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

METHOD: 1450, Issue 3 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 3: 15 March 2003

OSHA : Table 1
NIOSH: Table 1
ACGIH: Table 1

PROPERTIES: Table 1

COMPOUNDS:

n-amyl acetate	1-butyl acetate	isobutyl acetate	ethyl acrylate
2-ethoxyethyl acetate	methyl isoamyl acetate	n-butyl acetate	
n-propyl acetate	sec-butyl acetate	isoamyl acetate	

SYNONYMS: See Table 1

SAMPLING

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

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 1 L @ OSHA PEL
-MAX: 10 L

SHIPMENT: Refrigerated

SAMPLE STABILITY: See EVALUATION OF METHOD

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.5 to 2x OSHA PEL[1]

ACCURACY: See EVALUATION OF METHOD

BIAS: See EVALUATION OF METHOD

OVERALL PRECISION ($\hat{S}_{r,T}$): See EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: Compounds referenced above

DESORPTION: 1 mL CS_2, 30 min

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTION: 200 - 225 °C
-DETECTOR: 250 - 300 °C
-COLUMN: 50 °C for 2 minutes, then up to 110 °C at a rate of 5 °C per minute, holding at 110 °C for 3 minutes.

CARRIER GAS: 4 mL/min, Helium

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

CALIBRATION: Solutions of compounds in CS_2

RANGE: See EVALUATION OF METHOD and Table 1.

LOD: See EVALUATION OF METHOD

PRECISION ($\hat{S}_r$): See EVALUATION OF METHOD [1]

APPLICABILITY: This method can be used for simultaneous analysis of all analytes. High humidity greatly reduces sampler capacity and breakthrough volume.

INTERFERENCES: None identified.

OTHER METHODS: This method, NMAM 1450, Issue 3 is an updated analytical procedure [5]. This method originally combined and replaced the NMAM 2nd edition Methods S31, S32, S35, S37, S41, S44 through S48, and S51 [3]. Estimated LOD for each analyte is approximately 10 times lower than that of the previous methods.

REAGENTS:

1. Desorbing solution: Carbon disulfide* (chromatographic grade) with 0.05% (v/v) n-hexane or other suitable internal standard.
2. Analyte, reagent grade.
3. Helium, 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 1450-1).
5. Vials, glass, 2-mL, PTFE-lined crimp caps.
6. Syringe, 10-µL, readable to 0.1 µL, 25-, 50- and 100-µL.
7. Volumetric flasks, 10-mL.
8. Pipet, volumetric, 1-mL, with pipet bulb or repipet.

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

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler tube in line.
2. Break the ends of the sampler tube immediately before sampling. Attach sampler tube 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.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment with bagged refrigerant.

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 to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.
   NOTE: The desorption efficiency of 2-ethoxyethyl acetate has been found to decrease with the resident time of the desorbed solution with charcoal [4]. After 30 min desorption transfer the supernatant solution of 2-ethoxyethyl acetate to a clean 2-mL vial and seal with a crimp cap.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.001 to 10 mg analyte per sample.
   a. Add known amounts of analyte to desorbing solution 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 lot of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a 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 1450-1. Inject sample aliquot with autosampler, or manually using solvent flush technique.
    NOTE: If peak area is above the linear range of the working standards, dilute with desorbing solution, 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 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):

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

EVALUATION OF METHOD:

Previous Evaluation

The original methods for S31 (sec-amylacetate), S47 (n-butyl acetate), S46 (sec-butylacetate), S32 (t-butyl acetate), S41 (2-ethoxy acetate), S35 (ethyl acrylate), S45 (isoamyl acetate), S44 (isobutyl acetate), S37 (methyl isoamyl acetate), S48 (n-propyl acetate) were issued on December 6, 1974, except for S51 (n-amyl acetate), which was issued on January 17, 1975 [3]. Atmospheres of each compound were generated in dry air by calibrated syringe drive and 10-L air samples were taken [1]. Collection efficiency in humid air and sample storage stability were not tested. Spiked samplers were used to study measurement precision and desorption efficiency (DE).

Current Evaluation

Methods for esters (n-amyl acetate, n-butyl acetate, sec-butyl acetate, t-butyl acetate, 2-ethoxyethyl acetate, ethyl acrylate, isoamyl acetate, isobutyl acetate, methyl isoamyl acetate, n-propyl acetate) were evaluated [5] using analytes fortified on Anasorb CSC sorbent tubes (Lot #2000). Desorption efficiency (DE) and precision are shown in Table 2. Sec-amyl acetate was evaluated in the previous issue of this method but it was not included in this current update.

Storage stability studies were performed on Anasorb CSC tubes (Lot #2000) at approximately 150 µg each analyte/sample. The samples were stored for up to 30 days at 4 °C. The recoveries of 30-day storage are summarized in Table 2.

REFERENCES:

[1] NIOSH [1977]. Documentation of the NIOSH Validation Tests. U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 77-185.
[2] UTBL [1983]. UTBL user check, NIOSH Sequence #4121-N (unpublished), November 15.
[3] NIOSH [1977]. NIOSH Manual of Analytical Methods, 2nd ed., V.2., U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 77-157-B.
[4] Corelson D [1988]. Menlo Park, CA., SRI. Personal communication with NIOSH.
[5] Yoon YH, Perkins JB, Reynolds JM [2002]. Back-up Data Report for Esters 1, DataChem Laboratories, Inc. under NIOSH contracts CDC-200-95-2955 and CDC 200-2001-08000.

PREVIOUS REVISION BY:

Robert W. Kurimo, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC 99-74-45.

METHOD REVISED BY:

Young Hee Yoon, Ph.D., James B. Perkins and John M. Reynolds, DataChem Laboratories, Inc., Salt Lake City, Utah.

Table 1. General Information

Compound, Formula and RTECS	Synonyms	M.W.	OSHA/NIOSH/ACGIH, ppm	BP, °C	VP @ 20 °C, kPa (mm Hg)	Liquid Density, g/mL @ 20 °C
n-amyl acetate $CH_3COO(CH_2)_4CH_3$; $C_7H_{14}O_2$ AJ1925000	acetic acid 1-pentanol ester; CAS #628-63-7	130.18	TWA (STEL) 100/100/100	149	0.5(4)	0.876
sec-amyl acetate $CH_3COOCHCH_3(CH_2)_2CH_3$; $C_7H_{14}O_2$ AJ2100000	acetic acid 2-pentanol ester; CAS #626-38-0	130.18	125/125/125	134	0.9(7)	0.866
n-butyl acetate $CH_3COO(CH_2)_3CH_3$; $C_6H_{12}O_2$ AF7350000	acetic acid butyl ester; CAS #123-86-4	116.16	150/150(200)/150(200)	126	1.3(10)	0.883
sec-butyl acetate $CH_3COOCH(CH_3)CH_2CH_3$; $C_6H_{12}O_2$ AF7380000	acetic acid 1-methyl propyl ester; CAS #105-46-4	116.16	200/200/200	112	1.3(10)	0.865
t-butyl acetate $CH_3COOC(CH_3)_3$; $C_6H_{12}O_2$ AF7400000	acetic acid 1, 1-dimethylethyl ester; CAS #540-88-5	116.16	200/200/200	98	not available	0.867
2-ethoxyethyl acetate $CH_3COO(CH_2)_2OCH_2CH_3$; $C_6H_{12}O_3$ KK8225000	Cellosolve acetate; acetic acid ethylene glycol monoethyl ether ester; CAS #111-15-9	132.16	100[a]/0.5[a]/5[a]	156	0.3(2)	0.973
ethyl acrylate $CH_2=CHCOOCH_2CH_3$; $C_5H_8O_2$ AT0700000	2-propenoic acid ethyl ester; CAS #140-88-5	100.11	25[a]/4 LOQ[b]/5[ab](15 ppm)	99	3.9(30)	0.923
isoamyl acetate $CH_3COO(CH_2)_2CH(CH_3)_2$; $C_7H_{14}O_2$ NS9800000	acetic acid 3-methyl-1-butanol ester; CAS #123-92-2	130.18	100/100/100	142	0.5(4)	0.876
isobutyl acetate $CH_3COOCH_2CH(CH_3)_2$; $C_6H_{12}O_2$ AI4025000	acetic acid isobutyl ester; CAS #110-19-0	116.16	150/150/150	117	1.7(13)	0.871
methyl isoamyl acetate $CH_3COOCH(CH_3)CH_2CH(CH_3)_2$; $C_8H_{16}O_2$ SA7525000	acetic acid 4-methyl-2-pentanol ester; 1,3-dimethyl butyl acetate; "sec-hexyl acetate;" CAS #108-84-9	144.22	50/50/50	146	0.5(3.8)	0.858
n-propyl acetate $CH_2COO(CH_2)_2CH_3$; $C_5H_{10}O_2$ AJ3675000	acetic acid n-propyl ester; CAS #109-60-4	102.13	200/200 (250)/200 (250)	102	3.3(25)	0.890

[a] Skin

[b] Carcinogen

Table 2. Current Method Evaluation

	Overall Method					Analytical Method				Storage Stability Study	
Compound	Range (mg/m^3)	Accuracy	Breakthrough[1] at 2 x OSHA PEL (≤)	Bias (%)	S_{RT}	Range Studied (µg/sample)	LOD (µg/sample)	Average DE	Measurement Precision ($\hat{S}_r$)	Levels (µg/sample)	Recovery (%)
n-amyl acetate	208-871	0.163	34.2 L	0.3	0.0831	14-440	0.9	0.96	0.0072	140	98
n-butyl acetate	352-1475	0.136	20.5 L	0.3	0.0691	15-440	0.9	0.96	0.0087	140	98
sec-butyl acetate	478-2005	0.116	16.5 L	-2.4	0.0539	14-440	0.9	0.97	0.0062	140	98
t-butyl acetate	424-1780	0.234	14.3 L	-8.6	0.0897	14-430	0.9	0.98	0.0052	140	98
2-ethoxyethyl acetate	262-1100	0.203	34.6 L	-9.6	0.0648	16-340	1	0.82	0.020	160	96
ethyl acrylate	50-210	0.162	>45 L	-7.1	0.0550	31-300	2	0.86	0.015	150	90
isoamyl acetate	208-874	0.195	32.3 L	-7.1	0.0750	14-430	0.9	0.97	0.0066	140	98
isobutyl acetate	306-1280	0.133	21.5 L	1.8	0.0656	14-440	0.9	0.97	0.0084	140	98
methyl isoamyl acetate	143-601	0.126	>45 L	-2.6	0.0590	14-280	0.9	0.81	0.015	140	95
n-propyl acetate	384-1610	0.162	17.9 L	6.9	0.0566	15-450	0.9	0.95	0.0091	140	98

[1]The values for these categories were taken from the original methods validation, see ref [1].