Withdrawn

Provided For Historical Reference Only

n-Octane

Method no:	PV2138
Control no:	T-PV2138-01-0403-CH
OSHA PEL:	500 ppm (2350 mg/m^3)
Procedure:	Samples are collected by drawing a known volume of air through glass sampling tubes containing coconut-shell charcoal. Samples are extracted with 1 mL of a solution of carbon disulfide: *N,N*-dimethylformamide (99:1) with 0.25 µL/mL *p*-cymene internal standard, and analyzed by GC using a flame ionization detector (FID).
Recommended sampling time and sampling rate:	80 min at 0.05 L/min (4.0 L)
Reliable quantitation limit:	200 ppb (933 µg/m^3)
Status of method:	Partially evaluated method. This method has been subjected to established evaluation procedures of the Methods Development Team and is presented for information and trial use.

March 2004

Anna Tang

Chromatography Team
Industrial Hygiene Chemistry Division
OSHA Salt Lake Technical Center

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

1. General Discussion

1.1 Background

1.1.1 History

OSHA Method 48 for Petroleum Distillates validated collection of a boiling fraction that contained n-octane on coconut shell charcoal[1]. NIOSH Method 1500 for sampling and analysis of n-octane requires sample collection on coconut shell charcoal, extraction with carbon disulfide, and analysis by gas chromatography with FID detection[2]. These two methods were used as a guide for selection of parameters for this partially-validated method for n-octane. Storage stability was not assessed in the NIOSH work. This work was done to confirm the NIOSH evaluation results using the OSHA partially-validated methods evaluation protocol and to perform a storage stability test. Samples in this method are collected with coconut shell charcoal, extracted with 1 mL of carbon disulfide: *N,N*-dimethylformamide (99:1 CS_2:DMF) and analyzed by GC/FID. The extraction, storage, and retention efficiency studies showed good recoveries.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)[3,4]

n-Octane is a mucous membrane, eye, and nose irritant. High concentrations can cause drowsiness, dermatitis, and narcosis. It is toxic by ingestion, inhalation, and skin contact.

1.1.3 Workplace exposure[3]

n-Octane has been used as a solvent, in organic synthesis, and in azeotropic distillations. The octanes are present in gasoline and petroleum solvents such as VM&P naphtha.

1.1.4 Physical properties and other descriptive information[3,5]

CAS number:	111-65-9	IMIS[6]:	1957
molecular weight:	114.23	vapor density:	3.86
melting point:	-56.8°C	boiling point:	127°C
appearance:	colorless liquid	vapor pressure:	1.4 kPa @20°C
odor:	gasoline	flash point:	22°C (72°F) (open cup)
solubility:	soluble in ethyl ether, ethyl alcohol and benzene	molecular formula:	$CH_3(CH_2)_6CH_3$
		density:	0.7028 g/mL
synonyms:	normal octane		

---

[1] OSHA Method 48 www.osha.gov (accessed 11/11/03).

[2] NIOSH Method 1500 www.CDC.gov/ NIOSH (accessed 11/11/03).

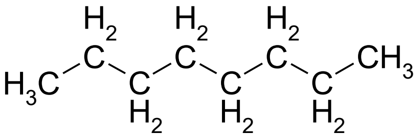
[3] *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 7th ed., American Conference of Governmental Industrial Hygienists Inc., Cincinnati, OH, 2001, Vol. 2.

[4] O' Neil, M. *The Merck Index*, 13th ed. Merck & Co Inc., Whitehouse Station, NJ, 2001, p. 6775.

[5] Lewis, R., Sr., *Hawley's Condensed Chemical Dictionary*, 14th ed., John Willy & Sons, Inc. NY, 2001, p. 812.

[6] OSHA Chemical Sampling Information, www.osha.gov (accessed 11/11/03).

structural formula:



This method was evaluated according to the OSHA SLTC “Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis”[7]. The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations, and acceptance criteria. The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters.

1.2 Detection limit of the overall procedure (DLOP) and reliable quantitation limit (RQL)

The DLOP is measured as mass per sample and expressed as equivalent air concentration, based on the recommended sampling parameters. Ten samplers were spiked with equally descending increments of analyte, such that the highest sampler loading was 3.5 µg of n-octane. This is the amount spiked on a sampler that would produce a peak about 10 times the response for a sample blank. These spiked samplers were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (standard error of estimate (SEE) and slope) for the calculation of the DLOP. The slope was 232.4 and the SEE was 86.2. The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters obtained for the calculation of the DLOP, providing 75% to 125% of the analyte is recovered. The DLOP and RQL were 1.11 µg (59.5 ppb) and 3.71 µg (198.9 ppb), respectively. The recovery at the RQL was 93.8%.

Table 1.2
Detection Limit of the Overall Procedure
for n-Octane

mass per sample (µg)	area counts (µV-s)
0.00	0
0.35	282
0.70	355
1.05	385
1.40	483
1.75	571
2.10	811
2.44	689
2.79	773
3.14	791
3.49	937

---

[7] Burright, D.; Chan, Y.; Edie, M.; Elskamp, C.; Hendricks, W.; Rose, M.C. Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis; OSHA Salt Lake Technical Center, U.S. Department of Labor, Salt Lake City, UT, 1999.

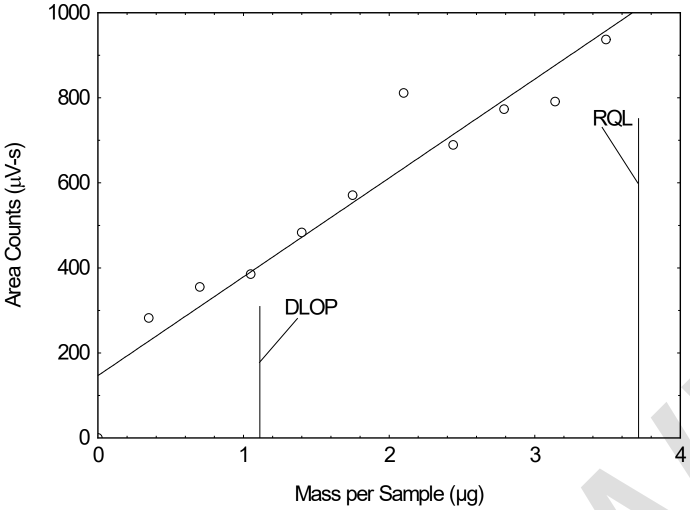


Figure 1.2.1. Plot of data to determine the DLOP/RQL for n-octane.
(y=232.41x + 146.58; SEE = 86.2)

Below is a chromatogram of the RQL level.

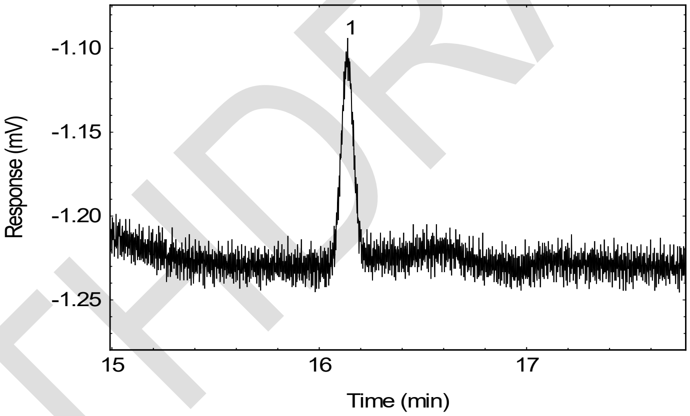


Figure 1.2.2 Chromatogram of the n-octane peak in a standard.
(Key: (1) n-octane)

2. Sampling Procedure

All safety practices that apply to the work area being sampled should be followed. The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

2.1 Apparatus

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

2.1.2 Samples are collected with 7-cm × 4-mm i.d. × 7-mm o.d. glass sampling tubes packed with two sections (100/50 mg) of charcoal. The sections are held in place with foam plugs and with a glass wool plug at the front. For this evaluation, commercially prepared sampling tubes were purchased from SKC, Inc. (catalog no. 226-01, lot 2000).

2.2 Reagents

None required.

2.3 Technique

2.3.1 Immediately before sampling break off the ends of the flame-sealed tube to provide an opening approximately half the internal diameter of the tube. Wear eye protection when breaking the tube. Use tube holders to minimize the hazard of broken glass. All tubes should be from the same lot.

2.3.2 The smaller section of the adsorbent tube is used as a back-up and is positioned nearest the sampling pump. Attach the tube holder to the sampling pump so that the adsorbent tube is in an approximately vertical position with the inlet facing down during sampling. Position the sampling pump, tube holder, and tubing so they do not impede work performance or safety.

2.3.3 Draw the air to be sampled directly into the inlet of the tube holder. The air being sampled is not to be passed through any hose or tubing before entering the sampling tube.

2.3.4 After sampling for the appropriate time, remove the adsorbent tube and seal it with plastic end caps. Seal each sample end-to-end with an OSHA-21 form as soon as possible.

2.3.5 Submit at least one blank sample with each set of samples. Handle the blank sample in the same manner as the other samples except draw no air through it.

2.3.6 Record sample air volumes (liters), sampling time (minutes), and sampling rate (L/min) for each sample, along with any potential interferences on the OSHA-91A form.

2.3.7 Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples at refrigerator temperature. Ship any bulk samples separate from the air samples.

2.4 Extraction efficiency

The extraction efficiency was determined by spiking front sections of sampling tubes with n-octane at 0.1 to 2 times the target concentration based on 4-L air samples. These samples were stored overnight at ambient temperature and then extracted for 30 minutes with shaking, and analyzed. The mean extraction efficiency over the studied range was 101.9%.

Table 2.4
Extraction Efficiency (%) of n-Octane

Level						
× target concn	mg per sample	1	2	3	4	mean
0.1	0.91	95.4	98.0	99.9	99.8	98.3
0.5	4.89	109.4	108.1	107.9	109.5	108.7
1.0	9.08	99.5	100.2	100.2	101.1	100.3
2.0	18.86	100.1	100.6	100.4	100.4	100.4

2.5 Retention efficiency

Eighteen charcoal sampling tubes were each spiked with 18.86 mg of n-octane on the front sections. This mass of n-octane is approximately equivalent to 2 times the OSHA PEL, based on a 4-L air volume. The test was performed by pulling humid air (absolute humidity 15.7 milligrams of water per liter of air, about 78% relative humidity at 23°C) through the tubes at approximately 0.05-L/min for increasing times. Pairs of samples were removed at approximately 0.5-L increments between 2 and 6-L and analyzed. The analytical results of the tube front and back charcoal sections were compared to detect breakthrough. These results show that the recommended air volume of 4-L, sampled at 0.05-L/min, provides an adequate safety margin against sampler saturation. The average of each pair of samples is presented for the air volumes shown in table 2.5.

Table 2.5
Retention Efficiency (%) of n-Octane

L of air	6.09	5.59	5.15	4.57	4.03	3.56	3.07	2.52	2.04
section A	104	105	110	107	107	109	105	106	105
section B	0	0	0	0	0	0	0	0	0

2.6 Sample storage

Fifteen charcoal tubes were each spiked with 9.08 mg (500 ppm) of n-octane, then they had 4-L of air, with an absolute humidity of 15.7 milligrams of water per liter of air (about 78% relative humidity at 23°C), drawn through them. Three samples were analyzed immediately, and the rest were sealed. Six were stored at room temperature (23°C), and the other six were stored at refrigerated temperature (4°C). The amounts recovered indicate good storage stability for the time period studied.

Table 2.6
Storage Test for n-Octane

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	97.5	97.0	96.1			
7	94.9	96.3	94.1	98.0	92.7	96.5
14	100.5	100.7	101.3	100.1	101.3	101.1

2.7 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 0.05 L/min for 80 minutes.

2.8 Interferences (sampling)

2.8.1 There are no known compounds which will severely interfere with the collection of n-octane.

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

3. Analytical Procedure

Adhere to the rules set down in your Chemical Hygiene Plan. Avoid skin contact and inhalation of all chemicals and review all appropriate MSDSs.

3.1 Apparatus

3.1.1 A gas chromatograph equipped with an FID detector. An Agilent 6890 Plus Gas Chromatograph equipped with a 7683 Injector was used in this evaluation.

3.1.2 A GC column capable of separating n-octane from the extraction solvent, internal standard, and any potential interferences. A 60-m × 0.32-mm i.d. DB-1 J & W (5.0-µm df) capillary column was used in this evaluation.

3.1.3 An electronic integrator or some other suitable means of measuring peak areas. A Waters Millennium^{32} Data System was used in this evaluation.

3.1.4 Glass vials with poly(tetrafluoroethylene)-lined caps. For this evaluation 2-mL vials were used.

3.1.5 A dispenser capable of delivering 1.0 mL of desorbing solvent to prepare standards and samples. If a dispenser is not available, a 1.0-mL volumetric pipet may be used.

3.1.6 Volumetric flasks – 10-mL and other convenient sizes for preparing standards.

3.1.7 Calibrated 10-µL or 20-µL syringe for preparing standards.

3.1.8 A mechanical shaker. An Eberbach mechanical shaker was used in this evaluation.

3.2 Reagents

3.2.1 n-Octane, reagent grade. ChemService lot FJ8667, 99% was used in this evaluation.

3.2.2 Carbon disulfide, reagent grade. EM Science lot 40298103, 99.9% was used in this evaluation.

3.2.3 *N,N*-dimethylformamide, reagent grade. Sigma-Aldrich lot 01340AB, 99.8% was used this evaluation.

3.2.4 *p*-Cymene, reagent grade. Aldrich lot 306PZ, 99% was used in this evaluation.

3.2.5 The extraction solvent solution was carbon disulfide: *N,N*-dimethylformamide (99:1) with 0.25µL/mL of *p*-cymene as internal standard.

3.3 Standard preparation

3.3.1 Prepare standards by spiking microliter quantities of n-octane from a microliter syringe into 2-mL vials, each containing 1 mL of the desorbing solution. For example, 13 µL of n-octane in 1 mL CS_2:DMF is equivalent to 9.14 mg/mL. For this evaluation, standards in the range of 0.0003 to 18.9 mg/mL were used. A check standard from a second source should be prepared to check the calibration.

3.3.2 Bracket sample concentrations with standard concentrations. If upon analysis, sample concentrations fall outside the range of prepared standards, prepare and analyze additional standards to confirm instrument response, or dilute high samples with extraction solvent and reanalyze the diluted samples.

3.4 Sample preparation

3.4.1 Remove the plastic end caps from the sample tubes and carefully transfer each adsorbent section to separate 2-mL vials. Discard the glass tube, urethane foam plug and glass wool plug.

3.4.2 Add 1.0 mL of extraction solvent to each vial using the same dispenser as used for preparation of standards.

3.4.3 Immediately seal the vials with poly(tetrafluoroethylene)-lined caps.

3.4.4 Shake the vials on a shaker for 30 minutes.

3.5 Analysis

3.5.1 Gas chromatographic conditions

<u>GC conditions</u>

Temperature:	
column:	initial 50°C, hold 3 min, program at 8°C/min to 185 °C, hold 5 min
injector:	225°C
detector:	250°C
run time:	24.6 min
column gas flow:	2.5 mL/min (hydrogen)
septum purge:	1.9 mL/min (hydrogen)
injection size:	1.0 µL (10:1 split)
column:	60-m × 0.32-mm i.d. capillary DB-1 (df = 5.0 µm)
retention times:	8.3 min (carbon disulfide) 14.6 min (*N,N*-dimethylformamide) 16.1 min (n-octane) 22.0 min (*p*-cymene)
Chromatogram:	Figure 3.5.1.

<u>FID conditions</u>

hydrogen flow:	35 mL/min
air flow:	450 mL/min
nitrogen makeup flow:	35 mL/min

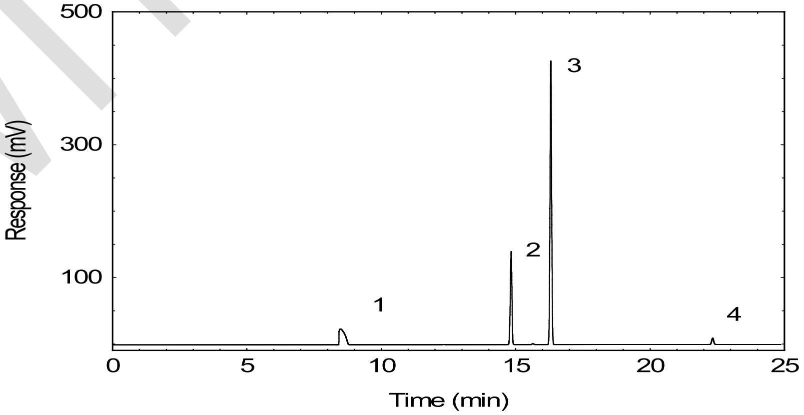


Figure 3.5.1 A chromatogram of 9136 µg/mL n-octane in 99:1 CS$_2$/DMF with 0.25µL/mL *p*-cymene internal standard. (Key: (1) CS$_2$; (2) DMF; (3) n-octane; and (4) *p*-cymene)

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

3.5.3 An internal standard (ISTD) calibration method is used. A calibration curve can be constructed by plotting response of standard injections versus micrograms of analyte per sample. Bracket the samples with freshly prepared analytical standards over the range of concentrations

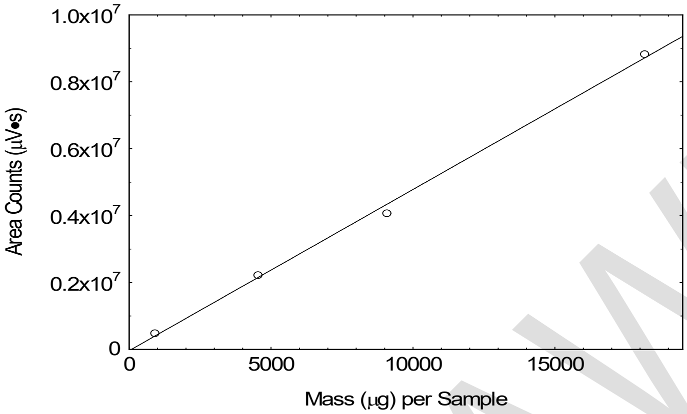


Figure 3.5.3 Calibration curve of n-octane. (y = 482x – 3.73E4)

3.6 Interferences (analytical)

3.6.1 Any compound that produces a GC 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 extracted. 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 spectrometry.

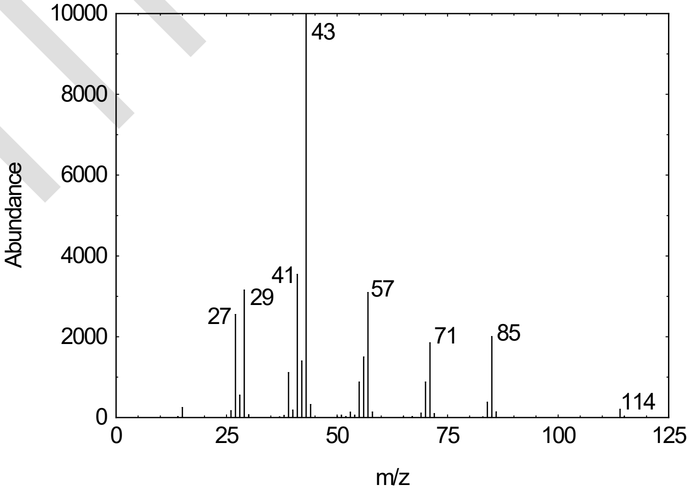


Figure 3.6.2 Mass spectrum of n-octane.

3.7 Calculations

The amount of analyte per sampler is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for extraction efficiency. This total amount is then corrected by subtracting the total amount (if any) found on the blank. The air concentration is calculated using the following formulas.

$$C_M = \frac{M}{VE_E}$$

where C_M is concentration by weight (mg/m^3)
M is micrograms per sample
V is liters of air sampled
E_E is extraction efficiency, in decimal form

$$C_V = \frac{V_M C_M}{M_r}$$

where C_V is concentration by volume (ppm)
V_M is molar volume at 25°C and 1 atm = 24.46
C_M is concentration by weight
M_r is molecular weight = 114.23

4. Recommendations for Further Study

Collection, reproducibility, and other detection limit studies need to be performed to make this a validated method.