

Table 1

MW: Table 1

CAS: Table 2

RTECS: Table 2

<b>METHOD:</b> 1400, Issue 2	<b>EVALUATION:</b> PARTIAL	<b>Issue 1:</b> 15 February 1984 <b>Issue 2:</b> 15 August 1994
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**OSHA :** Table 2  
**NIOSH:** Table 2  
**ACGIH:** Table 2

**PROPERTIES:** Table 1

**COMPOUNDS AND SYNONYMS:** (1) ethanol: ethyl alcohol.  
(2) isopropyl alcohol: 2-propanol.  
(3) tert-butyl alcohol: 2-methyl-2-propanol.

SAMPLING				MEASUREMENT	
<b>SAMPLER:</b>	SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)			<b>TECHNIQUE:</b>	GAS CHROMATOGRAPHY, FID
<b>FLOW RATE:</b>	0.01 to 0.2 L/min ( $\leq 0.05$ L/min for ethyl alcohol)			<b>ANALYTE:</b>	compounds above
<b>VOL-MIN:</b>	(1)	(2)	(3)	<b>DESORPTION:</b>	1 mL 1% 2-butanol in CS <sub>2</sub>
<b>-MAX:</b>	0.1 L	0.3 L	1.0 L	<b>INJECTION VOLUME:</b>	5 $\mu$ L
<b>SHIPMENT:</b>	cooled			<b>TEMPERATURE-INJECTION:</b>	200 °C
<b>SAMPLE STABILITY:</b>	unknown, store in freezer			<b>-DETECTOR:</b>	250-300 °C
<b>BLANKS:</b>	2 to 10 field blanks per set			<b>-COLUMN:</b>	65-70 °C
<b>ACCURACY</b>				<b>CARRIER GAS:</b>	N <sub>2</sub> or He, 30 mL/min
<b>RANGE STUDIED:</b>	see EVALUATION OF METHOD			<b>COLUMN:</b>	glass, 2 m x 4-mm ID, 0.2% Carbowax 1500 on 60/80 Carboxpack C or equivalent
<b>BIAS:</b>	not significant [1]			<b>CALIBRATION:</b>	solutions of analyte in eluent (internal standard optional)
<b>OVERALL PRECISION (<math>\hat{S}_{rt}</math>):</b>	see EVALUATION OF METHOD			<b>RANGE AND PRECISION:</b>	see EVALUATION OF METHOD
<b>ACCURACY:</b>	$\pm 14\%$			<b>ESTIMATED LOD:</b>	0.01 mg per sample [2]

**APPLICABILITY:** The working ranges are 16 to 1000 ppm ethanol (30 to 1900 mg/m<sup>3</sup>) for a 1-L air sample; 4 to 400 ppm isopropyl alcohol (10 to 1000 mg/m<sup>3</sup>) for a 3-L air sample; and 1 to 100 ppm t-butyl alcohol (3 to 300 mg/m<sup>3</sup>) for a 10-L air sample. This method employs a simple desorption and may be used to determine two or more analytes simultaneously by varying GC conditions (e.g., temperature programming).

**INTERFERENCES:** High humidity reduces sampling efficiency. The methods were validated using a 3 m x 3-mm stainless steel column packed with 10% FFAP on Chromosorb W-AW; other columns with equal or better resolution (e.g., capillary) may be used. Less volatile compounds may displace more volatile compounds on the charcoal.

**OTHER METHODS:** This method combines and replaces Methods S56, S65 and S63 [3].

**REAGENTS:**

1. Eluent: Carbon disulfide\* (chromatographic grade) with 1% (v/v) 2-butanol and 0.2% v/v n-undecane, 0.1% v/v ethyl benzene, or other suitable internal standard.
2. Analyte, reagent grade.
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, compressed, 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. Refrigerant, bagged (Blue Ice, or equivalent).
4. Gas chromatograph, FID, integrator and column (page 1400-1).
5. Vials, glass, 2-mL, PTFE-lined crimp caps.
6. Syringe, 10- $\mu$ L, readable to 0.1  $\mu$ L.
7. Volumetric flasks, 10-mL.

**SPECIAL PRECAUTIONS:** Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); all work with it must be done 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 of 0.1 to 1 L (ethanol), 0.3 to 3 L (isopropyl alcohol) or 1.0 to 10 L (t-butyl alcohol).
4. Cap the samplers with plastic (not rubber) caps and pack securely with bagged refrigerant for shipment.

**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 covering the range of the samples.
  - a. Add known amounts of analyte 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 analyte).
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 analyte 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 analyte 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 1400-1. Inject sample aliquot manually using solvent flush technique or with autosampler.  
NOTE: 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 analyte 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 analyte 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 S56, S65 and S63 were issued on January 17, 1975 [3], and validated using 1-, 3- and 10-L air samples, respectively, of atmospheres generated in dry air by calibrated syringe drive from absolute ethanol, 2-propanol and t-butyl alcohol [1]. No stability studies were done. Overall precision and recovery were as shown below, representing non-significant bias in each method:

Method	Overall Precision	Recovery (%)	Range Studied		Breakthrough @ 2X OSHA	Avg. DE	Measurement Precision ( $\bar{S}_r$ )
	( $\bar{S}_{r,r}$ )		mg/m <sup>3</sup>	mg per sample			
S56	0.065	103.6	900 to 3300	1 to 4	1.6 L	0.79*	0.027
S65	0.064	96.7	505 to 1890	1 to 5	6.0 L	0.93*	0.033
S63	0.075	100.3	165 to 600	1.5 to 6	17.0 L	0.91*	0.018

\*Over the range studied. Each laboratory must do their own DE determinations.

**REFERENCES:**

- [1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, (NIOSH) Publication No. 77-185 (1977).
- [2] User check, UBTL, NIOSH Sequence #3990-S (unpublished, November 3, 1983).
- [3] NIOSH Manual of Analytical Methods, 2nd ed., V. 2., S56, S65 and S63, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

**METHOD REVISED BY:**

George Williamson, NIOSH/DPSE; methods originally validated under NIOSH Contract 99-74-45.

**TABLE 1. PROPERTIES**

<u>Compound</u>	<u>Formula</u>	<u>mg/m<sup>3</sup> = 1 ppm @ NTP</u>	<u>M.W.</u>	<u>Density @ 20 °C (g/mL)</u>	<u>BP (°C)</u>	<u>VP @ 20 °C, kPa (mm Hg)</u>
Ethanol	CH <sub>3</sub> CH <sub>2</sub> OH; C <sub>2</sub> H <sub>6</sub> O	1.883	46.07	0.789	78.5	5.6 (42)
Isopropyl alcohol	CH <sub>3</sub> CH(OH)CH <sub>3</sub> ; C <sub>3</sub> H <sub>8</sub> O	2.46	60.09	0.785	82.5	4.4 (33)
tert-Butyl alcohol	(CH <sub>3</sub> ) <sub>3</sub> COH; C <sub>4</sub> H <sub>10</sub> O	3.03	74.12	0.786	82.4; MP = 25.6 °C	4.1 (31)

**TABLE 2. GENERAL INFORMATION.**

<u>COMPOUND</u>	<u>EXPOSURE LIMITS (ppm)</u>			<u>CAS#</u>	<u>RTECS#</u>
	<u>OSHA</u>	<u>NIOSH</u>	<u>ACGIH</u>		
Ethanol	TWA 1000	1000	1000	64-17-5	KQ6300000
Isopropyl alcohol	TWA 400	400 500 STEL	400 500 STEL	67-63-0	NT8050000
tert-Butyl alcohol	TWA 100	100 150 STEL	100	75-65-0	EO1925000