ALIPHATIC ALDEHYDES 2018

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

METHOD: 2018 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

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

PROPERTIES: Table 1

COMPOUNDS AND SYNONYMS: See Table 3

SAMPLING

SAMPLER:	CARTRIDGE (containing silica gel coated with acidified 2,4-dinitrophenylhydrazine)
FLOW RATE:	0.1 to 1.5 L/min
VOL-MIN:	1 L @ 0.68 to 1.3 mg/m^3
-MAX:	15 L @ 7.0 to 15 mg/m^3
SHIPMENT:	Ship cold (0 to 5 °C).
SAMPLE STABILITY:	≥30 days @ 5 °C [1]
BLANKS:	2 to 10 field blanks per set 6 to 10 media blanks per set

ACCURACY

RANGE STUDIED:	Not studied
BIAS:	Not determined
OVERALL PRECISION ($\hat{S}_{rT}$):	Not determined
ACCURACY:	Not determined

MEASUREMENT

TECHNIQUE:	HPLC; UV DETECTION
ANALYTE:	2,4-dinitrophenylhydrazones of aldehydes (Table 1)
EXTRACTION:	Elution with 10 mL of carbonyl-free acetonitrile
INJECTION VOLUME:	20 µL
MOBILE PHASE:	Acetonitrile:water (see Table 1 for percentages); 1.3 mL/min
COLUMN:	Stainless steel, 3.9 x 150 mm, packed with 5-µm C-18, Symmetry™ or equivalent
DETECTOR:	UV @ 360 nm
CALIBRATION:	Standard solutions of aldehyde-DNPH derivatives in acetonitrile
RANGE:	See Table 4 [1]
ESTIMATED LOD:	See Table 4
PRECISION ($\bar{S}_r$):	See Table 5 [1]

APPLICABILITY: Working ranges are approximately 0.05 to 15 mg/m^3 (approximately 0.02 to 4 ppm) for 15-L air samples for the four aldehydes. This method can be used for the determination of acetaldehyde and valeraldehyde for OSHA STEL and PEL exposures. Upper limits of the method for the Supelco sampler are 105, 183, 50, and 50 µg per sample for acetaldehyde, propionaldehyde, valeraldehyde, and isovaleraldehyde, respectively.

INTERFERENCES: Ozone has been observed to consume the 2,4-dinitrophenylhydrazine (2,4-DNPH) reagent and to degrade the DNPH derivative of formaldehyde [2]. Thus, ozone may degrade other aldehyde-DNPH derivatives. An ozone scrubber may be attached to the inlet of the sampler to remove ozone from the air; this scrubber may contain granular potassium iodide to reduce ozone to oxygen. Ketones and other aldehydes can react with 2,4-DNPH; the derivatives produced, however, generally are separated chromatographically from the analyte of interest.

OTHER METHODS: ASTM method D5197-97 and EPA compendium method TO-11A are applicable to the same four aldehydes and employ air samplers containing DNPH-coated silica gel [3,4]. NIOSH methods 2538 [5] and 3507 [6] and OSHA method 68 [7] are other methods for determination of acetaldehyde in air. OSHA method 85 is applicable to valeraldehyde and employs DNPH on glass fiber filters [8].

REAGENTS:

1. Aldehyde-DNPH derivatives, ≥99% pure (available from Supelco, Inc., or Aldrich Chemical Co.).
2. Acetonitrile, high purity solvent for HPLC and pesticide analysis, low carbonyl content.*
3. Calibration stock solutions. Accurately weigh 10 mg of DNPH derivatives in separate 10-mL volumetric flasks. Add acetonitrile to the 10-mL mark of each flask. Store at 5 °C in airtight containers 30 days or less.
4. Acetaldehyde, 99% pure.*
5. Propionaldehyde, 97% pure.*
6. Valeraldehyde, 97% pure.*
7. Isovaleraldehyde, 97% pure.*
8. Water, deionized (DI water).
9. Acetaldehyde fortification stock solution, 2.40 mg/mL. Measure 155 µL of cold (0 °C) acetaldehyde with a cold (0 °C) 500-µL syringe. Dissolve in 35 mL of cold DI water in a 50-mL volumetric flask. Add DI water (~20 °C) to the 50-mL mark. Use within 15 min of preparation.**
10. Propionaldehyde fortification stock solution, 2.40 mg/mL. Dissolve 154 µL of 97% propionaldehyde in 35 mL of acetonitrile in a 50-mL flask. Add acetonitrile to the 50-mL mark.***
11. Valeraldehyde fortification stock solution, 2.40 mg/mL. Dissolve 154 µL of 97% valeraldehyde in acetonitrile in a 50-mL volumetric flask. Add acetonitrile to the 50-mL mark.***
12. Isovaleraldehyde fortification stock solution, 2.40 mg/mL. Dissolve 152 µL of 97% isovaleraldehyde in acetonitrile in a 50-mL volumetric flask. Add acetonitrile to the 50-mL mark.***

* See SPECIAL PRECAUTIONS

** Cool a 500-µL syringe by placing in the freezer compartment of a refrigerator for at least 45 minutes. Make sure there is no water in the needle which would freeze and clog the needle.

*** Aldehyde stock solutions should be used within 30 minutes of preparation or kept chilled in an ice bath.

EQUIPMENT:

1. Sampler: Plastic holder containing 0.35 g of 150 to 250-µm (60-100 mesh) silica gel coated with 1.0 mg of 2,4-dinitrophenyl-hydrazine which has been acidified. Pressure drop across sampler should be less than 28 inches of water (7 kPa) at 1.5 L/min. Samplers are commercially available [Supelco S10 LpDNPH cartridge, cat. No. 2-1014; a similar type of sampler is manufactured by Waters Corp. (Sep-Pak XPoSure Aldehyde Sampler, part No. WAT047205)].
2. Personal sampling pump, 0.1 to 1.5 L/min, with flexible connecting tubing.
3. Vials, 20-mL, 4-mL, glass, PFTE-lined rubber septa in caps for airtight seals.
4. Liquid chromatograph with UV detector, recorder, integrator, and column. (See page 2018-1.)
5. Syringes, 100-µL, 500-µL, and 10-mL.
6. Volumetric flasks, 5-mL, 10-mL, and 50-mL.
7. Ozone scrubber (optional), available from Waters Corp., Milford, MA.
8. Aluminum foil, or black electrical tape (optional).

SPECIAL PRECAUTIONS: Acetaldehyde is a severe eye irritant, lachrymator, mutagen, confirmed animal carcinogen, human cancer suspect agent and possible sensitizer [9]. Contact of acetaldehyde with air may cause the formation of explosive peroxides, and contact of the peroxides with heat or flame may cause fires or explosions. Fire and explosion may result from contact of acetaldehyde with strong oxidizers. Acetaldehyde is an extreme fire hazard; flash point = -37.8 °C (closed cup). Allow excess acetaldehyde in the glass ampule to evaporate in a fume hood.
Propionaldehyde, valeraldehyde, and isovaleraldehyde are eye and skin irritants. Evidence for the potential carcinogenicity of propionaldehyde and valeraldehyde is inconclusive [9]. These three aldehydes are incompatible with strong oxidizers and are dangerous fire hazards (flash points = 17.8 °C, 12.2 °C and -1 °C, respectively). Bottles of these aldehydes should be flushed with nitrogen after use. Work with all aldehydes in a fume hood.
The DNPH reagent [11] and aliphatic aldehydes are light sensitive [10]. Also, DNPH is a suspect carcinogen. Acetonitrile is toxic and is a fire hazard (flash point = 12.8 °C).

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line. If desirable, attach a representative ozone scrubber to the inlet of the sampler. However this method has not been evaluated with an ozone scrubber in line.
2. Open sampler packet and remove end caps.
3. Attach sampler to the sampling pump with flexible tubing. The Waters sampler is bi-directional and can be connected at either end.
   NOTE: If sampling is to be performed in intense sunlight, protection of the DNPH-coated silica gel bed in the sampler from intense light would be suggested in order to prevent possible photodecomposition of the DNPH reagent [11] and the aldehyde derivatives. If desirable, wrap a portion of the sampler with aluminum foil or black electrical tape.
4. Sample 1 to 15 L of air at 0.1 to 1.5 L/min.
5. Place end caps onto the sampler and seal sampler in an envelope. Protect samples from heat.
6. Ship samples cold (0 to 5 °C). Ship blanks in a separate container.

SAMPLE PREPARATION:

7. a. Elute the aldehyde derivatives from the cartridge samplers with 10-mL quantities of acetonitrile. Collect effluent (ca. 9.5 mL) from each sampler in a separate 10-mL volumetric flask.
   b. Add acetonitrile to the 10-mL mark of the volumetric flask for each sample.
   NOTE: Carbonyl content of acetonitrile can be determined by passing 10 mL of the solvent through a cartridge of DNPH-coated silica gel and analyzing by HPLC. Contents of aldehydes of interest should be below the respective LODs.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of interest.
   a. Calculate the concentrations of the aldehyde-DNPH derivatives in the calibration stock solutions (about 1000 µg/mL). Calculate the equivalent concentrations of the free aldehydes in solution by multiplying the derivative concentrations by 0.197, 0.244, 0.324, and 0.324 (molecular weights of acetaldehyde, propionaldehyde, valeraldehyde and isovaleraldehyde divided by the molecular weights of the corresponding aldehyde-DNPH derivatives, respectively).
   b. Prepare a series of dilutions (working standards) from 0.01 to 10 or 20 µg/mL (ranges of equivalent concentrations of free aldehydes from values below the detection limits to values corresponding to upper limits of the analytical range). The working standards (standard solutions) are stable for more than a month when stored at 5 °C in the dark in airtight containers; however, it is suggested that fresh working standards be prepared weekly.
   c. Transfer 3-mL aliquots of working standards to 4-mL vials and analyze (steps 11, 13 and 14).
   d. Prepare calibration graphs, peak areas or heights vs. µg free aldehydes per sample.

9. Determine recoveries (R) of aldehydes from samplers in the calibration range (step 8). Prepare three sorbent beds at each of five concentration levels for each aldehyde plus three media blanks. Recovery is expected to be near 100% for acetaldehyde, propionaldehyde, and valeraldehyde and about 86% for isovaleraldehyde.
   a. Prepare series of dilutions of fresh fortification stock solutions in the range of 50 to 300 µg/mL in 20-mL vials (one dilution for each fortification level for each aldehyde). Cap vials tightly. Use acetaldehyde fortification solutions within 15 minutes of preparation or significant losses of acetaldehyde may occur. Use propionaldehyde, valeraldehyde and isovaleraldehyde fortification solutions within 30 minutes of preparation (a limit of 30 minutes is precautionary).
   b. Fortify beds of sorbent. Using a 100-µL syringe, measure 20 to 90 µL of the particular aldehyde solution. Penetrate the center of the frit at the inlet of the sampler with the needle of the syringe. Inject the solution into the center of the sorbent bed. It is recommended that each sampler be fortified with only one injection of 90 µL of less. Injection of an excessive volume of solution may lead to incomplete reaction of aldehyde with DNPH.
   c. Prepare the fortified samples (steps 7a and 7b).
   d. Transfer 3-mL aliquots of samples to 4-mL vials and analyze together with working standards (steps 11, 13 and 14).
   e. Prepare graph of peak height vs. concentration of aldehyde in µg/sample for each of the aldehydes.
   f. Calculate recovery (R) for each sample by dividing the quantity of aldehyde found in the sample by the quantity of aldehyde applied.
   g. Prepare graphs of R vs. µg of aldehyde found (recovered).
10. Fortify three quality control samples and three analyst samples with known quantities of free aldehyde and aldehyde-DNPH in separate experiments. Analyze these samples to ensure that the calibration and recovery graphs are in control.

MEASUREMENT:

11. Set the liquid chromatograph according to manufacturer's recommendations and to conditions given on page 2018-1 and in Table 1.
12. Transfer an aliquot of the sample solution from step 7.b. to a 4-mL vial. Cap the vial.
13. Inject a 20-µL sample aliquot.
14. Measure peak height or peak area. If a sample peak is larger than the largest standard peak, dilute an aliquot of the remaining sample solution, reanalyze, and apply appropriate dilution factor in the calculations.
15. To ensure validity of the samples, identify those samples which contain more than 105, 183, 50 or 50 µg of acetaldehyde, propionaldehyde, valeraldehyde or isovaleraldehyde per sample, respectively. The capacity of the samplers may have been exceeded for these samples, and collection of smaller samples would be warranted.

CALCULATIONS:

16. Determine mass, µg, of aldehyde, W, found in the sample and the average media blank, B, from the appropriate calibration graph.
17. Calculate concentration, C, of the aldehyde in the air volume sampled, V (L).

$$C = \frac{W - B}{V}, mg/m^3$$

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

The backup data report for this method development contains the data on recovery and breakthrough studies for each of the aldehydes.[1]

This method was evaluated with Supelco S10 LpDNPH samplers and free (underivatized) acetaldehyde, propionaldehyde, valeraldehyde, and isovaleraldehyde. Recoveries were determined after fortification of six samplers in each set with known quantities of free aldehyde (see Table 5). While acetaldehyde, propionaldehyde and valeraldehyde showed average recoveries greater than 90%, average recoveries of isovaleraldehyde in Table 5 were in the 80% range; the reason for these relatively low recoveries is unclear. For storage studies, six samplers in each set were fortified with 3.00-µg of free aldehyde and stored at 5 ^{o}C in the dark (see Table 6). Also, liquid standards (standard solutions of aldehyde-DNPH derivatives in acetonitrile) were stored at 5 °C in the dark in vials with airtight caps (see Table 6). Limits of detection and quantitation were determined by least squares calculations with series of six standard solutions of aldehyde-DNPH derivatives in acetonitrile (see Table 4).

This method also was evaluated for butyraldehyde-DNPH and free butryaldehyde on Supelco S10 LpDNPH samplers. Recoveries decreased from 98% to 79% when quantities applied increased from 1.5 µg to 20 µg. The negative slope caused difficulty or ambiguity in applying recovery factors to quantities found. This method is not recommended for butyraldehyde.

Crotonaldehyde and acrolein were also studied. The recoveries of crotonaldehyde (crotonaldehyde-DNPH) and acrolein (acrolein-DNPH) were found to be very low (less than 30%). This method is not recommended for either of these compounds [12].

In each breakthrough study, a pair of samplers in series was connected to an air pump. A glass U-tube (a Schwartz drying tube) preceded the front sampler. For dry air, an impinger of dried, indicating silica gel preceded the U-tube. For humid air, an impinger of water preceded the U-tube. Known quantities of free aldehyde in solution were placed into the U-tube, and the pump drew air through the system at 1 L/min.

Upper limits of the method for acetaldehyde and propionaldehyde were calculated as two-thirds of the smallest quantities of aldehyde placed into the U-tube which gave rise to 5% breakthrough. For these two aldehydes, breakthrough took place earlier in humid air than in dry air or laboratory air; this humidity effect was reversed in the case of formaldehyde [13].

However, quantities of valeraldehyde and isovaleraldehyde generally did not break through the front samplers, and excessive quantities of valeraldehyde and isovaleraldehyde remained on the front samplers without reaction with DNPH. Thus, upper limits of the method for valeraldehyde and isovaleraldehyde could not be determined from quantities of aldehyde which gave rise to 5% breakthrough. Upper limits of valeraldehyde and isovaleraldehyde were calculated as two-thirds of the largest quantities of aldehydes placed into the U-tube which gave rise to a mass balance or a near mass balance (see Backup Data Report [1]).

Since the sampler does not have a backup section for determination of breakthrough, the worker conducting sampling in the field may connect two samplers in series in the cases of acetaldehyde and propionaldehyde. The back pressure of the sampling train will be higher and a lower flow rate may be required. Use of backup samplers in the field for valeraldehyde and isovaleraldehyde would be meaningless because excessive quantities of these aldehydes are trapped on the front sampler without reaction with DNPH and breakthrough to backup samplers may never occur. Alternatively, sampling without a backup sampler may be conducted even when high concentrations of aldehydes and ketones are anticipated if the sampling period is minimal and the flow rate of the pump is low.

Although this method may be useful for determining aromatic aldehydes in the air, it would be very difficult or impossible to evaluate this method with free (underivatized) aromatic aldehydes. Aromatic aldehydes, such as benzaldehyde, undergo rapid oxidation in air to form the corresponding carboxylic acids, such as benzoic acid.

The capability to separate valeraldehyde-DNPH from isovaleraldehyde-DNPH by HPLC was investigated. Twenty microliters of a single acetonitrile solution containing valeraldehyde-DNPH at 2 µg/mL and isovaleraldehyde-DNPH at 1 µg/mL (equivalent concentrations of underivatized aldehydes) was injected into

the HPLC when the mobile phase consisted of 66:34 acetonitrile:water at 1.3 mL/min. Retention times of valeraldehyde-DNPH and isovaleraldehyde-DNPH were 7.82 and 7.32 min, respectively. Although two sharp peaks were observed, the separation was only partial.

This method can be used with SKC aldehyde samplers (DNPH-coated silica gel tubes, catalogue No. 226-119) for acetaldehyde, propionaldehyde, valeraldehyde, and isovaleraldehyde with modifications (see **APPENDIX**).

REFERENCES:

[1] Tucker SP [2002]. Aliphatic Aldehydes Backup Data Report for method 2018 for acetaldehyde, propionaldehyde, valeraldehyde, and isovaleraldehyde (butyraldehyde and crotonaldehyde), Cincinnati, OH: unpublished report. National Institute for Occupational Safety and Health, DART.

[2] Kleindienst TE, Corse EW, and Blanchard FT [1998]. Evaluation of the Performance of DNPH-Coated Silica Gel and C_{18} Cartridges in the Measurement of Formaldehyde in the Presence and Absence of Ozone. Environmental Science & Technology, *32*(1), 124-130.

[3] ASTM [2001]. Method D5197-97, Standard Test Method for Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology). Atmospheric Analysis, Occupational Health and Safety, Protective Clothing, *1103*, West Conshohocken, PA: American Society for Testing and Materials, ASTM International.

[4] U.S. EPA [1999]. Compendium Method TO-11A: Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC), Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, U.S. Environmental Protection Agency, Center for Environmental Research Information, Office of Research and Development, Washington, DC. EPA/625/R-96/010b.

[5] NIOSH [1994]. Acetaldehyde by GC, method 2538. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods, 4th ed., U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Cincinnati, OH. DHHS (NIOSH) Publication No. 94-113.

[6] NIOSH [1994]. Acetaldehyde by Bubbler and HPLC, method 3507. NIOSH Manual of Analytical Methods, 4th ed., Eller PM, Cassinelli ME, eds., U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Cincinnati, OH. DHHS (NIOSH) Publication No. 94-113.

[7] OSHA [1990]. Acetaldehyde, method 68, OSHA Analytical Methods Manual, 2nd ed., U.S. Department of Labor, Occupational Safety and Health Administration, Salt Lake City, UT.

[8] OSHA [1990]. Valeraldehyde, method 85, OSHA Analytical Methods Manual, 2nd ed., U.S. Department of Labor, Occupational Safety and Health Administration, Salt Lake City, UT.

[9] NIOSH [1991]. Current Intelligence Bulletin 55, Carciongenicity of Acetaldehyde and Malonaldehyde, and Mutagenicity of Related Low-Molecular-Weight Aldehydes. U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Cincinnati, OH. DHHS (NIOSH) Publication No. 91-112.

[10] Pacakova V, Konas M, and Kotvalova V [1985]. Reaction Gas Chromatography: Study of the Photodecomposition of Selected Substances, Chromatographia *20* (3), 164-172.

[11] Otson R and Fellin P [1998]. A Review of Techniques for Measurement of Airborne Aldehydes. Science of the Total Environment, *77* (2/3), 95-131.

[12] Risner CH [1995]. High Performance Liquid Chromatographic Determination of Major Carbonyl Compounds from Various Sources in Ambient Air, J. Chromatogr. Sci., *33* (4), 168-176.

[13] NIOSH [1994]. Formaldehyde by HPLC, method 2016, issue 2, NIOSH Manual of Analytical Methods, 4th ed., Eller PM, Cassinelli ME, eds., U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Cincinnati, OH. DHHS (NIOSH) Publication No. 94-113.

[14] NIOSH [1998]. NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Cincinnati, OH. DHHS (NIOSH) Publication No. 88-118, Supplement 1-OHG. For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

[15] Sax's Dangerous Properties of Industrial Materials [2000]. Vol. 3, 10th ed., Lewis RJ sr, ed., John Wiley & Sons, Inc., New York.
[16] Handbook of Toxic and Hazardous Chemicals and Carcinogens [1991]. Vol. 2, Sittig M, ed., GZ Noyes Publications, Park Ridge, NJ, p. 1633.

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TABLE 1. PROPERTIES AND OTHER INFORMATION

Compound	Formula	CAS	RTECS	MW	Density @ 20 °C (g/mL)	BP (°C)	Mobile Phase Percentages of Acetonitrile and Water (v/v)
acetaldehyde	CH_3-CHO	75-07-0	AB1925000	44.05	0.788[a]	20.8	51:49
propionaldehyde	CH_3-CH_2-CHO	123-38-6	UE0350000	58.09	0.807	49	54:46
valeraldehyde	CH_3-$(CH_2)_3$-CHO	110-62-3	YV3600000	86.13	0.8095	102	66:34
isovaleraldehyde	CH_3-CH(CH_3)-CH_2-CHO	590-86-3	ES3450000	86.13	0.803[b]	90	66:34

[a] Density of acetaldehyde at 16 °C
[b] The temperature for this density of isovaleraldehyde was not specified but is assumed to be room temperature.

TABLE 2. EXPOSURE LIMITS AND CONVERSION FACTORS.

Compound	Exposure Limits			Conversion Factor
	OSHA REL (ppm)	NIOSH PEL (ppm)	ACGIH TLV (ppm)	ppm to mg/m^3 @ NTP
acetaldehyde	200	lowest feasible level	25 ppm (ceiling)	1 ppm = 1.80 mg/m^3
propionaldehyde	none	none	none	1 ppm = 2.38 mg/m^3
valeraldehyde	50	50	50	1 ppm = 3.52 mg/m^3
isovaleraldehyde	none	none	none	1 ppm = 3.52 mg/m^3

TABLE 3. ALIPHATIC ALDEHYDES AND SYNONYMS

Aldehyde	Synonyms
acetaldehyde	ethanal, acetic aldehyde, ethylaldehyde, acetylaldehyde
propionaldehyde	propanal, propylaldehyde, methylacetaldehyde, propaldehyde, propylic aldehyde
valeraldehyde	n-valeraldehyde, pentanal, valeral, valeric aldehyde, amyl aldehyde, valeric acid aldehyde, butyl formal
isovaleraldehyde	isovaleral, isopentaldehyde, isovaleric aldehyde, 3-methylbutanal, 3-methylbutyraldehyde, isoamyl aldehyde

TABLE 4. ANALYTICAL LIMITS OF THE METHOD

Compound	LOD (µg/sample)	LOQ (µg/sample)	Calibration Range (µg/sample)	Maximum Sampler Capacity[a] (µg/sample)
acetaldehyde	0.2	0.68	0.68 to >150	105
propionaldehyde	0.3	0.89	0.89 to >150	183
valeraldehyde	0.4	1.30	1.30 to >150	50
isovaleraldehyde	0.2	0.79	0.79 to >150	50

[a] The maximum sampler capacity is the upper limit of the method (explained in text). The numbers shown apply to the Supelco sampler, which contains 1 mg of DNPH. Predicted capacities of the Waters sampler are 90% of these values.

TABLE 5. AVERAGE RECOVERIES AND POOLED PRECISION OF MEASUREMENT [a]

Compound	Average Recovery at the Level Shown (n = 6)					Pooled RSD[b]
	1.50 µg	3.00 µg	6.00 µg	12.0 µg	20.0 µg	
acetaldehyde	106%	99%	108%	106%	100%	0.031
propionaldehyde	84%	94%	91%	92%	95%	0.028
valeraldehyde	91%	97%	94%	94%	98%	0.021
isovaleraldehyde	83%	84%	85%	88%	85%	0.030

[a] Average recoveries were determined after fortification of Supelco samplers with free aldehydes in solution with a syringe.

[b] RSDs at all five levels for acetaldehyde and isovaleraldehyde were homogeneous by Bartlett's test; thus, all five RSDs for acetaldehyde and isovaleraldehyde were poolable. Other pooled RSDs were based on three or four individual RSDs.

TABLE 6. STABILITIES OF DNPH DERIVATIVES ON SAMPLER AND IN SOLUTION

Compound	Storage Period[a] (days)	Average Recovery from Sampler (n = 6)	Concentration of Liquid Std. (µg/mL[b])	Stability Period for Liquid Std. (days)[d]
acetaldehyde	30	102%	1.25	≥36
propionaldehyde	32	104%	2.20	≥35
valeraldehyde	30	105%	2.20	≥35
isovaleraldehyde	3	90%[c]	2.20	≥35

[a] Samplers were stored at 5 °C in the dark.
[b] Each liquid standard consisted of aldehyde-DNPH derivative in acetonitrile solution, and each concentration presented is the equivalent concentration of underivatized aldehyde.
[c] The average recovery of 90% is not an indication of deterioration of isovaleraldehyde-DNPH; compare the recovery of 90% with recoveries for isovaleraldehyde in Table 5.
[d] Liquid standards were stored at 5 °C in the dark in airtight containers.

TABLE 7. 5% BREAKTHROUGH DATA AND STOICHIOMETRIC QUANTITIES.

Compound	Amount of aldehyde found to show 5% breakthrough at a flowrate of 1L/min (µg/sample)			Stoichiometric Quantity ofAldehyde[d] (µg/sample)
	(in Dry Air[a])	(in Lab Air[b])	(in Humid Air[c])	
acetaldehyde	178	173	158	222 µg
propionaldehyde	322	290	274	293 µg
valeraldehyde	>>500	>>507	>>473	435 µg
isovaleraldehyde	>>400	>>498	>400	435 µg

[a] Estimated relative humidity of dry air was 10% at room temperature.
[b] The relative humidity of the laboratory air was not measured.
[c] Estimated relative humidity of humid air was 85% at room temperature.
[d] The stoichiometric quantities shown are the theoretical maximum quantities of aldehydes which can react with 1 mg of DNPH on the silica gel bed in the Supelco sampler.

APPENDIX

The SKC sampler for aldehydes (DNPH-coated silica gel tube, catalogue No. 226-119) may be used for acetaldehyde, propionaldehyde, valeraldehyde and isovaleraldehyde with modifications of this method. These modifications include the following. (a) The maximum recommended air volume sampled probably should be less than 15 L for an air concentration near 10 mg/m^3 (indicated on page 2018-1) because of the upper limits of the method for the SKC, Inc. sampler are probably smaller than the upper limits in this method (105, 183, 50 and 50 µg per sample for acetaldehyde, propionaldehyde, valeraldehyde, and isovaleraldehyde, respectively). However, the maximum recommended air volumes for the SKC sampler are unknown. (b) The procedure for recovery of analyte from the sorbent would be modified; i.e., placement of sorbent sections into vials and addition of solvent and possible use of ultrasonic bath. (c) A volume of solvent much smaller than 10 mL can be used for recovery. However, the minimum volume used should be tested for adequate recoveries. (d) Consequences of using a much smaller volume of solvent for recovery include a lower LOD, a lower LOQ, the need for a different range of calibration standards, and the need for a different range of levels of fortification (section 8). (e) The maximum volume of solution for fortification of the front sorbent bed must be smaller than 90 µL and should be determined (section 8).