

Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 1550, Issue 2

EVALUATION: FULL

Issue 1: 15 February 1984
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NIOSH: Table 1
ACGIH: Table 1

PROPERTIES: Table 1

SYNONYMS: Petroleum ether (benzin), rubber solvent, petroleum naphtha, VM&P naphtha, mineral spirits, Stoddard solvent, kerosene (kerosine), coal tar naphtha.

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)	TECHNIQUE:	GAS CHROMATOGRAPHY, FID
FLOW RATE:	0.01 to 0.2 L/min	ANALYTE:	naphtha hydrocarbons
VOL-MIN:	1.3 L @ 400 mg/m ³ ; 0.2 L @ 2500 mg/m ³	DESORPTION:	1 mL CS ₂ ; stand 30 min
-MAX:	20 L @ 400 mg/m ³ ; 3.2 L @ 2500 mg/m ³	INJECTION VOLUME:	5 µL (packed column); 0.1 to 1 µL (capillary column)
SHIPMENT:	routine	TEMPERATURE-INJECTION:	200 to 250 °C
SAMPLE STABILITY:	at least 1 week @ 25 °C	-DETECTOR:	250 to 300 °C
BLANKS:	2 to 10 field blanks per set	-COLUMN:	50 to 250 °C @ 8 °/min
BULK SAMPLE:	required; 5 to 10 mL	CARRIER GAS:	N ₂ or He, 30 mL/min
ACCURACY		COLUMN:	glass, 3 m x 6-mm, 10% SP-2100 on Supelcoport 80/100 or 30-m fused silica capillary, 0.325-mm ID, 1.0-µm DB-1 or equivalent
RANGE STUDIED:	see EVALUATION OF METHOD	CALIBRATION:	solutions of bulk naphtha in CS ₂
BIAS:	see EVALUATION OF METHOD	RANGE:	0.5 to 10 mg per sample [2,3,4]
OVERALL PRECISION (\hat{S}_{rT}):	0.05 [1]	ESTIMATED LOD:	0.1 mg per sample
ACCURACY:	see EVALUATION OF METHOD	PRECISION (\hat{S}_r):	0.01 [1]

APPLICABILITY: The working range is 100 to 2000 mg/m³ for a 5-L air sample. This is a general procedure for analysis of various types of hydrocarbon mixtures called "naphthas" which are used as thinners in paints and varnishes and as general purpose solvents.

INTERFERENCES: Most naphthas are quite complex. The components elute over a wide temperature range by gas chromatography, making interferences from other substances possible. Columns and conditions must be chosen to obtain the desired degree of separation for a given mixture.

OTHER METHODS: This method combines and replaces Methods S86 [2], S380 [3] and S382 [4]. A similar method appears in the criteria document [5].

REAGENTS:

1. Eluent: Carbon disulfide*, chromatographic quality, containing 0.1% (v/v) octane, 0.5% (v/v) hexadecane or other suitable internal standard.
NOTE 1: Use an internal standard which is not a major constituent of the sample.
NOTE 2: Use toluene in place of carbon disulfide for low-boiling analytes [5].
2. Naphtha bulk sample.
3. Nitrogen or helium, purified.
4. Hydrogen, prepurified.
5. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1550-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10- μ L (1- μ L syringe for capillary columns) and other convenient sizes for preparing standards, readable to 0.1 μ L.
6. Volumetric flasks, 10-mL.
7. Pipet, delivery, 1.0-mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size which contains between 0.5 and 8 mg naphtha.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment. Ship a bulk sample (5 to 10 mL) in a separate container from the sorbent tubes.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.1 to 10 mg naphtha per sample.
 - a. Add known amounts of naphtha bulk sample to eluent in 10-mL volumetric flasks and dilute to the mark.

- b. Analyze together with samples and blanks (steps 11 and 12).
- c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg naphtha).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
 - a. Remove and discard back sorbent section of a media blank sampler.
 - b. Inject a known amount of naphtha bulk sample directly onto front sorbent section with a microliter syringe.
 - c. Cap the tube. Allow to stand overnight.
 - d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
 - e. Prepare a graph of DE vs. mg naphtha recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1550-1. Inject sample aliquot manually using solvent flush technique or with autosampler.

NOTE 1: The columns and conditions given provide moderate to good separation of components. If less resolution is needed, use shorter, less efficient columns as were used in validation of Methods S86 [2], S380 [3] and S382 [4].

NOTE 2: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of naphtha found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.

NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of naphtha in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Methods S86 (Naphtha, Coal Tar), S380 (Petroleum distillate) and S382 (Stoddard Solvent) were issued on March 14, 1975 [2,3,4]. They were validated at 24 °C and approximately 755 mm Hg using 10-, 4- and 3-L air samples, respectively, of 2-50-W Hi-Flash Solvent (Neville Chemical Co.; BP 154 to 195 °C; d 0.893 g/mL), VM&P Naphtha (Amsco Product 1101; BP 120 to 147 °C; d 0.743 g/mL) and Stoddard Solvent (Fisher Scientific Co.; BP 159 to 176 °C; d 0.774 g/mL) [1]. Overall precision and recovery were as shown below, representing a non-significant bias in each method. Breakthrough tests in dry air showed a capacity of 20 to 25 mg of each solvent tested. Capacity at high relative humidity was not determined.

Method	Overall Precision (\hat{S}_{rT})	Bias	Range Studied		mg per sample	Avg. DE	Ref.
			Accuracy	mg/m ³			
S86 ^(b)	0.051	5.99%	±15.0%	193 to 809	2 to 8	0.88	[1,2]
S380 ^(a)	0.052	-4.37%	±12.5%	937 to 3930	4 to 16	0.96	[1,3]
S382 ^(b)	0.052	-3.10%	±11.4%	1417 to 5940	4.5 to 18	0.95	[1,4]

- NOTES: (a) Data based on experiments using an internal standard method with a 10 ft., 1/8" stainless steel column packed with 10% OV-101 on 100/120 mesh Supelcoport.
 (b) Data based on experiments using an internal standard method with a 6 ft., 1/8" stainless steel column packed with 1.5% OV-101 on 100/120 mesh Chromosorb W.

REFERENCES:

- [1] Documentation of the NIOSH Validation Tests, S86, S380, S382, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
 [2] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, Method S86, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
 [3] Ibid, V. 3, S380, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
 [4] Ibid, S382.
 [5] Criteria for a Recommended Standard...Occupational Exposure to Refined Petroleum Solvents, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-192 (July, 1977).

METHOD REVISED BY:

Ardith A. Grote, NIOSH/DPSE; S86, S380 and S382 originally validated under NIOSH Contract CDC-99-74-55.

Table 1. General information.

Exposure

<u>Limits, mg/m³</u> NAME		Vapor	
OSHA CAS #	Boiling NIOSH Range (°C)	Pressure, kPa (mm Hg) @ 20 °C	Liquid Density (g/mL @ 15 °C)
Predominant RETECS Hydrocarbon Species	ACGIH		
Petroleum ether (a) 8032-32-4 OI6180000	30 to 60 C ₅ -C ₆	13 (100) -- (13 °C)	0.63 to 0.66 aliphatic 350; C 1800 --
Rubber solvent (a) SE7449000 8030-30-6	45 to 125 C ₅ -C ₈	(c) 2000 (500 ppm)	0.67 to 0.85 aliphatic 350; C 1800 1590 (400 ppm)
Petroleum naphtha (b) (Petroleum distillates mixture) 8002-05-9 SE7449000	30 to 238 C ₆ -C ₈	5 (40) 2000 (500 ppm)	0.6 to 0.8 350; C 1800 --
VM&P naphtha (a) 8032-32-4 OI6180000	95 to 160 C ₇ -C ₁₁	0.3 to 3 (2 to 20) --	0.72 to 0.76 <20% aromatic 350, C 1800 1370 (300 ppm)
Mineral spirits (a) 8052-41-3 WJ89250000	150 to 200 C ₉ -C ₁₂	0.2758(2) 2900 (500 ppm)	0.77 to 0.81 <20% aromatic 350; C 1800 525 (100 ppm)
Stoddard solvent (a) 8052-41-3 WJ8925000	150 to 210 C ₉ -C ₁₂	0.2758 (2) 2900 (500 ppm)	0.75 to 0.80 <20% aromatic 350; C 1800 525 (100 ppm)
Kerosene (a) 8008-20-6 OA5500000	175 to 325 C ₉ -C ₁₆	(c) --	0.8 <20% aromatic 100 --
Coal tar naphtha (b)	110 to 190 C ₈ -C ₁₀	<0.7 (<5) 400 (100 ppm)	0.86 to 0.89

8030-30-6

aromatic

400 (100 ppm)

DE3030000 (NIOSH)

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- (a) As defined by NIOSH Criteria Document [5].
- (b) As defined for OSHA PEL.
- (c) Not available.

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