Volatile Organic Compounds, C1 to C10, Canister Method 3900

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

METHOD: 3900, Issue 1 **EVALUATION:** FULL **Issue 1:** 30 August 2018

OSHA: Table 3
NIOSH REL: Table 3
Other OELs: [1-3]

PROPERTIES: Table 1

ANALYTES: ethanol, 2-propanol, acetone, 2,3-butanedione, 2,3-pentanedione, 2,3-hexanedione, dichloromethane, trichloromethane, hexane, benzene, toluene, ethylbenzene, *o*-xylene, *m,p*-xylene, methyl methacrylate, α-pinene, *d*-limonene

SAMPLING

SAMPLER: FUSED-SILICA LINED STAINLESS STEEL CANISTER, 6 L, 450, or 400 mL

FLOW RATE: 0.06 to 50 mL/min. See SAMPLING section

VOL-MIN: Depends on canister volume. See SAMPLING section

SHIPMENT: Routine

SAMPLE STABILITY: 58 days @ 25 °C (30 days for ethanol, 2-propanol, and acetone @ 10 ppb; 21 days for α-pinene and *d*-limonene @ 0.8 ppm)

BLANKS: 1 field blank per set

ACCURACY

RANGE STUDIED: Tables 4a and 4b

BIAS: Tables 4a and 4b

OVERALL PRECISION ($\hat{S}_{rT}$): Tables 4a and 4b

ACCURACY: Tables 4a and 4b

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, MASS SPECTROMETRY

ANALYTE: Compounds listed in Table 1

PRECONCENTRATION VOLUME: 25 to 500 mL injection (ppb-levels) for a 6L canister, 25 to 250 mL injection (ppb-levels) for a 400/450 mL canister, 1 mL loop (ppm-levels)

PRECONCENTRATION CONDITIONS: Module 1 (empty): Focused @ -20° C, desorbed @ 10° C, baked @ 150° C (7 min); Module 2 (glass beads): Focused @ -80° C, desorbed @ 180° C, baked @ 190° C; Module 3 (focuser): Focused @ -150° C.

GC/MS CONDITIONS: Injection: preconcentrator transfer line 100°C
Detector: 280° C
Column: 35° C (2 min hold) to 170° C (ramp 8°C/min), ramp 20° C/min to 220° C (3 min hold)
MS Source: 230° C
Quadrupole: 150° C
Solvent delay: 4.5 min
MS Scan: 35-350 amu

CARRIER GAS: Helium, 1 mL/min

COLUMN: Capillary, fused silica, 60 m x 0.32-mm ID; 1-µm film 100% dimethylpolysiloxane

CALIBRATION: Gas phase analytes in canisters

RANGE: Tables 4a and 4b

ESTIMATED LOD: Tables 4a and 4b

PRECISION ($\bar{S}_r$): Tables 4a and 4b

APPLICABILITY: The method was developed for measuring a range of volatile organic compounds in healthcare settings [4], but may be used in other occupational settings. The method was developed to measure the following analytes: ethanol, acetone, 2-propanol, dichloromethane, hexane, trichloromethane, 2,3-butanedione, 2,3-pentanedione, and 2,3-hexanedione, benzene, methyl methacrylate, toluene, ethylbenzene, *m,p*-xylene, *o*-xylene, *α*-pinene, and *d*-limonene. The working range is 0.24 to 22 ppb

for ppb-level analysis and 0.07 to 2.0 ppm for ppm-level analysis depending on analyte (Table 4a). This method may be applicable for other volatile organic compounds that exhibit acceptable stability, bias, precision and accuracy. Alternate detectors (e.g., flame ionization detector, electron capture detector, thermal conductivity detector, time-of-flight or quadrupole time-of-flight mass spectrometer), canister volumes, GC columns, internal standards and equipment may be used after method performance has been assessed and shown to be within acceptable limits. Training on pressure dilution techniques and preconcentration systems as well as proficiency testing should be periodically conducted to ensure operating laboratories maintain optimal canister method performance.

INTERFERENCES: Other compounds with similar retention times and quantitation ions may interfere (e.g., alcohols, ketones, aromatics, beta-pinene). For example, vinyl acetate has the same molecular weight as 2,3-butanedione and has the same retention time elution on the recommended column. High humidity samples that are pressurized may form condensed water causing losses of water-soluble compounds. Water content should be managed during preconcentration of the sample by purging traps with helium, reducing the sample injection volume onto the preconcentrator, or splitting the sample stream prior to concentration and/or gas chromatograph injection.

OTHER METHODS: This is a method for the determination of VOCs, C1 to C10, in mixed exposure environments. The method has been modified from the Environmental Protection Agency (EPA) method TO-15 to include specific chemicals and low-ppm concentration volatile analysis [5]. ASTM D5466 is also available as guidance for canister sampling and analysis [6].

REAGENTS:

1. Ethanol, reagent grade*
2. 2-Propanol, reagent grade*
3. Acetone, reagent grade*
4. 2,3-Butanedione, reagent grade*
5. 2,3-Pentanedione, reagent grade*
6. 2,3-Hexanedione, reagent grade*
7. Dichloromethane, reagent grade*
8. Trichloromethane, reagent grade*
9. Hexane, reagent grade*
10. Benzene, reagent grade*
11. Toluene, reagent grade*
12. Ethylbenzene, reagent grade*
13. *o*-Xylene, reagent grade*
14. *m*-Xylene, reagent grade*
15. *p*-Xylene, reagent grade*
16. Methyl methacrylate, reagent grade*
17. *α*-Pinene, reagent grade
18. *d*-Limonene, reagent grade*
19. Ultra-high purity air
20. Ultra-high purity nitrogen
21. Ultra-high purity helium
22. Internal standard cylinder @ 20 ppb (bromochloromethane; 1,4-difluorobenzene; chlorobenzene-d5; and bromofluorobenzene)
23. Distilled, deionized water, 18 MOhm, low VOC content

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Gas chromatograph/mass spectrometer system capable of attaching to preconcentrator system
2. Whole-air preconcentrator system capable of variable injection volumes from 25 to 500 mL
3. Canister autosampler with 1-mL loop injection system
4. Gas dilution system capable of measuring pressure transfers
5. Heated canister cleaning system capable of evacuating canister to 0.0066 kPa prior to sampling and cycling between vacuum and humidified gas
6. Capillary or diaphragm flow controller for restricted flow sampling, or fitting for instantaneous sampling with 2-µm, sintered, stainless steel particle filter
7. 400 mL, 450 mL, or 6 L fused-silica lined coated canisters
8. Gas-tight syringes, 2.5 mL, 1 mL, 250 µL, 100 µL, 25 µl and 10 µL
9. Disposable glass pipets
10. 2 L glass bulb

SPECIAL PRECAUTIONS: Dichloromethane and trichloromethane are confirmed animal carcinogens and benzene is a confirmed human carcinogen (see International Agency for Research on Cancer (IARC)). Terpenes are flammable and considered irritants. Perform all standards preparation in a well-ventilated

hood. Wear appropriate personal protective equipment during sampling activities and analysis. It is essential that suitable gloves, eye protection, laboratory coat, etc. be used when working with the chemicals.

SAMPLING:

1. Evacuate canister to 0.0066 kPa prior to sampling.
2. Sampling may be performed with a flow controller (e.g., diaphragm or capillary) into a large canister (e.g., 6 L) for area sampling or a small canister (e.g., 400 or 450 mL) for personal sampling. Selection of the appropriate flow controller and flow rate will depend upon the size of canister being used and sampling period that is necessary to characterize exposures.
3. For diaphragm flow controllers, follow the manufacturers procedures for calibration to an appropriate flow rate (e.g., 10 mL/min for a 6 L canister for an 8-hour work shift) prior to each day of sampling; the final pressure in the canister should be less than 84.1 kPa.
4. For capillary flow controllers, the flow is governed by the length and internal diameter of the capillary. Use a flow controller that will fill the can volume to 30.4 kPa during your sampling period. Do not exceed a final sample pressure of 50.6 kPa.
5. Use a 2-µm, sintered, stainless steel particle filter to protect the flow controllers and canisters when sampling in dusty atmospheres.

SAMPLE PREPARATION:

6. For ppb-level analysis, attach the canister to the preconcentrator via an autosampler or direct transfer line. If sample needs to be pressurized to increase sample volume prior to analysis, perform pressure dilution with ultra-high purity (UHP) nitrogen or air and apply dilution factors in calculation. Final sample pressure after analysis should be greater than 50.6 kPa to limit potential for sample dilution due to system leakage.
7. For ppm-level analysis, pressurize the canister (e.g., 152 kPa or follow instrument manufacturer's recommendation) in order to obtain a sufficient excess pressure to flush the 1 mL loop. An alternative to using the loop for quantitation could be running a loop or low volume injection of the canister to investigate the analyte concentration range. Then, perform pressure dilutions into ppb-level calibration curve.

NOTE: Allow samples or calibration standards that are pressurized a minimum of 6 hours to equilibrate prior to analysis. Pressure dilutions greater than 50x should be performed with successive dilutions into additional canisters with equilibration time allowed at each step.

CALIBRATION AND QUALITY CONTROL:

8. Tune the mass spectrometer and calibrate with standards over the range 1 to 20 ppb (25 to 500 mL nominal injection volume) and 0.2 to 2 ppm (1 mL loop flushed with 100 mL of sample). Five to seven calibration points within the dynamic range should be used. Internal standard (50 mL at 20 ppb) is added to the preconcentrator prior to standard or sample transfer.
9. A mixture of the analytes must be produced before gas-phase standard preparation.
10. Gas-phase standards may be prepared in 2 L glass bulbs by adding a known volume of a neat chemical mixture (see Calculation section) to the vessels. The mass injected into the bulb is determined from the concentration of analyte in the mixture and the volume of mixture delivered to the vessel.

NOTE: Alcohols and ketones may react in the presence of heat. The heated-bulb preparation method is not recommended for alcohols and ketones when prepared in the same heated bulb as the reaction will change the gas concentration produced. Two alternatives to the heated-bulb

preparation method are generation without heat in a large inert bag (e.g., tedlar) protected from light or purchasing a calibration cylinder from a reference material supplier.

11. The vessel is heated to 60° C for 30 minutes and allowed to cool to room temperature before a small gas volume is transferred to evacuated-calibration canisters via a gas-tight syringe. An alternative to standard preparation by a heated glass bulb is to purchase gas standards at known concentrations and use a gas dilution system to measure pressure transfers. Gas standards should be purchased from a reputable, accredited reference material producer (e.g., ISO 17034 [7] accreditation recommended). A gas standard at approximately 2 ppm of each of the 17 compounds (balance nitrogen) has been stable for 2 years in a pressurized aluminum cylinder with only a ± 2% deviation from the original certified value.
12. Add 80 µl of clean distilled water to an evacuated 6 L canister, add gas standard, and dilute with UHP nitrogen or air to 172 kPa (i.e., ~40%RH).
13. Develop response factors for each analyte to the closest internal standard using the mass spectrometer quantitation software and the appropriate quantitation (primary) ion. Response factors (RF) are calculated as follows [8]:

$$RF = \frac{A_x * C_{is}}{A_{is} * C_x}$$

Where:
A_x = area of the quantitation ion for the analyte (counts);
A_{is} = area of the quantitation ion for the internal standard (counts);
C_{is} = concentration of internal standard (ppb); and
C_x = concentration of the analyte (ppb).

14. A humidified (e.g., ~40%RH) laboratory blank and humidified (e.g., ~40%RH) 10 ppb check standard must be analyzed within a 24 hour period of sample analysis. Perform a full calibration when the check standard falls outside established acceptance criteria as developed by the laboratory. Check standard recoveries of 90% to 110% are achievable but may be higher or lower depending on instrumentation. A replicate sample analysis should be conducted every 10 samples, when possible, to assess measurement repeatability. A check standard should be analyzed near the end of the analytical sequence to ensure recoveries of each compound are within 80% to 120%.

MEASUREMENT:

15. Set preconcentrator/GC/MS according to manufacturer's recommendations and to conditions given on page 3900-1.
16. Inject 50 mL of internal standard at 20 ppb.
17. Inject between 200 and 500 mL of sample for ppb-level analysis and 1 mL of sample for ppm-level analysis. Alternative injection volumes may be used as long as performance is verified prior to sample analysis.

NOTE 1: If peak area is above linear range of the working standards, dilute with UHP nitrogen using a gas dilution system or inject smaller sample volumes, reanalyze and apply the appropriate dilution factor in calculations.

NOTE 2: *m*- and *p*-Xylene isomers co-elute on the specified column and should be analyzed/reported together.

CALCULATIONS:

18. Calculation for the concentration of analyte in calibration standard (C_{bulb}; ppm) in the glass bulb:

$$C_{bulb} = \frac{C_a V_m Y * 22.4}{MW_s * V_{bulb}} * \frac{T_{lab}}{273.15} * \frac{760}{P_{lab}}$$

Where:
C_a = concentration of analyte in the mixture (mg/mL);
V_m = volume of mixture injected in bulb (mL);
Y = purity of analyte (scale 0 to 1);
MW_s = molecular weight of analyte (g/mol);
V_{bulb} = volume of glass bulb (m^3) determined experimentally;
T_{lab} = temperature of the laboratory (K);
P_{lab} = pressure of the lab (mm Hg).
NOTE: 760 is assuming standard atmospheric pressure. 273.15 is International Union of Pure and Applied Chemistry (IUPAC) standard temperature and 22.4 is molar volume at STP.

19. Transfer a small aliquot of the gas from the bulb to an evacuated canister for calibration standards.
20. Calculate the final concentration in the canister (C_{final}; ppb) based on:

$$C_{final} = C_{bulb} * 1000 * \frac{V_{inj}}{V_{can}} * \frac{P_{atm}}{P_f}$$

Where:
C_{bulb} = concentration in glass bulb (ppm);
V_{inj} = volume transferred to the canister (mL);
V_{can} = volume of the canister (mL);
P_{atm}=atmospheric pressure (kPa); and
P_f = final canister pressure (kPa).

21. Determine the analyte concentration (C_x) in ppb or ppm according to the following equation:

$$C_x = \frac{A_x * C_{is}}{A_{is} * RF}$$

Where:
A_x = area of the primary ion for the analyte (counts);
A_{is} = area of the primary ion for the internal standard (counts);
C_{is} = concentration of internal standard (ppb);
RF = response factor calculated using linear regression.

Note: Most data analysis software packages will calculate analyte concentration provided you enter the calibration information in the quantification database. Blank correction may be necessary when instrument or field blank results are consistent and above the analyte detection limit.

22. Dilution factors (ratio of final volume to initial volume) must be applied to standards or samples as applicable.

EVALUATION OF METHOD:

Method Accuracy

Bias, precision, accuracy and stability for 14 volatile organic compounds (ethanol, acetone, 2-propanol, dichloromethane, hexane, trichloromethane, benzene, methyl methacrylate, toluene, ethylbenzene, *m,p*-xylene, *o*-xylene, α-pinene, and *d*-limonene) at ppb-level and ppm-level concentrations [4] were determined using Kennedy et al. [9]. Three additional analytes (2,3-butanedione, 2,3-pentanedione, and

2,3-hexanedione) were added to the target list after this study and accuracy has been assessed during chamber studies (see section below). The upper and lower 95% confidence limits of the average bias were calculated (i.e., ±1.96*standard error). To be acceptable either both bias limits must have an absolute value less than 10%, or an absolute value of 10% must fall between the limits. For a method to meet the NIOSH "25% accuracy" criterion, the 95% confidence statistic for accuracy estimated with the hyperbolic approximation formula must be below 25%. The stability metric is a measure of bias comparing average concentration on day 30 or greater to average concentration on day zero; the absolute value of the stability metric must be less than 10% to be acceptable. Day 30 stability was obtained from LeBouf et al. [4]. Day 58 stability was obtained from NIOSH [10]. While method performance varied by analyte, the validation results demonstrate that this method is a viable air sampling and analytical methodology for measuring a wide range of air concentrations of select volatile organic compounds in mixed exposure environments.

For the preconcentration method used to measure ppb-level concentrations, all accuracy criteria were within acceptable limits for 16 of the 17 target analytes (Table 4a). 2-Propanol failed the 95% accuracy criterion at ppb-level concentrations and accuracy validation results are considered inconclusive, perhaps because the water management step in the preconcentration may have affected the concentrations of this analyte due to its polar nature. Ethanol, however, passed the accuracy criterion despite its similar polarity. Bias was acceptable for all 17 analytes. The average bias values for 2-propanol and methyl methacrylate were greater than 10% but still within acceptable parameters when 95% confidence limits were calculated; further evaluation to confirm or refute this excessive bias result is warranted, particularly because bias values may have been influenced by error introduced during the preparation of standards (e.g., liquid injection into glass bulb or concentration dilution). Storage stability of the 17 analytes was confirmed for 58 days at approximately 10 ppb for most analytes with the exception of ethanol, 2-propanol, and acetone (stable for 30 days) (Table 4a) [4, 10].

Because trichloromethane failed Bartlett's test of homogeneity [9] (i.e., precision varied across concentrations) for ppb-level, the accuracy value for this analyte displayed in Table 4a was not calculated based on a value for precision that was pooled across all concentrations investigated. Rather, the accuracy value was calculated based on the worst-case concentration-specific precision and bias and a modified accuracy calculation that accounts for the reduced degrees of freedom. Further investigation of the precision for trichloromethane using the ppb-level method is warranted. In the meantime, the method can be used to quantify this analyte, but the analyst must be cognizant of the concentration-dependence of measurement variability.

For the loop method used to measure ppm-level concentrations, all accuracy and bias criterion were within acceptable limits for each analyte (Table 4b). Bartlett's test demonstrated that measurement precision was non-homogeneous over concentrations for both dichloromethane and methyl methacrylate. The accuracy values for these two analytes were calculated based on the worst-case concentration-specific precision and bias and a modified accuracy calculation that accounts for the reduced degrees of freedom. All analytes were stable for 30 days, except α-pinene and *d*-limonene, which remained stable for 21 days (Table 4b). The shorter acceptable storage time for α-pinene and *d*-limonene may be due to losses from chemical reactions with other components of canister contents, particularly oxidizing species such as ozone or hydroxyl and nitrate radicals naturally found in indoor air [11, 12].

Inter-laboratory Study

An inter-laboratory study was conducted to estimate precision from nine laboratories [10]. Laboratories were recruited from American Industrial Hygiene Association (AIHA)-accredited or National Environmental Laboratory Accreditation Program (NELAP)-accredited laboratories which had the experience and equipment necessary to analyze canister samples. Precision estimates for repeatability ranged from 0.04 to 0.55 at ppb concentrations and from 0.1 to 0.47 for ppm concentrations. Precision estimates for

reproducibility ranged from 0.1 to 0.62 at ppb concentrations and from 0.19 to 0.58 at ppm concentrations, depending on analyte and nominal level. Plots of h and k statistics which measure between and within laboratory consistency indicated inconsistencies with reported results from laboratories 5, 6, and 7. These laboratories were investigated to determine the cause of the inconsistent results. Issues with storage time and adherence to the method protocol were encountered but results were retained due to the low number of laboratories participating. Training on pressure dilution techniques and preconcentration systems as well as proficiency testing should be periodically conducted to ensure operating laboratories maintain optimal canister method performance.

Chamber Studies

The canister method was challenged in laboratory chamber studies [10] under varying environmental conditions and concentrations of alpha-diketones to assess sampling and analytical accuracy following ASTM D6246 [13]. The following conditions were assessed: temperature, humidity, wind speed, and concentration. Bias pulse tests were performed to assess the bias associated with a known drop in flow rate (~13% over the sampling period) for capillary flow controllers. Flow rate bias (bias pulse) was assessed using the difference in measurements for peak exposures occurring at the beginning and end of the sampling period. Tests were also performed to assess inter-day and inter-sampler variation. A dynamic volatile organic compound generation and sampling system was used to produce known concentrations of challenge agents in a glass sampling chamber with 18 sampling ports. The system was placed in a large walk-in environmental control chamber to regulate temperature. Capillary flow controllers were constructed using Swagelok connections and deactivated fused-silica tubing to collect air samples at 15 mL/min for 15 minutes into a 450 mL canister to test the maximum recommended sampling fill pressure of 50.6 kPa. Canisters were pressurized with ultra-high purity nitrogen and analyzed using an autosampler/preconcentrator system attached to a gas chromatograph/mass spectrometer. Results were corrected for pressure dilution and compared to a theoretical concentration calculated from flow dilution of the gas standard used in the generation system. Accuracy was calculated for each target analyte for all conditions combined. Variance estimates for each factor influencing accuracy were used to apportion the relative influence of each test condition on the overall performance of the method. Upper confidence limits on accuracy (A95) were below 0.25 for all analytes: 0.085 for diacetyl, 0.142 for 2,3-pentanedione, and 0.194 for 2,3-hexanedione. Overall precision was largest for 2,3-hexanedione at 0.061 with 27.4% of the total variance due to inter-day variability. The peak exposure condition (i.e., effect of a bias pulse given the flow rate drop over the sampling period) accounted for less than 6% of the variability regardless of analyte, meaning the known drop in flow rate from the capillary flow controller did not overly influence air sampling results. Additional VOCs (ethanol, acetone, isopropyl alcohol, dichloromethane, trichloromethane, methyl methacrylate, hexane, benzene, toluene, xylenes, α-pinene, *d*-limonene) were present during low and high humidity trials to assess the effect of humidity on method performance. For the high humidity trial (n=10), A_{95} for the additional VOCs were below 0.25 except for ethanol and methyl methacrylate. For the low humidity trial (n=5), A_{95} for the additional VOCs were below 0.25 except for ethanol and isopropyl alcohol. Canister method is a reliable, robust sampling and analytical method that may be used for a variety of analytes (e.g., C1 to C10) under varying environmental conditions.

Flow Controllers for Personal Sampling

Diaphragm flow controllers are heavy due to the stainless steel body holding the diaphragm making them inconvenient for personal sampling. The capillary flow controllers are light weight and provide a broad dynamic range of flow rates that enables full-shift (8-12 hours) sample collection in a 400/450mL canister [8]. With capillary flow controllers, the flow is governed by the length and internal diameter of the capillary and the pressure in the canister [8, 14]. As the canister fills with sample, the pressure differential between the atmosphere and the inside of the canister decreases. This decrease causes a slight, non-linear reduction in flow rate over time. The effect of the change can be mitigated by keeping the final sample volume in the canister at around 30% (but no greater than 50%). The effect of a known, decrease in flow

rate on bias has been assessed and will not overly influence time-integrated measurements of analyte concentration even when a peak concentration at the beginning or end of the sampling period is collected [10, 14].

Additional Guidance

Follow EPA guidelines for cleaning canisters, sampling train cleanliness, canister cleanliness, leak testing, and canister pressurization [5, 15]. Do not clean fused silica lined canisters with humidified air and heat above 80°C. Use humidified nitrogen and heat to clean fused silica lined canisters. ASTM D5466 is also available as guidance for canister sampling and analysis [6].

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TABLE 1. SYNONYMS, FORMULAE, MOLECULAR WEIGHTS AND PHYSICAL PROPERTIES

IUPAC Name / Synonym	CAS # / RTECS	Empirical formula	Molecular Weight	Boiling Point (°C)	Vapor Pressure @ 20° C (mm Hg)	Vapor Pressure @ 20° C (kPa)
ethanol / ethyl alcohol	64-17-5/ KQ6300000	C_2H_6O	46.07	78.3	44	5.87
2-propanol / isopropyl alcohol	67-63-0/ NT8050000	C_3H_8O	60.1	82.3	33	4.4
acetone / 2-propanone	67-64-1/ AL3150000	C_3H_6O	58.08	56.1	180	24
2,3-butanedione / diacetyl	431-03-8/ EK2625000	$C_4H_6O_2$	86.09	88	52.2	6.96
2,3-pentanedione / acetyl propionyl	600-14-6/ SA1850000	$C_5H_8O_2$	100.12	110-112	21.4	2.85
2,3-hexanedione / acetyl butyryl	3848-24-6	$C_6H_{10}O_2$	114.14	128	10	1.33
dichloromethane / methylene chloride	75-09-2/ PA8050000	CH_2Cl_2	84.93	40	350	46.7
trichloromethane / chloroform	67-66-3	$CHCl_3$	119.38	61.2	160	21.3
hexane / n-hexane	110-54-3/ MN9275000	C_6H_{14}	86.18	68.7	124	16.5
benzene / benzol	71-43-2/ CY1400000	C_6H_6	78.11	80.1	75	10
toluene / methylbenzene	108-88-3/ XS5250000	C_7H_8	92.14	110.6	22	2.93
ethylbenzene / phenylethane	100-41-4/ DA0700000	C_8H_{10}	106.17	136.2	7	0.93
o-xylene / 1,2-dimethylbenzene	95-47-6/ ZE2450000	C_8H_{10}	106.17	144.5	7	0.93
m-xylene / 1,3-dimethylbenzene	108-38-3/ ZE2275000	C_8H_{10}	106.17	139.1	9	1.2
p-xylene / 1,4-dimethylbenzene	106-42-3/ ZE2625000	C_8H_{10}	106.17	138.2	9	1.2
methyl-2-methyl-2-propenate / methyl methacrylate	80-62-6/ OZ5075000	$C_5H_8O_2$	100.12	100.5	29	3.87
4,6,6-trimethylbicyclo[3.1.1]hept-3-ene / *α*-pinene / 2-pinene	80-56-8/ DT7000000	$C_{10}H_{16}$	136.23	156.2	4.75 (25° C)	0.63
(4R)-1-methyl-4-prop-1-en-2-ylcyclohexene / *d*-limonene / p-mentha-1,8-diene, ("R")	5989-27-5/ OS8100000	$C_{10}H_{16}$	136.23	178	1.43	0.19

TABLE 2. CHARACTERISTIC MASSES (M/Z) USED FOR QUANTITATION

Substance	Primary Ion	Secondary Ion
ethanol	45	46, 43
2-propanol	45	43
acetone	43	58
2,3-butanedione	86	43
2,3-pentanedione	100	57, 43
2,3-hexanedione	71	43, 114
dichloromethane	84	49, 86
trichloromethane	83	85, 47
hexane	57	41, 43
benzene	78	77, 52
toluene	91	92
ethylbenzene	91	106
***o*-xylene**	91	106, 105
***m,p*-xylene**	91	106, 105
methyl methacrylate	69	41, 100
***α*-pinene**	93	91, 92
***d*-limonene**	68	93, 67
bromochloromethane[A]	130	49, 93
1,4-difluorobenzene[A]	114	63, 88
chlorobenzene-d5[A]	117	82, 119

[A]internal standards

TABLE 3. EXPOSURE LIMITS (PPM) [16,17]

Substance	OSHA TWA	OSHA Peak	NIOSH TWA	NIOSH STEL	mg/m³ per ppm
ethanol	1000	-	1000	-	1.89
2-propanol	400		400	500	2.46
acetone	1000	-	250	-	2.38
2,3-butanedione	-	-	0.005	0.025	3.52
2,3-pentanedione	-	-	0.0093	0.031	4.09
2,3-hexanedione	-	-	-	-	4.67
dichloromethane	25	125	N/A[A]	(ca[B])	3.47
trichloromethane	-	50	-	2 (60 min)	4.88
hexane	500	-	50	-	3.53
benzene	1	5	0.1 (ca)	1 (ca)	3.19
toluene	200	500	100	150	3.77
ethylbenzene	100	-	100	125	4.34
***o*-xylene**	100	-	100	150	4.34
***m*-xylene**	100	-	100	150	4.34
***p*-xylene**	100	-	100	150	4.34
methyl methacrylate	100	-	100	-	4.09
***α*-pinene**	-	-	-	-	5.57
***d*-limonene**	-	-	-	-	5.57

[A]N/A = not applicable

[B]ca = carcinogen

TABLE 4A. RANGE, OVERALL BIAS, PRECISION AND ACCURACY FOR PPB LEVELS [4, 10]

Substance	Range of generated samples	Overall Bias (%)	Overall Precision (S_{rT})	Overall Accuracy (%)	58 day Stability (%)
ethanol	1.3 - 9.9	-9.3	0.058	±22.2	-0.5 (30 days)
2-propanol	1.3 - 10.0	-12.3	0.098	±28.9	7.8 (30 days)
acetone	1.3 - 10.0	-3.2	0.064	±18.6	3.1 (30 days)
2,3-butanedione	21.5 - 381	2.2	0.032	±8.5	4.1
2,3-pentanedione	20.8 - 377	4.8	0.048	±14.2	2.7
2,3-hexanedione	20.4 - 368	-6.0	0.061	±19.4	-2.9
dichloromethane	1.3 - 9.8	2.9	0.017	±7.1	0.22
trichloromethane	1.3 - 9.8	-0.3	0.020*	±16.5*	3.1
hexane	1.3 - 9.9	-0.1	0.020	±5.5	3.6
benzene	1.3 - 9.8	-3.0	0.022	±8.3	3.6
toluene	1.3 - 9.9	-4.0	0.020	±8.6	1.6
ethylbenzene	1.3 - 9.9	-4.4	0.020	±9.1	-0.6
***o*-xylene**	1.3 - 9.8	-6.0	0.027	±12.3	-3.5
***m,p*-xylene**	1.3 - 9.8	-6.7	0.025	±12.6	-8.1
methyl methacrylate	1.3 - 9.9	-10.2	0.066	±24.9	1.5
***α*-pinene**	1.3 - 9.8	-4.7	0.028	±11.4	-3.3
***d*-limonene**	1.3 - 9.8	-4.6	0.069	±21.1	-1.9

*worst-case precision estimate since failed Bartlett's test of homogeneity of variance across concentrations

S_{rT} = pooled precision as relative standard deviation across multiple concentration levels

Overall Accuracy=upper confidence limit on accuracy, A_{95}

Stability (%) = ((Concentration at storage day)/(Concentration at day 0)-1)*100%

TABLE 4B. RANGE, OVERALL BIAS, PRECISION AND ACCURACY FOR PPM-LEVELS [4]

Substance	Range of generated samples	Overall Bias (%)	Overall Precision (S_{rT})	Overall Accuracy (%)	30 day Stability (%)
ethanol	0.81 - 1.8	9.4	0.028	±17.0	-9.2
2-propanol	0.82 - 1.8	8.9	0.027	±16.1	-2.9
acetone	0.82 - 1.8	8.7	0.019	±13.8	-1.6
dichloromethane	0.79 - 1.8	3.0	0.041*	±17.8*	-4.7
trichloromethane	0.80 - 1.8	5.7	0.012	±8.9	-1.9
hexane	0.81 - 1.8	6.1	0.012	±9.4	0.1
benzene	0.80 - 1.8	6.3	0.011	±9.3	7.3
toluene	0.81 - 1.8	5.5	0.015	±9.3	6.4
ethylbenzene	0.81 - 1.8	4.7	0.017	±9.2	0.8
***o*-xylene**	0.80 - 1.8	5.4	0.019	±10.3	-0.3
***m,p*-xylene**	0.80 - 1.8	3.9	0.019	±8.8	-2.1
methyl methacrylate	0.81 - 1.8	5.7	0.016*	±15.6*	1.4
***α*-pinene**	0.81 - 1.8	6.7	0.022	±12.5	0.1 (21 days)
***d*-limonene**	0.80 - 1.8	13.1	0.039	±24.0	-0.03 (21 days)

*worst-case precision estimate since failed Bartlett's test of homogeneity of variance across concentrations
S_{rT} = pooled precision as relative standard deviation across multiple concentration levels
Overall Accuracy=upper confidence limit on accuracy, A_{95}
Stability (%) = ((Concentration at storage day)/(Concentration at day 0)-1)*100%

TABLE 5A. LIMITS OF DETECTION (LOD), MEASUREMENT RANGE, AND PRECISION FOR PPB-LEVELS [4, 10]

Substance	LOD (ppb)	Range (ppb)	Precision ($RMSE^A$)	Linearity R^2
ethanol	0.4	0.25 – 21.4	0.272	0.999
2-propanol	0.5	0.27 – 22.0	0.077	0.998
acetone	0.4	0.27 – 20.6	0.080	0.999
2,3-butanedione*	0.3	0.26 – 21.0	0.033	0.999
2,3-pentanedione*	0.2	0.24 – 18.4	0.148	0.999
2,3-hexanedione*	0.4	0.24 – 18.0	0.238	0.999
dichloromethane	0.2	0.26 – 20.8	0.049	0.999
trichloromethane	0.1	0.27 – 21.6	0.044	0.999
hexane	0.2	0.27 – 21.8	0.030	0.999
benzene	0.2	0.27 – 21.6	0.032	0.999
toluene	0.3	0.27 – 21.4	0.023	0.999
ethylbenzene	0.3	0.26 – 21.0	0.019	0.999
***o*-xylene**	0.3	0.26 – 21.0	0.019	0.999
***m,p*-xylene**	0.4	0.27 – 22.0	0.015	0.999
methyl methacrylate	0.5	0.25 – 20.4	0.035	0.999
***α*-pinene**	0.5	0.26 – 21.0	0.019	0.999
***d*-limonene**	0.8	0.26 – 20.8	0.136	0.999

*Selected ion monitoring mode used to improve detection limits
[A]RMSE= root mean square error

TABLE 5B. LIMITS OF DETECTION (LOD), MEASUREMENT RANGE, AND PRECISION FOR PPM-LEVELS [4]

Substance	LOD (ppm)	Range (ppm)	Precision (SEE[A])	Linearity R^2
ethanol	0.2	0.07 - 1.9	0.058	0.998
2-propanol	0.2	0.07 - 2.0	0.066	0.998
acetone	0.3	0.08 - 2.0	0.071	0.998
dichloromethane	0.4	0.15 - 1.9	0.099	0.999
trichloromethane	0.3	0.11 - 1.9	0.093	0.999
hexane	0.2	0.11 - 2.0	0.072	0.999
benzene	0.2	0.11 - 1.9	0.064	0.999
toluene	0.3	0.11 - 1.9	0.101	0.998
ethylbenzene	0.3	0.11 - 1.9	0.108	0.998
***o*-xylene**	0.1	0.11 - 1.3	0.031	0.998
***m,p*-xylene**	0.3	0.11 - 1.9	0.110	0.998
methyl methacrylate	0.2	0.11 - 1.9	0.089	0.998
***α*-pinene**	0.3	0.11 - 1.9	0.116	0.999
***d*-limonene**	0.4	0.11 - 1.9	0.156	0.999

[A]SEE = standard error of estimate from regression curve