continuous exposure of animals at 250 ppm has also caused neurotoxic effects.

1.1.3 Workplace exposure (Ref.5.3, 5.4)

No data were available for exposure to n-Hexane. It is a widely used chemical as a solvent, especially for vegetable oils, in low temperature thermometers, in polymerization reactions, in paint dilution, and as an alcohol denaturant.

1.1.4 Physical properties and other descriptive information (Ref. 5.3, 5.4)

CAS number:	110-54-3
IMIS:	1380
RTECS:	MN9275000; 39449
Synonyms:	Normal hexane; Hexyl hydride
DOT:	UN1208 Flammable Liquid
Molecular weight:	86
Flash point:	- 30.56 °C (-23 °F) (cc)
Boiling point:	68.95 ^{0}C
Color:	Clear
Density:	0.66
Molecular formula:	$CH_3(CH_2)_4CH_3$

The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm are referenced to 25 °C and 101.3 kPa (760 mmHg).

1.2 Limit defining parameters

1.2.1 Detection limit of the overall procedure (DLOP)

The detection limit of the overall procedure is 0.81 µg per sample (0.06 ppm or 0.2 mg/m^3). This is the amount of analyte spiked on the sampler that will give a response

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that is significantly different from the background response of a sampler blank. The DLOP is defined as the concentration of analyte that gives a response (Y_{DLOP}) that is significantly different (three standard deviations (SD_{BR})) from the background response (Y_{BR}).

$$Y_{DLOP} - Y_{BR} = 3(SD_{BR})$$

The direct measurement of Y_{BR} and SD_{BR} in chromatographic methods is typically inconvient, and difficult because Y_{BR} is usually extremely low. Estimates of these parameters can be made with data obtained from the analysis of a series of samples whose responses are in the vicinity of the background response. The regression curve obtained for a plot of instrument response versus concentration of analyte will usually be linear. Assuming SD_{BR} and the precision of data about the curve are similar, the standard error of estimate (SEE) for the regression curve can be substituted for SD_{BR} in the above equation. The following calculations derive a formula for the DLOP:

$$SEE = \sqrt{\frac{\sum (Y_{obs} - Y_{est})^2}{(n-k)}}$$

Y_{obs} = observed response
Y_{est} = estimated response from regression curve
n = total number of data points
k = 2 for a linear regression curve

At Point Y_{DLOP} on the regression curve

$$Y_{DLOP} = A(DLOP) + Y_{BR}$$

A = analytical sensitivity (slope)

Therefore:

$$DLOP = \frac{(Y_{DLOP} - Y_{BR})}{A}$$

Substituting $3(SEE) + Y_{BR}$ for Y_{DLOP} gives

$$DLOP = \frac{3(SEE)}{A}$$

The DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten samplers were spiked with equal descending increments of analyte, such that the highest sampler loading was 7.11 µg/sample. This is the amount, when spiked on a sampler, that would produce a peak approximately 10 times the background response for the sample blank. These spiked samplers, and the sample blank were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (A and SEE) for the calculation of the DLOP. Values of 232.7 and 62.9 were obtained for A and SEE respectively. DLOP was calculated to be 0.81 µg/sample (0.06 ppm or 0.2 mg/m^3).

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Table 1.2.1
Detection Limit of the Overall Procedure

mass/sample (µg)	area counts (µV-s)
0	0
0.72	152
1.44	327
2.16	345
2.88	514
3.60	804
4.32	986
5.04	1162
5.76	1280
6.48	1485

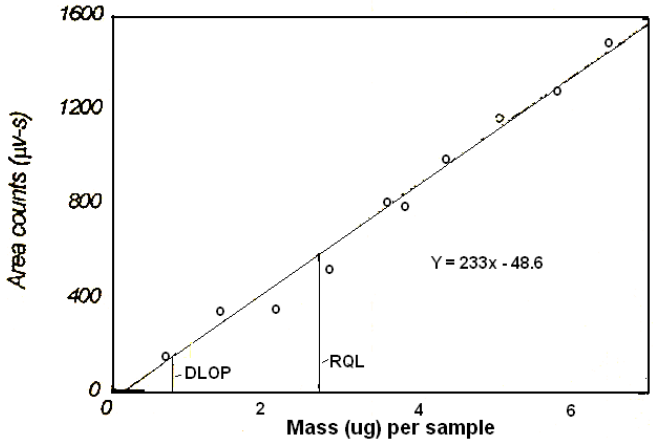

Figure 1.2.1. Plot of data to determine the DLOP/RQL.

1.2.2 Reliable quantitation limit (RQL)

The reliable quantitation limit is 2.71 µg per sample (0.19 ppm). This is the amount of analyte spiked on a sampler that will give a signal that is considered the lower limit for precise quantitative measurements.

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line data obtained for the calculation of the DLOP (Section 1.2.1), providing at least 75% of the analyte is recovered. The RQL is defined as the concentration of analyte that gives a response (Y_{RQL}) such that

$$Y_{RQL} - Y_{BR} = 10(SD_{BR})$$

Therefore:

$$RQL = \frac{10(SEE)}{A}$$

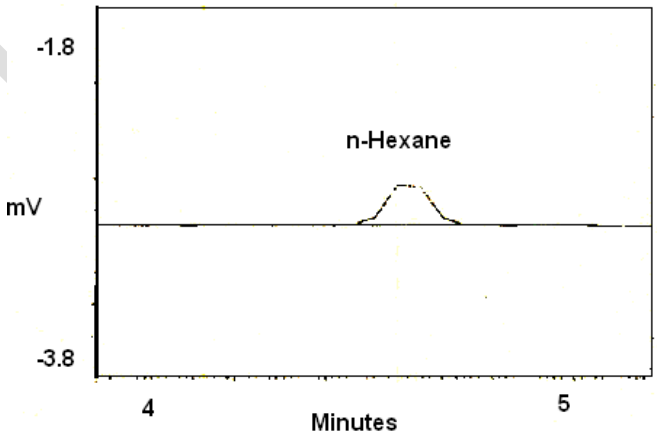

Figure 1.2.2. Chromatogram of the RQL.

The RQL is the lowest loading at which 75% of the analyte can be recovered as determined from the regression line of the plotted data.

RQL = 2.71 µg per sample (0.19 ppm or 0.68 mg/m^3)

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2 Sampling procedure

2.1 Apparatus

2.1.1 Samples are collected using a personal sampling pump, calibrated with a sampling device attached, to within ±5% of the recommended flow rate.

2.1.2 Samples are collected with 7-cm x 4-mm i.d. x 6-mm o.d. glass sampling tubes packed with two sections of coconut shell charcoal. The front section contains 100 mg and the back section contains 50 mg of coconut shell charcoal. The sections are held in place with glass wool plugs and are separated by a urethane foam plug. For this evaluation, commercially prepared sampling tubes were purchased from SKC Inc, Eighty-Four, PA, Catalog No 206-01, Lot 120.

2.2 Technique

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

2.2.2 Attach the sampling tube to the pump with flexible tubing. It is desirable to utilize a sampling tube holder which has a protective cover to shield the employee from the sharp, jagged end of the sampling tube. Position the tube so that sampled air passes through the front section of the tube first.

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

2.2.4 Attach the sampler vertically with the front section pointing downward, in the worker's breathing zone, and positioned so it does not impede work performance or safety.

2.2.5 After sampling for the appropriate time, remove the sample and seal the tube with plastic end caps. Wrap each sample end-to-end with a Form OSHA-21 seal.

2.2.6 Submit at least one blank sample with each set of samples. Handle the blank sampler in the same manner as the other samples (break ends, seal, & transport) except draw no air through it.

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

2.2.8 Ship any bulk samples in a separate package from the air samples.

2.2.9 Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples in a refrigerator.

2.3 Desorption efficiency

The desorption efficiency of n-Hexane was determined by liquid spiking the charcoal tubes with the analytes ranging in concentration from 2 to 0.1 times the target concentration. The loadings on the tubes were 1440, 720, 360 and 72 µg of n-Hexane. These samples were stored overnight at ambient temperature, then desorbed, and analyzed. The average desorption efficiency over the studied range was 100.8%.

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Table 2.3
n-Hexane
Desorption Efficiency

tube #	% recovered			
	0.1 x 72 µg	0.5 x 360 µg	1.0 x 720 µg	2.0 x 1440 µg
1	101.7	101.4	104.4	101.8
2	104.9	99.8	101.0	100.3
3	102.2	100.5	101.3	100.9
4	100.7	101.5	99.1	101.5
5	98.2	l02.3	101.2	100.6
6	101.4	96.8	98.3	98.4
average	101.5	100.4	100.9	100.6

overall average = 100.8%
standard deviation = ±1.79

2.4 Retention efficiency

The sample tubes were spiked with 1440 µg of n-Hexane, allowed to equilibrate for 24 hours at room temperature, and then had 4 L humid air (80% RH at 22 °C) pulled through them at 0.2 Lpm. They were then opened, desorbed, and analyzed by GC-FID. The retention efficiency averaged 99.6 %. There was little or no n-Hexane found on the back sections of the tubes.

Table 2.4
n-Hexane
Retention Efficiency

tube #	% recovered		total
	front section	back section	
1	99.9	0.0	99.9
2	98.6	0.0	98.6
3	100.7	0.0	100.7
4	100.0	0.0	100.0
5	99.1	0.0	99.1
6	99.1	0.0	99.1

average = 99.6%

2.5 Sample storage

The front sections of six sampling tubes were each spiked with 1440 µg of n-Hexane. Six more tubes had 4 liters of humid air (80% RH at 22°C) drawn through them before they were spiked with n-Hexane. They were sealed and stored at room temperature. Three of each type of samples were analyzed after 7 days and the remaining three samples of each type after 14 days. The amounts recovered indicate good storage stability for the time period studied and had an average recovery of 99.7%.

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Table 2.5
n-Hexane
Storage Study

time (days)	% recovered (humid)	% recovered (dry)
7	102.3	101.4
7	100.7	100.6
7	100.3	100.2
17	97.6	97.7
17	98.0	97.1
17	99.8	100.1
average	99.8	99.5

2.6 Recommended air volume and sampling rate.

Based on the data collected in this evaluation, 4 L air samples should be collected at a sampling rate of 0.2 L/min.

2.7 Interferences (sampling)

2.7.1 It is not known if any compounds will severely interfere with the collection of n-Hexane on the sample tubes. In general, the presence of other contaminant vapors in the air will reduce the capacity of the charcoal tube to collect n-Hexane.

2.7.2 Suspected interferences should be reported to the laboratory with submitted samples.

2.8 Safety precautions (sampling)

2.8.1 Attach the sampling equipment to the worker in such a manner that it will not interfere with work performance or safety.

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

2.8.3 Wear eye protection when breaking the ends of the glass sampling tubes.

3 Analytical Procedure

3.1 Apparatus

3.1.1 The instrument used in this study was a gas chromatograph (GC) equipped with a flame ionization detector (FID), specifically a Hewlett Packard model 5890.

3.1.2 A GC column capable of separating the analyte from any interferences. The column used in this study was a 60-m x 0.32-mm i.d. capillary column coated with 1-µm film of Stabilwax.

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

3.1.4 Two milliliter vials with PTFE-lined caps.

3.1.5 A 10-µL syringe or other convenient sizes for sample preparation and sample injection.

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3.1.6 Pipettes for dispensing the desorbing solution. A 10-mL dispenser was used in this study.

3.1.7 Volumetric flasks, 5-mL or 10-mL and other convenient sizes for preparing standards.

3.2 Reagents

3.2.1 Nitrogen, Hydrogen, and Air - GC grade

3.2.2 n-Hexane (analyte), reagent grade.

3.2.3 Carbon disulfide (desorbing solvent), reagent grade.

3.2.4 p-Cymene (internal standard), reagent grade.

3.2.5 Desorbing solution was Carbon disulfide with 0.25 µL/mL p-Cymene internal standard.

3.3 Standard preparation

3.3.1 At least two separate stock standards are prepared by diluting a known quantity of n-Hexane with the desorbing solution. The concentration of these stock standards was 1 µL/mL or 660 µg/mL.

3.3.2 For this study, two analytical standards were prepared at a concentration of 1 µL/mL (660 µg/mL), and one at 3 µL/mL (1980 µg/mL) n-Hexane in the desorbing solution. A third standard at a higher concentration was prepared to check the linearity of the calibration.

3.4 Sample preparation

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

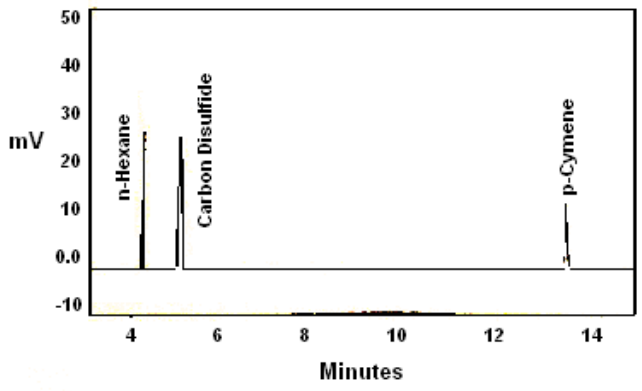
3.4.2 Each section is desorbed with 1 mL of the desorbing solution of Carbon disulfide with 0.25 µL/mL p-Cymene as internal standard.

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

3.5 Analysis

3.5.1 Gas chromatograph conditions.

Injection size:	1 µL
<u>Flow rates</u>	<u>(mL/min)</u>
Nitrogen (make-up):	30
Hydrogen (carrier):	1.5
Hydrogen (detector):	30
Air:	360
<u>Temperatures</u>	<u>(°C)</u>
Injector	200
Detector:	240



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Column 80 ^{0}C for 4 min, program rate 14 ^{0}C/min to 180 ^{0}C, hold 4 min.

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

3.6 Interferences (analytical)

3.6.1 Any compound that produces a response and has a similar retention time as the analyte is a potential interference. If any potential interferences were reported, they should be considered before samples are desorbed. Generally, chromatographic conditions can be altered to separate an interference from the analyte.

3.6.2 When necessary, the identity or purity of an analyte peak may be confirmed by GC-mass spectrometer or by another analytical procedure.

3.7 Calculations

3.7.1 The instrument was calibrated with a standard of 720 µg/mL n-Hexane in the desorbing solution. The linearity of the calibration was checked with a standard of 1728 µg/mL.

3.7.2 If the calibration is non-linear, two or more standards at different concentrations must be analyzed, bracketing the samples, 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 the following formula.

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

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, 1.0 mL
L = Air volume, 4.0 L
DE = Desorption efficiency, decimal

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

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3.8 Safety precautions (analytical)

3.8.1 Avoid skin contact and inhalation of all chemicals.

3.8.2 Wear safety glasses, gloves and a lab coat at all times while in laboratory areas.

4 Recommendations for Further Study

Collection studies need to be performed from a dynamically generated test atmosphere.

5 References

5.1 "Documentation of the Threshold Limits Values and Biological Exposure Indices" Fifth Edition, American Conference of Governmental Industrial Hygienists Inc., Cincinnati, OH 1986, p. 305.

5.2 "NIOSH Manual of Analytical Methods", U.S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National institute for Occupational Safety and Health, third Edition, Vol. 21 (E-N) Method 1500 .

5.3 Lewis, R., "Hawley's Condensed Chemical Dictionary," Twelfth Edition, Van Nostrand Reinhold Co., New York, 1993, p 600.

5.4 Windholz, M., "The Merck Index," Eleventh Edition, Merck & Co., Rahway N.J., 1989, p. 714

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