Kerosene

Method no:	PV2139

Control no: T-PV2139-01-0408-CH

Target concentration: 100 mg/m^3
NIOSH REL: 100 mg/m^3
ACGIH TLV: 200 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 99:1 carbon disulfide (CS$_2$):*N,N*-dimethylformamide (DMF) and analyzed by GC using a flame ionization detector (GC/FID).

Recommended sampling time
and sampling rate: 200 min at 0.1 L/min (20 L)

Reliable quantitation limit: 4.79 mg/m^3

Status of method: Partially validated method. This method has been subjected to the established evaluation procedures of the Method Development Team and is presented for information and trial use.

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1. General Discussion

    1.1   Background

        1.1.1   History

            OSHA presently uses NIOSH Method 1550[1] (Naphtha) for kerosene. That method requires sampling on coconut-shell charcoal, sample extraction with carbon disulfide, and analysis by GC-FID. Kerosene is defined as "A refined petroleum solvent (predominantly C_9-C_{16} hydrocarbon, which is typically a mixture of 25% normal paraffins, 11% branched paraffins, 30% monocycloparraffins,12% dicycloparaffins, 1% tricycloparrafins, 16% mononuclear aromatics and 5% dinuclear aromatics"[2].

            This partially-validated method work was performed to document analytical practices detailed in OSHA Method 48[3] (Petroleum Distillate Fractions) for kerosene. An important analytical practice discussed in Method 48 was the use of "non-source" petroleum distillate fractions (PDF) as analytical standards. Source PDF was defined as the bulk material actually in use at the workplace and that was presumed to be the source of the workplace contamination. Non-source PDF was defined as a substitute for the same generic PDF, but not the actual material in use at the workplace. Method 48 showed that non-source PDF can be used as analytical standards in place of source PDF. This is permissible because similar FID responses are observed for different hydrocarbons. Results presented in Method 48 showed that no significant differences were obtained in sample analysis when using either a source or non-source PDF to calibrate the FID response.

            A single number representing FID response to kerosene is obtained by summing detector response of GC peaks that elute in the "kerosene envelope". The kerosene envelope is determined with the professional judgment of the analyst by comparison of analytical standard chromatograms to air sample chromatograms. Any major component (or components) observed in air samples can be identified by GC/MS and then quantitated separately from kerosene. The FID response for this component(s) is then subtracted from the summed response for the air sample. The FID response of extraction solvent components is also subtracted from the summed response for the air sample and also for the analytical standards. An in-house computer program has been developed at SLTC for this purpose.

            The target level selected for this evolution was 100 mg/m^3 (the NIOSH REL) because of kerosene's designation by ACGIH as an A3 substance, "Confirmed Animal Carcinogen with Unknown Relevance to Humans"[4].

            The results of an extraction efficiency study for kerosene extracted from charcoal tubes with 99:1(CS_2:DMF) was 98.2%. Kerosene was found to be well retained on charcoal tubes, with 98.6% retention efficiency after 20 L of air had been drawn through the each tube, and the ambient storage stability recovery was 98.6% on day 14.

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[1] NIOSH Manual of Analytical Methods, 4th ed; U.S. Department of Health and Human Services, Center for Disease Control and Prevention, National Institute for Occupational Safety and Health : Cincinnati, OH, Method 1550.

[2] NIOSH Pocket Guide, www.cdc.gov (accessed 08/15/04).

[3] OSHA Method 48, Petroleum Distillate Fractions, www.osha.gov (accessed 05/15/2003).

[4] 2004 TLV and BEIs, Threshold Limit values for Chemical Substances and Physical Agents, American Conference of Governmental Industrial Hygienists, (ACGIH): Cincinnati, OH, 2004.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.) [5,6]

ACGIH lists kerosene as an A3 substance, "Confirmed Animal Carcinogen with Unknown Relevance to Humans". The major effects of exposure to kerosene are headache, drowsiness, and irritation of the eyes, nose and lungs. Contact dermatitis (skin irritation) may occur with prolonged and repeated contact. Target organs include the respiratory system, nervous system and mucous membranes. The LD_{50} is 2835 mg/kg orally in rabbits.

1.1.3 Workplace exposure[7,8]

Kerosene is used as a fuel in kerosene lamps, flares, and stoves. It is also used as a degreaser. Kerosene is used as a fuel in jet-propelled aircraft and also as a fuel in some other engines.

1.1.4 Physical properties and other descriptive information[9,10]

CAS number:	8008-20-6
IMIS[11]:	K107
RTECS number:	OA5500000
molecular weight:	170 (approximately, C_9 to C_{16} hydrocarbons)
melting point:	-51 °C
boiling point:	175-325 °C
appearance:	colorless to pale straw
density:	0.8 - 0.81g/mL
odor:	odorless
flash point:	65-85 °C
molecular formula:	C_9 to C_{16} hydrocarbon
synonyms:	kerosine; coal oil; fuel oil no.1; range oil
solubility:	Insoluble in water, miscible in all petroleum solvents
structural composition:	composition varies greatly and includes C_9 to C_{16} hydrocarbons (aliphatic and aromatic) with a boiling range of about 175 to 325 °C

This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Air sampling Methods utilizing Chromatographic analysis"[12]. 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.

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5   Budavari,S. Ed, The Merck Index, 12th edition, Merck & Co. Inc., Rawhay, N.J., 1997, p 903.
6   MSDS: Brown oil, www.brownoil.com/msdskerosene.htm (accessed 06/08/2003).
7   Budavari,S. The Merck Index , 12th edition Merck & Co. Inc., Rawhay, N.J., 1997, p 903.
8   MSDS: Brown oil, www.brownoil.com/msdskerosene.htm (accessed 06/02/2004).
9   MSDS: Brown oil, www.brownoil.com/msdskerosene.htm (accessed 06/02/2004).
10   Budavari,S. Ed, The Merck Index , 12th edition Merck & Co. Inc., Rawhay, N.J., 1997, p 903.
11   OSHA Chemical Sampling Information, http://www:osha.gov (accessed 06/02/2004).
12   Burright, D.; Chan, Y.; Eide, 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.

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

Different kerosenes may have similar constituents but not have similar concentrations of these constituents, therefore, no single representative component can be used to determine DLOP or RQL. 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 200 µg of kerosene. These spiked samplers were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (standard error of estimate and slope) for the calculation of the DLOP. The slope was 300 and the SEE was 2875.4. The RQL is considered to be 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 28.8 µg and 95.8 µg, respectively. The recovery at the RQL was 93.2%.

Table 1.2.
DLOP and RQL for Kerosene

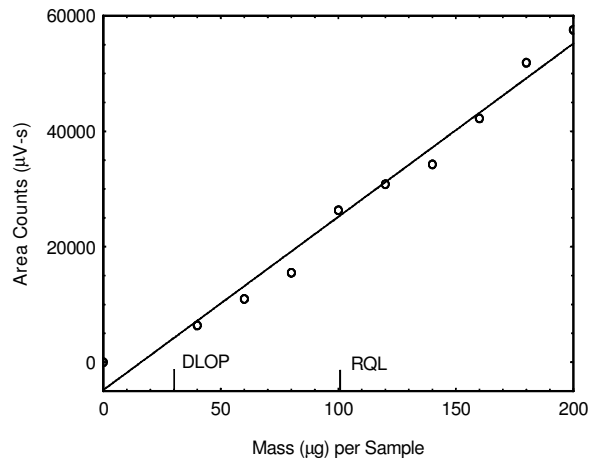| mass per sample (μg)	area counts (μV·s)
0	0
40	6374
60	10949
80	15490
100	26314
120	30828
140	34276
160	42240
180	51870
200	57569

Figure 1.2.1 DLOP and RQL for kerosene.

Below is a chromatogram of kerosene near the RQL concentration.
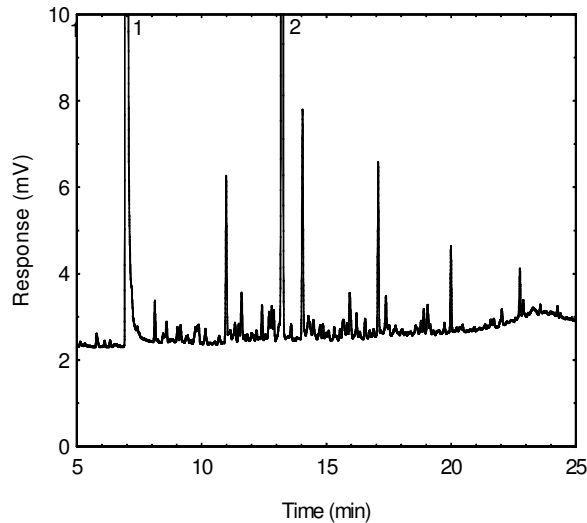

Figure 1.2.2 Chromatogram of kerosene near the RQL.
(Key: (1) DMF, (2) *P*-cymene. Kerosene is the series of unnumbered peaks eluting between 7 and 25 min.)

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 x 4-mm i.d. x 7-mm o.d. glass sampling tubes packed with two sections (100/50 mg) of coconut shell charcoal. The sections are held in place and separated with glass wool plugs. 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 tube ends. 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 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 liquid-spiking front sections of charcoal tubes with kerosene at 0.1 to 2 times the target concentration. These samples were stored overnight at ambient temperature and then extracted for 30 minutes with occasional shaking, and analyzed.

The mean extraction efficiency over the studied range was 98.2 %. The wet extraction efficiency was determined at 1 times the target concentration by liquid spiking the analyte onto charcoal tubes which had 20 L humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity at 22.2 °C) drawn through them. The mean recovery for the wet samples was 100.5%.

Table 2.4
Extraction Efficiency (%) of Kerosene

level		sample number					
x target concn	mg per sample	1	2	3	4	5	mean
0.1	0.2	96.0	98.0	93.0	95,0	95.0	95.4
0.2	0.4	97.3	99.0	98.8	100.0	97.3	98.5
0.5	1.0	100.0	100.7	99.6	100.5	99.6	100.1
1.0	2.0	99.5	99.2	99.3	99.2	95.1	98.5
2.0	4.0	101.3	95.2.	100.2	100.4	95.4	98.5
1.0 (wet)	2.0	99.4	100.6	100.6	102.4	99.4	100.5

2.5   Retention efficiency

Six charcoal tubes were spiked with 4.0 mg of kerosene in the front section of the tubes and allowed to equilibrate for 6 h. The tubes had 20 L humid air (absolute humidity of 15.9 mg/L of water, about 80% relative humidity at 22.2 °C) pulled through them at 0.1 L/min. The samples were extracted and analyzed. The mean retention recovery was 98.6%. There was no analyte found on the backup section of any of the tubes.

Table 2.5
Retention Efficiency (%) of Kerosene

	sample number						
section	1	2	3	4	5	6	mean
front of spiked tube	99.8	99.0	99.2	98.6	97.2	97.8	98.6
rear of spiked tube	0.0	0.0	0.0	0.0	0.0	0.0	0.0
total	99.8	99.0	99.2	98.6	97.2	97.8	98.6

2.6   Sample storage

Nine charcoal tubes were each spiked with 2.0 mg of kerosene. They were allowed to equilibrate for 6 h, then 20 L of air, with an absolute humidity of 15.7 milligrams of water per liter of air (about 80% relative humidity at 22.2 °C), was drawn through them. Three samples were analyzed immediately, and the rest were sealed and stored at room temperature. Three more were analyzed after 7 days of storage and the remaining three after 14 days of storage.

Table 2.6
Storage Test for Kerosene (% Recovery)

	sample number			
time (days)	1	2	3	mean
0	99.4	100.9	100.6	100.3
7	97.3	98.8	98.0	98.0
14	99.6	96.6	99.5	98.6

2.7   Recommended air volume and sampling rate

Based on the data collected in this evaluation, 20-L air samples should be collected at a sampling rate of 0.1 L/min for 200 minutes.

2.8   Interferences (sampling)

2.8.1   There are no known compounds that will severely interfere with the collection of kerosene.

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. An Agilent 6890 plus Series Gas Chromatograph equipped with a 7683 Automatic Sampler was used in this evaluation.

3.1.2   A GC column capable of separating kerosene from the extraction solvent, internal standard and any potential interference. A 60-m x 0.32-mm i.d. capillary RT_X Volatiles with a 0.5 µm df (Restek Corporation, Bellefonte PA) was used in the 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. An in-house computer program for summing and subtracting selected solvent peaks was used to calculate kerosene FID response.

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

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

3.1.7   Volumetric flasks. Ten-milliliter and other convenient sizes for preparing standards.

3.1.8   Calibrated 10-µL syringe for preparing standards.

3.2   Reagents

3.2.1   Kerosene, reagent grade. Aldrich 99% (lot 06411KU) was used in this evaluation.

3.2.2   Carbon disulfide, reagent grade. Omni-Solv® 99.99% (lot CX0397-3) was used in this evaluation.

3.2.3   *N,N*-Dimethylformamide (DMF), reagent grade. Aldrich 99.9% (lot DU010523) was used in this evaluation.

3.2.4   *p*-Cymene, reagent grade. Aldrich 99% (lot 11703TR) was used in this evaluation.

3.2.5   The extraction solvent was 0.25 µL/mL *p*-cymene as internal standard in CS_2/DMF (99/1). *p*-Cymene was used as the internal standard because it did not interfere with

kerosene peaks. n-Hexyl benzene was not used as the internal standard because it eluted with kerosene peaks.

3.2.6   GC grade nitrogen, air, and hydrogen.

3.3   Standard preparation

3.3.1   Prepare working analytical standards by injecting microliter amounts of kerosene into volumetric flasks containing the extraction solvent. An analytical standard at a concentration of 2 mg/mL is equivalent to 100 mg/m^3 based on a 20-L air volume.

3.3.2   Bracket sample results with working standard concentrations. If sample concentrations are higher than the concentration range of prepared standards, prepare and analyze additional standards with at least as high a concentration as the highest sample to confirm the linearity of response. Otherwise, dilute the sample with extracting solvent to obtain a concentration within the existing standard range. The range of standards used in this study was from 0.2 to 4 mg/mL, which is equivalent to 0.1 to 2 times target concentration based on a 20-L air sample.

3.4   Sample preparation

3.4.1   Remove the plastic end caps from the sample tubes and carefully transfer the adsorbent sections to separate 2-mL vials. Discard the glass tube, glass wool and foam 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 vigorously by hand several times during the next 30 minutes.

3.5   Analysis

3.5.1   Analytical conditions.

GC conditions
column: 100 °C for 5 min, 5 °C /min to 220 °C, final time 2 min
zone
 temperatures: 220 °C (injector)
                       250 °C (detector)
run time: 31 min
column gas flow: 3.0 mL/min (hydrogen)
injection size: 1.0 µL (10:1 split)
column: 60-m x 0.32-mm i.d. capillary RT$_X$ Volatiles (0.5-µm df)
retention times: 3.2 min (carbon disulfide); 4.4 min (benzene contaminate in the carbon disulfide); 7.1 min (DMF); 13.3 min (p-cymene); (kerosene is the series of unnumbered peaks eluting between 7 and 30 min)

FID conditions
hydrogen flow: 30 mL/min
air flow: 400 mL/min
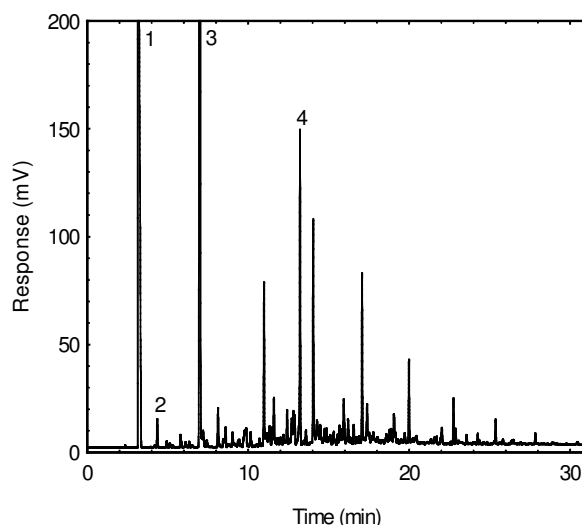makeup flow: 25 mL/min (nitrogen)

Figure 3.5.1 Chromatogram of 2.0 mg/mL kerosene
in the extraction solvent. (key: (1) CS_2, (2) benzene,
(3) DMF, (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 ISTD-corrected response of standard injections versus
micrograms of analyte per sample. An in-house computer program for summing of
peaks and subtracting solvent peaks was used to calculate kerosene values. Bracket
the samples with freshly prepared analytical standards over a range of concentrations.

3.6   Interferences (analytical)

3.6.1   Any compound that produces a GC response and has a elution time in the kerosene
peak envelope is a potential interference.   If any potential interferences were reported,
they should be considered before samples are extracted. If any large unknown peak is
observed and is identified, or if a chemical was identified as an interference by the IH,
its GC response can be subtracted from the summed kerosene value and then
quantitated as an individual analyte.

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

4. 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 formula.

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

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

5. Recommendations for Further Study

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