ALCOHOLS COMBINED 1405

Formulas: Table 1 MW: Table 1 CAS: Table 2 RTECS: Table 2

METHOD: 1405, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA : Table 2
NIOSH: Table 2
ACGIH: Table 2

PROPERTIES: Table 1

COMPOUNDS:
(1) *n*-butyl alcohol
(2) *sec*-butyl alcohol
(3) isobutyl alcohol
(4) *n*-propyl alcohol
(5) allyl alcohol
(6) diacetone alcohol
(7) cyclohexanol
(8) isoamyl alcohol
(9) methyl isobutyl carbinol

SYNONYMS: See Table 3.

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(Coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

Compounds:	(1-3)	(4-9)
VOL-MIN:	2 L	1 L
-MAX:	10 L	10 L

SHIPMENT: Routine

SAMPLE STABILITY: See Evaluation of Method.

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Not studied [1, 2].

BIAS: Not determined

OVERALL PRECISION ($\hat{S}_{rT}$): Not determined

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: Compounds above

DESORPTION: 1 mL 5% 2-propanol in CS_2

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTION: 220 °C
-DETECTOR: 250 - 300 °C
-COLUMN: 35 °C (7 minutes), to 60 °C at 5 °C/minute, hold 5 minutes, up to 120 °C at 10 °C /minute, hold 3 minutes.

CARRIER GAS: He, 4 mL/min

COLUMN: Capillary, fused silica, 30 m x 0.32-mm ID; 0.5 µm film polyethylene glycol, DB-wax or equivalent

CALIBRATION: Solutions of analyte in eluent (internal standard optional)

RANGE: See EVALUATION OF METHOD.

ESTIMATED LOD: 1 µg each analyte per sample

PRECISION: See EVALUATION OF METHOD.

APPLICABILITY: This method may be used to determine two or more of the specified analytes simultaneously.

INTERFERENCES: High humidity reduces sampling capacity. Less volatile compounds may displace more volatile compounds on the charcoal.

OTHER METHODS: This method combines and updates Methods 1401 and 1402, NMAM, Fourth Edition, Issue 2. Estimated LOD for each analyte is approximately ten times lower than that of the old methods.

REAGENTS:

1. Carbon disulfide, chromatographic grade.*
2. 2-Propanol, chromatographic grade.*
3. Hexane, chromatographic grade.*
4. Heptane, chromatographic grade.*
5. Desorbing solution: Carbon disulfide with 5% (v/v) 2-propanol and 0.05% (v/v) hexane as an internal standard.
   NOTE: n-Undecane, 0.1 (v/v) or other suitable standard can be used.
6. Analyte(s).
7. Stock solution, 100 mg/mL. Prepare solutions of each analyte in heptane.
8. Nitrogen, purified.
9. Hydrogen, prepurified.
10. 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 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 1405-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 2 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. Propanol, hexane, and heptane are flammable. Analytes should be handled in a fume hood. Wear gloves, safety glasses, and appropriate protective clothing.

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 1 to 10 L (2 to 10 L for n-butanol, sec-butanol, and isobutyl alcohol).
4. Cap the samplers with plastic (not rubber) caps and pack securely 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 desorbing solution (DS) 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 samples.
   a. Add known amounts of analyte to DS in 2-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. µg 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 tree media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of stock solution 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. µg analyte recovered.

10. Analyze three quality control bind 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 1405-1. 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, µg (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 (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):

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

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

Previous Evaluations [2]

This method, NIOSH 1405, combines and updates NIOSH Methods 1401 and 1402. Methods 1401 an 1402 were based on the 2nd edition NMAM Methods S66 (n-butyl alcohol), S53 (sec-butyl alcohol), S64 (isobutyl alcohol), S62 (n-propyl alcohol), S52 (allyl alcohol), S55 (diacetone alcohol), S54 (cyclohexanol), S58 (isoamyl aocohol), and S60 (methyl isobutyl carbinol) which were issued on January 17, 1975 [3] and validated using 10-L air samples of atmospheres generated by injection of the pure alcohol into dry air using a calibrated syringe drive [1]. No storage stability studies were performed. Overall precision and recoveries are shown Table 4, representing non-significant bias in each method.

Current Evaluation [4]

Methods for alcohols (n-butyl alcohol, sec-butyl alcohol, isobutyl alcohol, n-propyl alcohol, allyl alcohol, diacetone alcohol, cyclohexanol, isoamyl alcohol) were evaluated using analytes fortified on Anasorb CSC sorbent tubes (Lot #2000). Table 5 lists the desorption efficiency (DE) and precision for the compounds tested in the evaluation.

Storage stability studies were performed at two different concentration levels: one at approximately 10 µg each analyte/sample for the low level, and the other at approximately 150 µg each analyte/sample for the high level. The samples were stored for 7, 14, 21, and 30 days at 5 °C. The results are summarized in Table 5.

REFERENCES:

[1] NIOSH [1977]. Documentation of the NIOSH Validation Tests. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185.
[2] NIOSH [1994]. Methods 1401 and 1402. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods, 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.
[3] Taylor DG, eds [1977]. NIOSH Manual of Analytical Methods, 2nd ed., V.2., Cincinnati, OH: U.S. Department of Health, Education, and Welfare. DHHS (NIOSH) Publication No. 77-157-B.
[4] Yoon YH, Perkins JB, Reynolds JM [2002]. Back-up Data Report for Alcohols Combined. DataChem Laboratories, Inc. under NIOSH contracts CDC-200-95-2955 and CDC 200-2001-08000 (August).

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TABLE 1. PROPERTIES

Compound	Formula	mg/m^3 = 1 ppm @ NTP	M.W.	Density (g/mL)	BP (°C)	VP @ 20°C, kPa (mm Hg)
n-Butyl alcohol	$CH_3CH_2CH_2CH_2OH$; $C_4H_{10}O$	3.03	74.12	0.810 @ 20 °C	117	0.56 (4.2)
sec-Butyl alcohol	$CH_3CH(OH)CH_2CH_3$; $C_4H_{10}O$	3.03	74.12	0.808 @ 20 °C	99.5	1.7 (13)
Isobutyl alcohol	$(CH_3)_2CHCH_2OH$; $C_4H_{10}O$	3.03	74.12	0.806 @ 15 °C	108	1.2 (9)
n-Propyl alcohol	$CH_3CH_2CH_2OH$; C_3H_8O	2.46	60.09	0.805 @ 20 °C	97	2.0 (15)
Allyl alcohol	$CH_2=CHCH_2OH$; $C_3H_6O_2$	2.37	58.08	0.854	96-97	2.3 (17)
Diacetone alcohol	$(CH_3)_2C(OH)CH_2COCH_3$; $C_6H_{12}O_2$	4.75	116.16	0.931 @ 25 °C	167.9	0.1 (0.8)
Cyclohexanol	$C_6H_{12}O$	4.09	100.16	0.962	161: MP=24	0.13 (1.0)
Isoamyl alcohol	$(CH_3)_2CHCH_2CH_2OH$; $C_5H_{12}O$	3.60	88.15	0.813 @ 15 °C	132	3.7 (28)
Methyl isobutyl carbinol	$(CH_3)_2CHCH_2CH(OH)CH_3$; $C_6H_{14}O$	4.18	102.18	0.802	132	0.4 (3)

TABLE 2. GENERAL INFORMATION

			Exposure Limits		
Compound	**CAS #**	**RETECS #**	**OSHA (ppm)**	**NIOSH (ppm)**	**ACGIH (ppm)**
n-Butyl alcohol	71-36-3	EO1400000	100 TWA	C 50 (skin)	C 50 (skin)
sec-Butyl alcohol	78-92-2	EO1750000	150 TWA	100 TWA; 150 STEL	100 TWA
Isobutyl alcohol	78-83-1	NP9625000	100 TWA	50 TWA	50 TWA
n-Propyl alcohol	71-23-8	UH8225000	200 TWA	200 TWA; 250 STEL(skin)	200 TWA; 250 STEL (skin)
Allyl alcohol	107-18-6	BA5075000	2 TWA; (skin)	2 TWA; 4 STEL (skin) (Group 1 Pesticide)	2 TWA; 4 STEL (skin)
Diacetone alcohol	123-42-2	SA9100000	50 TWA	50 TWA	50 TWA
Cyclohexanol	108-93-0	GV7875000	50 TWA	50 TWA (skin)	50 TWA (skin)
Isoamyl alcohol	123-51-3	EL5425000	100 TWA	100 TWA; 125 STEL(skin)	100 TWA; 125 STEL
Methyl isobutyl carbinol	108-11-2	SA7350000	25 TWA; (skin)	25 TWA; 40 STEL (skin)	25 TWA; 40 STEL (skin)

TABLE 3. SYNONYMS

Compound	Synonyms
(1) n-butyl alcohol	1-butanol; n-butanol; propyl carbinol.
(2) sec-Butyl alcohol	2-butanol; methyl ethyl carbinol; 2-hydroxybutane.
(3) isobutyl alcohol	2-methyl-1-propanol; isopropyl carbinol; IBA.
(4) n-propyl alcohol	1-propanol; ethyl carbinol.
(5) allyl alcohol	2-propen-1-ol; 2-propenol; vinyl carbinol.
(6) diacetone alcohol	4-hydroxy-4-methyl-2-pentanone; 2-methyl-2-pentanol-4-one.
(7) cyclohexanol	hexalin; hydralin; hydroxycyclohenane; anol.
(8) isoamyl alcohol	3-methyl-1-butanol; isobutylcarbinol; isopentyl alcohol.
(9) methyl isobutyl carbinol	MIBC; 4-methyl-2-pentanol; methyl amyl alcohol.

TABLE 4. PREVIOUS METHOD EVALUATION

			Range Studied [1]				
Method	Overall Precision (ŝrT)	Recovery (%)	(mg/m3)	(µg / sample)	Breakthrough[a] @ 2X OSHA PEL	Avg. DE	Measurement Precision (ŝr)
S66	0.065	100.0	170 to 610	1,500 to 6,000	35 L	0.89	0.021
S53	0.066	107.2	270 to 850	2,200 to 9,000	15 L	0.92	0.028
S64	0.073	100.0	180 to 620	1,500 to 6,000	31 L	0.85	0.023
S62	0.075	103.5	225 to 835	2,500 to 10,000	19 L	0.89	0.016
S52	0.111	98.8	1.8 to 8.4	20 to 100	>48 L	0.90	0.023
S55	0.104	91.8	140 to 510	1,100 to 4,700	>48 L	0.78	0.054
S54	0.080	98.9	95 to 380	1,000 to 4,000	>48 L	0.99	0.015
S58	0.077	107.6	195 to 680	1,800 to 7,000	34 L	0.99	0.020
S60	0.080	101.8	45 to 175	500 to 2,000	>48 L	0.99	0.035

a) sampling done in dry air

TABLE 5. CURRENT METHOD EVALUATION

Compound	Range Studied (µg / sample)	Average DE	Measurement Precision ($\hat{S}_r$)	Storage Stability Levels	
				Low (day)	High (day)
n-Butyl Alcohol	8 to 3,040	0.91	0.025	<7	30
sec-Butyl alcohol	8 to 3,030	0.96	0.016	30	30
Isobutyl alcohol	8 to 3,020	0.94	0.015	30	30
n-Propyl alcohol	8 to 3,020	0.92	0.015	14	30
Allyl alcohol	9 to 152	0.80	0.026	<7	14
Diacetone alcohol	9 to 3,260	0.88	0.013	<7	7
Cyclohexanol	10 to 1,710	0.95	0.017	30	30
Isoamyl alcohol	8 to 1,450	0.92	0.017	14	30
Methyl isobutyl carbinol	8 to 1,430	0.96	0.018	30	30