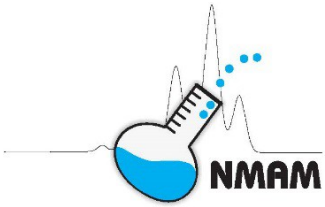

BACKUP DATA REPORT

NIOSH Method No. 3900

Title: Volatile Organic Compounds, C1 to C10, Canister Method

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

Author/developer: Ryan LeBouf, NIOSH

Date: 8/30/2018

BACKUP DATA REPORT
NMAM Method No 3900
Volatile Organic Compounds, C1 to C10, Canister Method

Substance

C1-C10 volatile organic compounds

Chemicals Used for Evaluation

Specific chemicals tested were 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, *a*-pinene, *d*-limonene. Custom gas standards (Linde, Braddock, PA) were diluted with ultra-high purity nitrogen. Distilled/deionized water (18 MOhm, low VOC content) was produced using a Milli-Q Advantage A10 system (Millipore, Burlington, MA). The water should have a low enough residual VOC content to not interfere with analysis.

Exposure Limits

Table 1. Exposure Limits (ppm) [1, 2]

Substance	OSHA TWA	OSHA Peak	NIOSH TWA	NIOSH STEL	mg/m^3 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	NA	(ca)	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

Note: ca = carcinogen; NA = not applicable

Synopsis

Traditional occupational exposure monitoring for volatile organic compounds uses sorbent tubes to collect analytes from an air stream. Sorbent-based techniques require the user to have some prior knowledge of the target analytes and approximate concentrations to effectively sample exposures. Whole-air sampling into evacuated canisters requires no prior knowledge of air concentrations as breakthrough is not an issue, can handle part per billion (ppb) and part per million (ppm) analyte concentrations, and the technique is amenable to a wide range of compounds using a single technique. Canisters coupled with restricted flow controllers makes sampling easier for the field industrial hygienist because the flow controllers require no onsite pre- or post-calibration. NIOSH developed the canister method for occupational exposure monitoring of seventeen volatile organic compounds. The method was adapted from EPA Method TO-15 [3] and has been designated as NMAM Method 3900.

The focus of the canister method development was to validate an evacuated canister-based (passive) sampling approach followed by preconcentration of samples (for ppb-level VOCs) and loop injection (for ppm-level VOCs) into a gas chromatograph/mass spectrometer (GC/MS). Spiking experiments, LODs/LOQs, and 30-day storage stability were assessed [4]. An additional 58-day storage stability experiment is presented here along with an interlaboratory study to assess method performance by other laboratories and a chamber study to assess the canister method coupled with restricted flow controllers for time-integrated sampling during varying environmental conditions.

Sampling

The canister must be evacuated to 0.0066 kPa prior to sampling using a system equipped with a rough pump and a high vacuum pump. Sampling may be performed with a fitting for instantaneous samples or 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. 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. 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 (30% full) during your sampling period. Do not exceed a final sample pressure of 50.6 kPa (50% full) as the flow rate will become increasingly non-linear. Use a 2-µm, sintered, stainless steel particle filter to protect the canisters when sampling in dusty atmospheres.

Pressure Dilutions

Calibration and sample canisters generally require pressure dilutions with ultra-high purity (UHP) nitrogen or air. A receiving canister is partially filled to between 5 and 7 psia to reduce the vacuum in the canister prior to sample transfer which allows for a less aggressive introduction of the sample and also places the pressure differential measurement in the optimal range of the pressure transducer. A portion of the sample, in terms of a pressure differential, from the calibration cylinder or sample (e.g., 0.3 to 8 psia) is added to the receiving canister at a slow rate (e.g., 0.03 to 0.3 psia/sec depending on the desired pressure differential). Then UHP nitrogen or air is added to the receiving canister at a slow rate until the final pressure is reached. The ratio of the final pressure to the sample pressure differential is equal to the dilution factor (e.g., 25 psia final/2.5 psia sample pressure differential = 10x dilution). Final pressure should not exceed 30 psia to keep the pressure of the sample flow path (including sample transfer lines, fittings, traps, and loop if used) to similar pressures as those used to calibrate the system, otherwise the volume transferred to the preconcentration system may be different than

requested and require pressure correction factors. Final pressures of 25 psia are recommended for routine analysis. While pressure dilutions of up to 100x may be achievable, they are not as reproducible as multiple, lower dilutions (e.g., two 10x dilutions for a 100x final dilution). Allow the canisters to equilibrate for a minimum of 6 hours after pressurization to allow time for mixing.

Sample Preparation

Pressurize canister samples with UHP nitrogen or air to 152 kPa to obtain a sufficient excess pressure for a 250 mL nominal injection volume or to flush a 1 mL loop with approximately 100 mL of samples. Final sample pressure after analysis should be greater than 50.6 kPa (50% empty) to limit potential for sample dilution due to system leakage. 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 followed by pressure dilutions to place the diluted concentration into the range of the ppb-level calibration curve.

Sample Analysis

Sample analysis requires a whole-air preconcentration system to manage water content and reduce the transfer volume to the GC. Some water content is necessary to mimic humidity seen in field samples.

MS Scan and selected ion monitoring (SIM) mode have been previously shown to provide roughly equivalent detection limits for aromatics, alkanes, and terpenes when using a thermal desorption/GC/MS system [5]. Using MS scan mode allows unknown chemicals to be qualitatively identified and concentrations estimated based on the closest internal standard and an assumed response factor. Limits of detection could be improved by using SIM mode.

Spiking Experiments

Method bias, precision, and accuracy 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) were determined at ppb-level and ppm-level concentrations [4]. Backup data tables are presented for ppb-levels (Table A1, Appendix A) and ppm-levels (Table A2, Appendix A). Three additional analytes (2,3-butanedione, 2,3-pentanedione, and 2,3-hexanedione) were added to the target list after this study and method accuracy has been assessed during chamber studies (see section below). The upper and lower 95% confidence limit of the average bias was 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. While method performance varied by analyte, the validation results demonstrated 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. 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).

Because trichloromethane failed Bartlett's test of homogeneity (i.e., precision varied across concentrations) for ppb-level, the accuracy value for this analyte 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. 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.

LOD/LOQ Assessment

The initial assessment of LODs/LOQs for the original 14 compounds was completed in 2012 (Table 2) [4]. For the preconcentration method used to quantify ppb levels of the target analytes, LODs/LOQs for each analyte were determined using five low-level calibration spikes ranging from 0.03 to 1.1 ppb (depending on the analyte) prepared in 6 L canisters and analyzed with a nominal injection volume of 500 mL (Table A3, Appendix A) [4]. For the loop method used to quantify ppm levels, LODs and LOQs were determined with five calibration spikes ranging from 0.1 to 2 ppm (depending on the analyte) (Table A4, Appendix A) [4]. The LOD was calculated as 3 times the standard error of the regression divided by the slope of the regression, while the LOQ was calculated as 3.33 times the LOD [6].

LODs/LOQs have continued to be assessed over time as the condition of the instruments changed due to age and instruments were upgraded or replaced. Current LODs/LOQs for ppb-level as listed in NMAM Method 3900 appear in Table 3. The values for ppb-level have been updated with an assessment conducted in July 2017 (Table A5, Appendix A) using seven separately-prepared, low-level concentrations including 0.1, 0.3, 0.5, 1.0, 2.0, 3.0, and 6.0 ppb; each of these levels were produced in 6 L canisters and injected once at 250 mL. The nominal injection volume for ppb-level analysis has been reduced from 500 mL to 250 mL for all canisters since the original LOD/LOQ assessment in 2012. A nominal injection volume of 250 mL has been found to be amenable for both 450 mL canisters and 6 L canisters with minimal effect on sensitivity.

The LODs for ppm-level were not updated from those produced in the initial LOD assessment since loop injection is fairly uncommon now. The current recommended strategy for higher concentration samples is pressure dilutions into the ppb-level calibration range or loop injection with a dilution factor correction for volume injected onto the preconcentrator compared to a nominal 250 mL injection volume.

Table 2a&b. Limits of detection (LODs) and limits of quantitation (LOQs) for target analytes, ppb and ppm levels

Table 2a ppb level

Analyte	Intercept	slope	RMSE	LOD (ppb)	LOQ (ppb)
ethanol	0.073	0.911	0.088	0.3	0.97
2-propanol	0.001	1.093	0.109	0.1	0.23
acetone	0.148	1.037	0.115	0.3	1.1
dichloromethane	0.068	1.113	0.113	0.3	1.0
trichloromethane	-0.024	0.989	0.063	0.2	0.64
hexane	-0.025	0.958	0.067	0.2	0.70
benzene	-0.018	0.950	0.061	0.2	0.64
toluene	-0.015	0.959	0.056	0.2	0.58
ethylbenzene	-0.012	0.989	0.064	0.2	0.65
m,p-xylene	-0.003	0.958	0.065	0.2	0.68
o-xylene	-0.006	0.968	0.071	0.2	0.73
methyl methacrylate	-0.015	1.002	0.079	0.3	0.79
α-pinene	-0.022	0.996	0.073	0.2	0.73
d-limonene	-0.011	0.984	0.099	0.3	1.0

Note: RMSE=root mean square error

Table 2b ppm level

Analyte	Intercept	slope	RMSE	LOD (ppm)	LOQ (ppm)
ethanol	-0.019	1.008	0.062	0.2	0.60
2-propanol	-0.029	1.028	0.068	0.2	0.63
acetone	0.002	0.938	0.078	0.3	0.76
dichloromethane	-0.002	0.923	0.099	0.4	1.1
trichloromethane	-0.035	1.043	0.093	0.3	0.89
hexane	-0.087	1.181	0.072	0.2	0.61
benzene	-0.075	1.163	0.064	0.2	0.55
toluene	-0.121	1.303	0.101	0.3	0.77
ethylbenzene	-0.121	1.299	0.108	0.3	0.83
m,p-xylene	-0.120	1.288	0.110	0.3	0.85
o-xylene	-0.055	1.155	0.031	0.1	0.27
methyl methacrylate	-0.126	1.341	0.089	0.2	0.66
α-pinene	-0.154	1.397	0.116	0.3	0.83
d-limonene	-0.210	1.526	0.156	0.4	1.0

Note: RMSE=root mean square error

Table 3. LODs for ppb-levels

Analyte	Intercept	Slope	RMSE	LOD (ppb)	LOQ (ppb)
ethanol	0.082	0.426	0.060	0.4	1.3
2-propanol	-0.023	0.799	0.121	0.5	1.7
acetone	0.019	0.916	0.111	0.4	1.3
2,3-butanedione*	-0.137	0.984	0.085	0.3	1.0
2,3-pentanedione*	-0.095	0.988	0.056	0.2	0.67
2,3-hexanedione*	-0.141	0.935	0.134	0.4	1.3
dichloromethane	-0.076	0.953	0.047	0.2	0.67
trichloromethane	-0.087	0.914	0.028	0.1	0.33
hexane	-0.092	0.936	0.049	0.2	0.67
benzene	-0.086	0.946	0.058	0.2	0.67
toluene	-0.091	0.945	0.107	0.3	1.00
ethylbenzene	-0.096	0.958	0.102	0.3	1.00
m,p-xylene	-0.114	0.975	0.119	0.4	1.3
o-xylene	-0.119	0.972	0.091	0.3	1.00
methyl methacrylate	-0.128	0.931	0.149	0.5	1.7
α-pinene	-0.110	0.920	0.160	0.5	1.7
d-limonene	-0.123	0.862	0.241	0.8	2.7

Note: RMSE=root mean square error

*Selected ion monitoring mode used to improve detection limits

Storage Stability Testing

Sample storage stability at room temperature was assessed for 14 analytes at 5 ppb and 0.6 ppm over a period of 30 days [4]. For the 5 ppb concentration, a total of twelve 6 L canisters were stored and analyzed repeatedly on days zero, 7, 14, 21, and 30. For the 0.6 ppm concentration, 30 canisters were generated and analyzed only once according to the following schedule: 12 canisters on day zero, six canisters on day 7, and three canisters each on days 14, 21, and 30. The stability metric is bias comparing average concentration on day 30 to average concentration on day zero; the absolute value of the stability metric must be less than 0.10 to be acceptable per NIOSH guidance [6]. If the analyte is not stable for 30 days, the method is still acceptable as long as a shorter stability time is confirmed.

All 14 analytes at ppb-level were stable (i.e., less than 10% change) over a period of 30 days (Table A6, Appendix A). All 14 analytes at ppm-levels were stable for 30 days, except α-pinene and *d*-limonene, which remained stable for 21 days (Table A7, Appendix A). 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 [7, 8].

Additional Storage Stability Testing

Sample storage stability at room temperature was assessed for 17 analytes (14 original analytes plus 2,3-butanedione, 2,3-pentanedione, and 2,3-hexanedione) at 10 ppb over a period of 58 days (Table A8, Appendix A). A total of twelve 6 L canisters were individually prepared, stored, and analyzed repeatedly on days zero, 9, 14, 22, 29, and 58. 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 according to the first storage stability test) (Table 4).

Table 4. Additional storage stability for 58 days

Analyte	**58 day Stability, Bias (%)**
ethanol	-0.5 (30 days)
2-propanol	7.8 (30 days)
acetone	3.1 (30 days)
2,3-butanedione	4.1
2,3-pentanedione	2.7
2,3-hexanedione	-2.9
dichloromethane	0.22
trichloromethane	3.1
hexane	3.6
benzene	3.6
toluene	1.6
ethylbenzene	-0.6
o-xylene	-3.5
m,p-xylene	-8.1
methyl methacrylate	1.5
α-pinene	-3.3
d-limonene	-1.9

Dynamically-generated Samples: Chamber Studies

Canister method was challenged using alpha-diketones in chamber studies under varying environmental conditions to assess sampling and analytical accuracy following ASTM D6246 [9]. The following conditions were assessed: temperature, humidity, wind speed, and concentration. Additional VOCs (ethanol, acetone, 2-propanol, dichloromethane, trichloromethane, methyl methacrylate, hexane, benzene, toluene, *o*-xylene, *m*,*p*-xylene, α-pinene, *d*-limonene) were present during low and high humidity trials to assess the effect of humidity on method performance for these analytes. 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. 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 certified 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 (A_{95}) were below 0.25 for all analytes: 0.085 for 2,3-butanedione, 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 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 adversely affect air sampling. 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.

Chamber Study Methods

Chamber Study protocol

The VOC generation system was constructed in a large walk-in environmental chamber (Nor-Lake Scientific, Hudson, WI) to control temperature close to the test condition. The test chamber was a glass cylinder with nine ports for sampling (replica of OSHA test chamber). VOC concentration homogeneity was assessed by sampling silica gel sorbent tubes (SKC cat no. 226-183) at each port. Tubes were analyzed using a modified OSHA 1016 method (mass spectrometry instead of flame ionization detection) [10]. Variability between ports was 4.1% for 2,3-butanedione, 4.4% for 2,3-pentanedione, and 3.9% for 2,3-hexanedione. The temperature, humidity, and flow rate of the dilution air to test chamber was controlled by a Miller-Nelson unit (Model HCS-501, Assay Technology, Livermore, CA). The VOC concentration was generated by flow dilution of a certified calibration gas cylinder at approximately 2 ppm (±5% analytical accuracy) (Linde Spectra Environmental Gases, Alpha, NJ) using a mass flow controller (Aalborg, Orangeburg, NY). Blank samples collected prior to conducting the studies ensured system cleanliness. No alpha-diketones were detected above the MDL (0.01 µg/sample which is 0.95 ppb 2,3-butanedione for a 15 minute air sample collected at 200 mL/min). Trials were conducted at a constant concentration. For the bias pulse experiments, the sampler was attached to the test chamber for 1 out of 15 minutes at the beginning or end of the sampling period. For the rest of the trial, the sampler was placed in a tedlar bag filled with UHP nitrogen gas.

NIOSH draft canister method was used to analyze canister samples. Briefly, canisters were pressurized to 1.5 times atmospheric pressure with UHP nitrogen prior to analysis on an Entech 7200/7032

preconcentrator/autosampler (Simi Valley, CA) attached to an Agilent 6890/5975 gas chromatograph/mass spectrometer. Canister injection volume was 25, 50, or 250 mL adjusted to produce a mass loading on the column within the calibration curve. Calibration curve dynamic range was from 0.2 to 40 ppb. Canisters were allowed to equilibrate for at least three hours prior to analysis. Each analyte response was referenced to an internal standard response and compared to a calibration curve. Internal standards were bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d5 at 25 ppb with a 50 mL loading on the preconcentrator module prior to sample loading. A pressure dilution factor was applied to the measure concentration for final reporting. Bias was calculated as the difference between the final result and the flow dilution theoretical value (assuming no error in the theoretical value). Bartley calculation was employed for point estimate accuracy and confidence limits on accuracy [11]. Variance estimates for each trial as well as aggregate bias and overall inter-sampler variation were used to apportion the relative percentage effect (squared error over total squared error) of each of the conditions on method performance. Bias pulse was calculated as the difference between the beginning and end pulse measurements divided by the sum of the measurements [9].

Chamber Study Design

The effect of environmental conditions on method performance in terms of bias and precision were assessed using different trials based on ASTM D6246 [9]. The experimental trials included humidity, wind speed, concentration, inter-day, beginning pulse, and end pulse (Table 5). High wind speed was difficult to achieve with the VOC generation system, so a low wind speed (0.009 m/s) was substituted. The rest of the trials were conducted between 0.033 and 0.042 m/s depending on VOC generation needs. Additional VOCs (ethanol, acetone, 2-propanol, dichloromethane, trichloromethane, methyl methacrylate, hexane, benzene, toluene, *o*-xylene, *m,p*-xylene, α-pinene, *d*-limonene) were present during low and high humidity trials at the same nominal concentration as the alpha-diketones (400 ppb). Trial sample sizes ranged from 5 to 12 due to constraints on the analytical system at the time of analysis (i.e., other projects like NIOSH Health Hazard Evaluation samples took precedence) and lost samples or outlier results. Lost samples were due to low liquid nitrogen pressure during analysis causing a failed injection. For the high humidity trial, 12 samples were collected but one was lost; one was visually identified as an outlier (bias -0.33 for 2,3-butanedione, -0.64 for 2,3-pentanedione, and -0.81 for 2,3-hexanedione) and removed. For the high temperature trial, 6 samples were collected; one was visually identified as an outlier (bias -0.18 for 2,3-butanedione, -0.39 for 2,3-pentanedione, and -0.79 for 2,3-hexanedione) and removed. For the low humidity trial, 6 samples were collected; one was visually identified as an outlier (bias -0.01 for 2,3-butanedione, -0.22 for 2,3-pentanedione, and -0.37 for 2,3-hexanedione) and removed. For the end pulse trial, 9 samples were collected; one sample was lost.

Table 5. Summary of Environmental Conditions

Trial Name	N	Mean Temperature (°C)	Mean Relative Humidity (%RH)	Target Concentration (ppb)	Theoretical Concentrations of 2,3-Butanedione (ppb)	Theoretical Concentrations of 2,3-Pentanedione (ppb)	Theoretical Concentrations of 2,3-Hexanedione (ppb)
high humidity	10	24.9	71.0	400	381	377	367
normal humidity	9	25.9	49.5	70	73.7	74.8	69.8
low humidity	5	24.9	19.5	400	381	377	368
low wind speed	12	21.8	26.1	20	21.5	20.8	20.4
low concentration	6	25.8	40.0	20	22.2	21.4	21.0
high temperature	5	36.0	13.0	20	22.2	21.4	21.0
Inter-day #1	12	25.5	42.5	100	98.6	95.3	93.4
Inter-day #2	12	25.5	42.8	100	98.6	95.3	93.4
beginning pulse	9	25.6	42.0	450	465	450	441
end pulse	8	25.9	42.5	400	409	396	388

Chamber Study Results/Discussion

2,3-Butanedione upper confidence limit on accuracy (A_{95}) was 0.085 with a mean bias of 0.022 and an overall precision of 0.032 (Table 6). Humidity had a negligible effect on the method performance (0.5 to 2.6% effect). The greatest effect on method performance was due to inter-day variability (33.2% effect), followed by high temperature (32.1% effect). Bias pulse had a negligible effect on method performance (5.1% effect).

Table 6. Bias, Precision, and Accuracy Estimates for 2,3-Butanedione

Trial Name	N	Mean Bias	Precision	%effect
high humidity	10	0.070	0.010	0.7
normal humidity	9	-0.052	0.008	0.5
low humidity	8	0.027	0.020	2.6
low wind speed	12	0.053	0.034	7.6
low concentration	6	0.050	0.069	32.1
high temperature	5	0.010	0.070	33.2
inter-day	24	-0.007	0.031	6.3
bias pulse	17		0.047	5.1
bias				3.2
inter-sampler				8.8
	Overall	0.022	0.032	
	A	0.075		
	A_{95}	0.085		

2,3-Pentanedione A_{95} was 0.142 with a mean bias of 0.048 and an overall precision of 0.048 (Table 7). Humidity had a negligible effect on method performance (0.2 to 1.3% effect). High temperature had the greatest effect on method performance presumably due to variable test results (41.3% effect). Low concentration had a 21.4% effect on method performance. The effect of bias pulse was minimal (5.4% effect).

Table 7. Bias, Precision, and Accuracy Estimates for 2,3-Pentanedione

Trial Name	N	Mean Bias	Precision	%effect
high humidity	10	0.012	0.011	0.5
normal humidity	9	0.034	0.019	1.3
low humidity	8	-0.019	0.006	0.2
low wind speed	12	0.054	0.039	5.6
low concentration	6	0.114	0.077	21.4
high temperature	5	0.082	0.107	41.3
inter-day	24	0.061	0.047	8.0
bias pulse	17		0.066	5.4
bias				8.5
inter-sampler				7.9
	Overall	0.048	0.048	
	A	0.127		
	A_{95}	0.142		

2,3-Hexanedione A_{95} was 0.194 with a mean bias of -0.060 and an overall precision of 0.061 (Table 8). Humidity had a variable effect on method performance (0.3 to 7.9% effect). Inter-day variability and low windspeed had the greatest effect on method performance presumably due to a few test results in this trial that were inconsistent with the rest of the observations. Bias pulse had little effect on method performance (5.9% effect).

Table 8. Bias, Precision, and Accuracy Estimates for 2,3-Hexanedione

Trial Name	N	Mean Bias	Precision	%effect
high humidity	10	-0.010	0.015	0.9
normal humidity	9	-0.013	0.043	7.9
low humidity	8	-0.041	0.008	0.3
low wind speed	12	-0.087	0.076	24.2
low concentration	6	-0.106	0.027	3.1
high temperature	5	-0.147	0.040	6.7
inter-day	24	-0.018	0.081	27.4
bias pulse	17		0.065	5.9
bias				15.1
inter-sampler				8.3
	Overall	-0.060	0.061	
	A	0.168		
	A_{95}	0.194		

Additional VOCs were present during low and high humidity trials at a target concentration of 400 ppb. For the high humidity trial (n=10), A_{95} for the additional VOCs were below 0.25 except for ethanol and methyl methacrylate (Table 9). The lower confidence limit for ethanol was 0.39 meaning the method did not pass the accuracy criterion for this analyte during this specific trial. Polar, early-eluting compounds like ethanol are notoriously challenging to quantify in the presence of humidity for two reasons. During the water management step of some preconcentrators, water is removed on a cold trap and some polar analytes are also lost. Preconcentrator operating conditions need to be optimized to remove water while minimizing the removal of polar compounds. In the case of ethanol at high humidity, the mean bias was low at -0.347 but the precision was good at 0.04 indicating a consistent loss of ethanol (and presumably water) during the water management step. Reducing the cold trap temperature to reduce the amount of water removed may be an effective strategy to reduce the loss of polar compounds during the water management steps. Another strategy would be to separate the analyte of interest from the water peak by adjusting chromatographic and/or preconcentration conditions. It is recommended to work with the manufacturer on optimizing the operating conditions of the preconcentrator for your analytes. The lower confidence limit for methyl methacrylate was 0.15 meaning the method was inconclusive for this analyte during this specific trial. For the low humidity trial (n=5), A_{95} for the additional VOCs were all below 0.25 meaning the method passed the 95% accuracy criterion (Table 9).

Table 9. Additional VOC Accuracy Results for High (n=10) and Low (n=5) Humidity Trials

	High Humidity			Low Humidity		
Analyte	**Mean Bias**	**Precision**	**A_{95}**	**Mean Bias**	**Precision**	**A_{95}**
2,3-Butanedione	0.070	0.010	0.099	0.027	0.020	0.110
2,3-Hexanedione	-0.010	0.015	0.052	-0.041	0.008	0.075
2,3-Pentanedione	0.012	0.011	0.045	-0.019	0.006	0.046
Acetone	0.063	0.020	0.122	0.023	0.015	0.088
α-Pinene	0.045	0.008	0.069	0.007	0.032	0.134
Benzene	0.024	0.016	0.071	0.040	0.013	0.096
Trichloromethane	0.136	0.025	0.209	0.085	0.026	0.196
d-Limonene	0.020	0.012	0.055	-0.014	0.040	0.172
Ethanol	-0.347	0.040	**0.465**	-0.096	0.035	0.241
Ethylbenzene	0.034	0.011	0.065	0.024	0.008	0.058
2-Propanol	0.083	0.021	0.143	0.075	0.025	0.181
m,p-Xylene	0.028	0.012	0.064	0.003	0.005	0.023
Methyl Methacrylate	0.051	0.093	**0.331**	-0.002	0.013	0.052
Dichloromethane	0.059	0.015	0.104	0.032	0.013	0.087
Hexane	0.054	0.046	0.187	0.020	0.019	0.102
o-Xylene	0.054	0.011	0.084	0.012	0.007	0.041
Toluene	0.009	0.010	0.037	-0.003	0.010	0.043

Chamber Study Conclusions

Upper confidence limits on accuracy (A_{95}) were below 0.25 for all analytes: 0.085 for 2,3-butanedione, 0.142 for 2,3-pentanedione, and 0.194 for 2,3-hexanedione. Absolute value of bias was less than 0.10 for each analyte. Known flow rate drop over the sampling period did not affect overall accuracy as seen in the bias pulse trial which accounted for less than 6% of the variance regardless of analyte. Additional VOCs (ethanol, acetone, 2-propanol, methylene chloride, chloroform, methyl methacrylate, hexane, benzene, toluene, xylenes, alpha-pinene, d-limonene) were present during low and high humidity trials. Humidity did not have an effect on method performance for most analytes. Canister method is a reliable, robust sampling and analytical method that may be used for a variety of airborne analytes (e.g., C1 to C10) under varying environmental conditions.

Interlaboratory Study (ILS)

Authors: Ryan F. LeBouf, H. Amy Feng, and Stanley A. Shulman

An evacuated canister method for sampling and analysis of select volatile organic compounds was developed at the NIOSH Respiratory Health Division Organic Laboratory in Morgantown, WV. An inter-laboratory study was conducted to assess repeatability and reproducibility of the test method prior to incorporation of the method in the NIOSH Manual of Analytical Methods. Nine laboratories completed the study on the test mix containing 17 analytes: ethanol, 2-propanol (isopropyl alcohol), acetone, dichloromethane (methylene chloride), trichloromethane (chloroform), hexane, 2,3-butanedione, 2,3-pentanedione, 2,3-hexanedione, benzene, toluene, ethylbenzene, *o*-xylene, *m,p*-xylene, methyl methacrylate, α-pinene, and *d*-limonene. Blind spiked test samples were shipped to each laboratory. Spikes consisted of two concentration ranges, three nominal levels, and three replicates per combination (n=18 samples per laboratory, except for the reference laboratory who analyzed between three and six replicates). For quality control, two samples containing UHP nitrogen were included as laboratory blanks for each round. Spikes were produced in batches to accommodate each round which included one to three laboratories at the same time depending on laboratory availability and feasibility in sample preparation. Reference canisters were produced with each batch and analyzed in-house to ensure spike generation was acceptable prior to shipment. Precision estimates for repeatability ranged from 0.04 to 0.55 at ppb concentrations and from 0.10 to 0.47 for ppm concentrations over all analytes and nominal levels. Precision estimates for reproducibility ranged from 0.10 to 0.62 at ppb concentrations and from 0.19 to 0.58 at ppm concentrations, depending on analyte and nominal levels. Plots of h and k statistics which measure the between- and within-laboratory consistency indicated inconsistencies with reported results from laboratories 5, 6, and 7. All results were retained due to the low number of participating laboratories. 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.

ILS Methods

ILS Participating Laboratories

The canister method was based on a validation study by a single laboratory [4]. 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. Ten laboratories were engaged with one lost due to attrition. Laboratories were scheduled together to receive the test samples when possible to reduce the number of reference samples needed for quality assurance. Laboratories were numbered 0 to 8 for anonymity at aggregation, where laboratory 0 was the reference laboratory. Individual laboratory results were given to each participating laboratory upon completion. A protocol, a draft NMAM method, and a results template were provided by email to each participating laboratory along with a certified gas standard to construct a preliminary calibration curve at least two weeks prior to receiving the test samples.

Laboratories conducted the study between September 2013 and August 2014 with one laboratory (laboratory 6) repeating the study in October 2015 due to poor performance with biases ranging from -1.0 to 2.75, attributable to instrument variability and exceeding the recommended sample storage time (30 days). After the ILS study, sample storage stability was demonstrated to be 58 days for most analytes.

For the most part, contract laboratories were equipped to analyze canisters using EPA Method TO-15 which is a sensitive method for analyzing ambient air toxics. Analysis of TO-15 canister samples requires the use of a preconcentrator with a large injection volume ranging from 250 to 500 mL. The reference laboratory injected 250 mL for ppb-level samples. Most participating laboratories did not have a loop available for ppm-level analysis necessitating pressure or volume dilutions to decrease instrument mass loading into their ppb-level

quantitation range. The reference laboratory, therefore, used two techniques to assess ppm-level concentrations: nitrogen pressure dilution and loop injection. Since most laboratories performed pressure dilutions (except laboratory 3 which used a 1 mL loop injection), these data are included for ppm-level reference laboratory data (laboratory 0).

ILS Study Design

The test method was challenged at two concentration ranges (ppb and ppm) with three nominal levels (low, medium, high) per concentration range. The nominal levels were 5, 10, and 15 ppb and 0.8, 1.3 and 1.7 ppm. Three replicate canisters at each concentration were tested including a set analyzed in-house to assess spike generation. Each canister contained a mixture of 17 analytes. Two laboratory blanks with ultra-high purity nitrogen were shipped with the samples. The first round of testing involved two laboratories and served as a pilot study to identify any issues with the study protocol or method instructions. No issues were revealed during the pilot study.

ILS Spike Preparation

PPB-range samples were prepared from a gas standard (Linde, Braddock, PA) using flow dilution with nitrogen or using pressure dilutions with nitrogen. Linde is an ISO 17034-accredited reference material provider. PPM-range samples were prepared using pressure dilutions with nitrogen. Most samples were prepared in 450 mL canisters, except for laboratory three who requested 6 L canisters for ppb-range spikes to enable multiple injections. Two canisters for each laboratory were pressurized with nitrogen for laboratory blanks. Each canister was spiked with all 17 analytes. Example canister data are shown for laboratory 6 at 0.8 ppm in Table 10. Multiple spike batches were required due to canister equipment inventory and logistics in preparation: five spike batches for ppb-level and eight spike batches for ppm-level. Except for the reference laboratory, each laboratory analyzed canisters from just one spike-batch. For ppm-level each lab 1 to 8 analyzed canisters from a different spike-batch. For ppm-level spike batch 6 and 7, the generation procedure was changed from a manifold system that simultaneously produced up to nine canisters at a given concentration to a master cylinder preparation of a given concentration followed by pressure transfers. For ppb-level, laboratories 1 and 2 analyzed canisters from the same batch, and laboratories 3, 4 and 5 analyzed canisters from the same batch. Laboratories 6, 7, and 8 each had their own spike-batches. For the statistical analysis each laboratory except the reference laboratory received three canisters at each of the three ppb levels and three canisters at each of the three ppm levels. The reference laboratory received more for some batches.

Table 10. Example canister data for laboratory 6 at 0.8 ppm nominal concentration

Analyte	Theoretical Value (ppb)	Can 526 Reported Value	Can 883 Reported Value (ppb)	Can 974 Reported Value (ppb)
2,3-Butanedione	0.8036	0.25	0.56	1.0
2,3-Hexanedione	0.7756	0.30	0.04	1.3
2,3-Pentanedione	0.7956	0.25	0.59	1.0
Acetone	0.8676	0.24	0.53	1.0
Benzene	0.8396	0.27	0.32	1.1
Trichloromethane	0.7796	0.28	0.63	1.2
d-Limonene	0.7716	0.21	0.21	1.1
Ethanol	0.7916	0.18	0.45	0.88
Ethylbenzene	0.8396	0.28	0.24	1.2
2-Propanol	0.8116	0.21	0.55	0.93
Methyl Methacrylate	0.8116	0.24	0.48	0.93
Dichloromethane	0.8116	0.26	0.52	1.1
Toluene	0.8436	0.28	0.28	1.1
α-pinene	0.7876	0.24	0.26	1.1
m,p-Xylene	0.8636	0.26	0.11	1.1
Hexane	0.8476	0.28	0.55	1.1
o-Xylene	0.8396	0.27	0.24	1.2

ILS Data Analysis

SAS version 9.3 (SAS Institute Inc., Cary, NC) was used to manage data and perform statistical analyses. JMP version 12 (SAS Institute Inc.) was used for graphics. The decision was made to include reference laboratory data from just one spike-batch, because there was no reason to give more weight to the reference laboratory than to other laboratories. The reference laboratory results from the first spike batches of ppm and ppb were used. In addition, whereas the ppm data had three replicates per batch for the reference lab, the ppb reference laboratory data for the first spike batch had six replicates. For consistency and in order to maintain equal numbers of analyses for each lab, as is done in ASTM E691 [12], only three of the six replicates for the first spike batch of reference lab data were used to obtain the variance estimates. As a check, after the above analyses were completed, the model was refitted with all six ppb replicates from the first spike batch for the reference lab. With just one exception, acetone at 10 ppb, estimated relative standard deviations never differed by more than 0.032 from those given in Table 12. (For acetone at 10 ppb, the difference of total RSD is within the 0.032 bound but the two other components differ by more.) This size difference is considered negligible. Total observations (excluding blanks) used for the results in Tables 13 and 14 equaled 2754 (9 laboratories × 17 analytes × 2 ranges × 3 levels × 3 replicates).

The 2754 observations were divided into 102 sets of 27 values, formed from the nine laboratories with three replicates at each of the six concentration levels for each analyte used in the study. For each of these 102 sets, the within-laboratory (repeatability), between-laboratory, and total (reproducibility) standard deviations were computed for the statistical model using the method provided by ASTM E691. Furthermore, since theoretical values varied slightly by batch, each standard deviation was divided by the average of the batch theoretical values for the given analyte and concentration level combination to obtain the relative standard deviation (RSD). E691 uses the analysis of variance method (ANOVA) to estimate the required standard deviations using eqs (6),

(7), (8), and (10) in ASTM E691. Example calculations of the RSDs are given in Table 11 for benzene at the 0.8 ppm level. The ASTM statistical models do not deal with samples from canisters. However, some discussion of the canister data is presented below.

Table 11. Example calculations for relative standard deviations and outlier tests for benzene at 0.8 ppm level

Batch	Lab	Theoretical Value (ppm)	Can	Reported Value (ppm)	Note	Within lab variance	Note	Lab means
1	0	0.868	895	0.763		0.014	hi mean	0.896
1	0	0.868	546	0.932				
1	0	0.868	893	0.993				
1	1	0.868	901	0.83		0		0.839
1	1	0.868	902	0.84				
1	1	0.868	946	0.847				
2	2	0.848	519	0.727		0.002		0.715
2	2	0.848	523	0.666				
2	2	0.848	532	0.753				
3	3	0.8623	964	0.83		0		0.812
3	3	0.8623	517	0.81				
3	3	0.8623	535	0.795				
4	4	0.8601	955	0.898		0	2nd largest mean	0.891
4	4	0.8601	534	0.896				
4	4	0.8601	968	0.88				
5	5	0.8597	953	0.859		0.001		0.888
5	5	0.8597	965	0.876				
5	5	0.8597	531	0.928				
8	6	0.8396	526	0.27	largest variance	0.217	low mean	0.563
8	6	0.8396	883	0.32				
8	6	0.8396	974	1.1				
6	7	0.8043	995	0.85		0.001		0.877
6	7	0.8043	534	0.88				
6	7	0.8043	533	0.9				
7	8	0.8044	906	0.658		0	2nd lowest mean	0.655
7	8	0.8044	947	0.662				
7	8	0.8044	979	0.645				
	theoretical average	0.846044			Avg within lab variance	0.026	variance of means	0.0146
							Between lab variance	0.0058
							Stdev	0.077
	Within lab std dev	0.16	Between lab std dev	0.077	Total std dev	0.18		
	within lab RSD	0.19	between lab RSD	0.09	total RSD	0.211	mean lab mean	0.793

	Test Statistics			1% values
Grubbs1,hi =	0.855	(hi mean-mean average)/stdev	<	2.387
Grubbs1, low=	1.901	Abs((low mean-mean average)/stdev)	<	2.387
Grubbs2, hi=	0.776	6/8*var(without 2 highest mns)/var of means	>	0.0851
Grubbs2, low=	0.219	6/8*var(without 2 lowest mns)/var of means	>	0.0851
Cochran	0.92	largest variance/variance sum; significant for lab 6	>	0.573

ASTM E691 was also used to develop h (between-laboratory) and k (within-laboratory) consistency statistics prior to outlier removal. Critical values are 2.23 and -2.23 for h-statistic and 2.09 for k-statistic (from Table 5 of ASTM E691). Data were screened for possible outliers by investigating data points in h,k-plots. Outlier tests were performed for each analyte, concentration level combination for which the total RSD was greater than 0.6, using a two-step removal rule, adapted from ISO 5725 [13]. In step one, the highest and lowest laboratory means were used in separate Grubbs tests for comparison to the two-tailed critical value (2.387, for 9 laboratories, 1% level from Table 5 of ISO 5725, see Table 11 for example calculation). If the critical value was exceeded in either test, then all data from the responsible laboratory were removed (n=51 removed) for the particular analyte, concentration level combination. In step two, if no outliers were removed in step one, an additional Grubb's test was done by computing the statistic based on the two largest or two lowest laboratory means. If these statistics are less than the 1% critical value (0.0851, for 9 laboratories, from Table 5 of ISO 5725, see Table 11 for example calculation) then all of the data from responsible laboratories were removed (n=24 removed). A total of 2.7% (75/2754) were removed, leaving 2679 data points. After removal, only one analyte, 2,3-Hexanedione at 5 ppb, had total RSD greater than 0.6 (Table 13). Measurements that were removed by this removal rule were not used in subsequent computations of the RSDs, which are shown in Tables 13 and 14. Laboratories with poor performance were contacted regarding these data to investigate potential causes for outlying data.

In the process described above, the aim was not to systematically remove all outliers. The procedure was only applied to analytes with very large total RSDs, those greater than 0.6. The largest RSD was about 1.9. The 75 values mentioned above were taken from 21 different analyte, nominal combinations. For the 18 (of the 21) different ppb-range combinations, the ratio of between-laboratory to within-laboratory RSD was at least 1.55, while for the remaining three ppm-range combinations, two of them had between-laboratory RSDs less than within-laboratory RSD. The bulk of the data suggested that the main reason for the large total RSDs was large between-laboratory variability, for which outliers are identified by the two Grubbs tests. These identified outliers were always outliers larger than the other data. (Recall that the tests are two-sided.) In addition, all except six of the outliers were from two labs which each made some changes to the method instructions (discussed below). After removal, all total RSDs were less than 0.51, with one exception with an RSD greater than 0.6, 2,3-Hexanedione at 5 ppb. Neither Grubbs outlier test gave a significant result. The decision was made not to remove the data. It happens that the Cochran test (from Table 4 of ISO 5725) did identify one outlying laboratory, but removal of that laboratory changed the RSDs by very little.

The above procedure differs somewhat from that in ISO 5725 which suggests that the Cochran test for outliers in within-laboratory variability be used first. It happens that of the 21 different analyte, nominal combinations, 18 had significant results by Cochran's test. For 15 of these 18, the laboratories with the largest variances were also responsible for the large Grubbs statistics (which included the two ppm analytes for which between RSD was less than within RSD). Thus, by both Grubbs and Cochran tests there were three laboratories for which a different laboratory was identified by the Cochran test than by the Grubbs tests, in which case the within RSD is larger than it would be if the laboratory had been removed. In summary, by the two-step removal rule used here, most of the extremely large outliers were removed by simple application of the rule.

ILS Results/Discussion

ILS Blank Canisters

Laboratories 5 – 7 reported analyte concentrations in UHP nitrogen blank canisters. The highest blank level reported by laboratory 7 was 19 ppb for m,p-xylene. The same UHP nitrogen tested by the reference laboratory during the same period showed m,p-xylene below the detection limit (<0.28 ppb). Most laboratories reported analyte concentrations in the blanks less than detectable or less than one ppb. No blank corrections were used on reported spike canister results.

Variation of Spike Batches and Estimation of Bias, Based on Reference Laboratory Canisters

It is possible that the estimates in Tables 13 and 14 are larger than they would be if all samples at each concentration level had been collected in a single batch for ppb and a single batch for ppm. Recall that the reference laboratory made measurements in every spike batch, but only the reference laboratory results from the first batch were included in the data used for Tables 13 and 14. If only that laboratory's data are used and if that laboratory is not overly variable, we would expect that the between batch RSD, would be much smaller than those from the inter-laboratory study results. When a laboratory is used only in one batch and a batch includes only one laboratory, there is no way to know whether the data indicate something about the laboratory or about the batch. This issue makes the data analysis more complicated, as discussed below. Only the reference laboratory data avoid this problem.

The statistical models of interest for measurements (x) of an analyte at a concentration level are given below. These models, for both ppb and ppm (102 data sets with 27 measurements in each set) refer to nine laboratories and three samples per laboratory

M1: $x_{ls} = \mu + a_l + b_{ls}$,

where μ is the true mean of the analyte, a_l is the difference from the overall mean of laboratory l, and b_{ls} is the difference from the lab l mean of the sth sample of lab l. a_l and b_{ls} are normally distributed with means 0, and variances σ^2_l and σ^2_{ls} respectively.

It is convenient to express the variances relative to the mean. We do not know the overall mean, but we think that the average of the batch theoretical values, M, for the analyte at the concentration level is a good guess. We rewrite model M1 as:

M2: $x_{ls}/M = \mu/M + a_l/M + b_{ls}/M$.

From model M2, we refer to σ_l/M and σ_{ls}/M, respectively, as the between laboratory and within laboratory relative standard deviations (RSD).

In Table 11, the within, between, and total laboratory standard deviations were computed and then converted to RSDs by dividing these estimates by the average of the spike batch theoretical means, 0.846. This approach corresponds to model M1. In model M2 estimation, the reported values (ppm) are divided by 0.846, and the same calculations are carried out, as is done for model M1. However, the estimates for within, between, and total laboratory standard deviations are actually the RSDs because we have already divided by 0.846.
There is another source of variation here, that between batches:

M3: $x_{ls}/M = \mu/M + a_l/M + c_b/M + b_{ls}/M$,

where σ_b/M is the RSD for between batch variability component, c_b, which is normally distributed with mean 0.

The concern is that between lab RSDs from the inter-laboratory analysis may be increased due to the batch variability, which is due to batch generation changes over time. The statistical model used in E691 (M1 or equivalently M2) gives just two RSD estimates - between and within laboratory. For the ppm data only batch 1 has two laboratories (laboratory 1 and the reference laboratory.) The other batches each have measurements from just one laboratory and each laboratory is in just one batch. For this case the estimated between laboratory RSD from the E691 model will include all between laboratory variability and almost all between batch variability, because there is no way to separate these two sources because of the design. The ppb data are more complicated because batches 1 and 2 each include three laboratories; batches 3, 4, and 5 each have just one laboratory. (Batch 3 originally included laboratories 6 and 7 data, but those data were removed and laboratory 6

was evaluated again in batch 5.) We must assess here how much the batch RSDs increases the between laboratory estimate from models M1 and M2.

The statistical model including the variable “batch” (M3) has been fitted, but estimates are not reliable. This model will not work for ppm because almost every laboratory is in its own batch, and between batch and between laboratory variability cannot be separated. For ppb, there is some replication of laboratory in batch, but, there are also three laboratories which are each used in one batch. The resulting estimates from this larger model for both batch and laboratory are difficult to interpret.

In fact, for our purposes, we do not require precise estimates of between batch RSDs. Also, there is reason to think that these RSDs are small. For every batch of analyte and concentration level for both ppb and ppm, a theoretical concentration was specified. For ppb, the 51 RSDs of the theoretical concentrations (relative to their average) for the 51 analyte, concentration levels never exceeded 0.1. The corresponding limit for ppm was 0.05. These estimates indicate small between batch variability, but we also want a more data-based estimate for the batches. The E691 model can give sensible estimates if we can show that the batch RSDs do not enlarge the between laboratory variability by much.

For both ppm and ppb the issue is whether we can use the estimates of model M2 when the data come from model M3. For ppm, as stated above, we know that the ppm between laboratory estimates will be inflated by the variability associated with the between batch RSD. For ppb the design is more complicated. Computer simulations using the E691 model (M2) indicate that, on average, the between batch relative variances (squares of RSDs) do not increase the between laboratory relative variance estimates (squares of the RSDs) more than the true value of the between batch variance. A summary of the simulations is in Table 12. Columns 2, 3, 4, and 5 give the specified values needed for the simulations.

Table 12: Computer simulations of between batch influence on between laboratory relative variance estimates

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7	Column 8
	RSD, within Laboratories	RSD, between batches	RSD between laboratories	Square root of sum of RSD^2(s) from columns 3 and 4	Estimated between laboratory RSD	Estimated within laboratory RSD	True between laboratory RSD, from formula
Simulation 1	0.1	0.1	0.5	**0.510**	**0.507**	0.11	**0.508**
Simulation 2	0.2	0.2	0.4	**0.447**	**0.438**	0.2	**0.440**
Simulation 3	0.2	0.2	0.3	**0.361**	**0.354**	0.2	**0.351**
Simulation 4	0.15	0.15	0.15	**0.212**	**0.205**	0.15	**0.203**
Simulation 5	0.1	0.075	0.075	**0.15**	**0.101**	0.1	**0.102**

Note: For column 2-5 RSDs, specified parameter settings for the 2500 normally distributed data samples. For column 6 and 7, average RSD Estimates from simulations from Model M2 (square root of simulations mean value for either between lab or within lab variance)

Following the structure of most of the ppb data, each simulation sample had 27 simulated values, three values for each of nine laboratories with specified between laboratory RSD. In addition, there were five batch values, which follow the structure of the ppb data, using the specified RSD for batch, and are consistent with model M3. There were 27 residual error values using the RSD specified by the simulation. Note that the RSD corresponding to the sum of the true between batch and between laboratory relative variances (Column 5) always exceeds the RSD corresponding to the estimated laboratory relative variance (Column 6). It was determined mathematically that the statistical expected value of the between laboratory mean square for laboratories equals the square root of the sum of the RSD^2 for laboratories + 5/6 RSD^2 for batches (Column 8) (See Appendix A for a derivation of this result). Columns 6 and 8 agree very well, which supports the accuracy of the formula used in Column 8. Columns 2 and 7 agree very well, showing that the estimate of average within laboratory RSD is close to the true value. Thus, the overestimate in the between laboratory RSD does not exceed that associated with the between batch RSD. Thus, for both ppm and ppb the overestimate in laboratory RSD will not exceed that associated with the between batch RSD. (Because of removal of outliers, some analytes had fewer than nine laboratories. For those situations, too, computations indicate that the overestimate in laboratory RSD will not exceed that associated with the between batch RSD.)

In order to get a data-based estimate of batch variability, the reference laboratory analyses from every batch were used to calculate RSD estimates for the between batch variability and within batch variability for each analyte, concentration level combination for ppb and ppm. The model used for these variances is analogous to model M2, except that in place of a_l / M and b_{ls} /M, we use a_b / M and b_{bs} /M, which, respectively, denote between batch and within batch components. The variabilities associated with these data would include both the batch variability over time and that of the reference laboratory variability. In the analyses discussed here the data include ppb data for six canisters from batches 1, 2 and 5 and three canisters from batches 3 and 4. Two

measurements at 5 ppb for each of three analytes were removed because of Grubbs tests. PPM results are based on three canisters for each of seven batches, except that at the 0.8 ppm level, two canisters were removed based on Grubbs tests.

We are interested in determining how much the between laboratory RSD is inflated by the between batch variability. Recall that the RSD values are relative to the average of the batch theoretical values for the given analyte and concentration level. Thus, all RSDs for each analyte, concentration level combination are divided by this average theoretical value. Each RSD can be converted to a standard deviation by multiplying it by the theoretical average. This is correct for both the model M2 for the laboratory data and the model discussed in the previous paragraph for the reference laboratory data. In accordance with the results shown above for ppm and ppb, a modified result for the laboratory RSD_ILS was calculated as:

lab RSD_ILS (mod) = $[(\text{lab RSD\_ ILS})^2 - (\text{batch RSD\_Reflab})^2)]^{0.5}$,

In terms of the Table 11 data, lab RSD_ILS squared value is $(0.077/0.846)^2 = 0.09^2 = 0.0081$, where 0.846 is the average theoretical value for the analyte at the given concentration, and 0.077 is the estimated standard deviation from the ILS. From the reference laboratory analysis, the batch RSD Reflab value is 0.024 / 0.846 and $(0.024/0.846)^2 = 0.028^2 = 0.00078$. Thus, lab RSD_ILS (mod) = sq. rt$((0.077/0.846)^2 - (0.024/0.846)^2)$ = sq. rt. (0.0081- 0.00078) = 0.086. The lab RSD_ ILS value was 0.09. Thus the modified value differs from the estimated RSD by 0.09-0.086 = 0.004, a small difference. This supports the idea that the between batch variability is small compared to the between laboratory variability. The estimate 0.086 represents the estimate of the between laboratory RSD, after removing the variability associated with the between batch variability. We know from the statistical analysis results above that, on average, the estimated between laboratory RSD^2 from the ILS study will not exceed the true between laboratory RSD^2 by more than the between batch RSD^2 (here 0.00078); by removing this excess we can determine the effect of between batch variability on the between laboratory RSD estimates.

The aim of this work is not to replace the RSDs of the ILS by the modified values. We wish to see if the modified ("mod") estimates support the reasonableness of the unmodified estimates. We will assess this by determining the size of the difference between the original estimates and the modified estimates. Note that there are models for which the RSDs from the reference laboratory data exceeded those from the ILS study, which led to negative differences of $[(\text{lab RSD\_ ILS})^2 - (\text{batch RSD\_Reflab})^2)]$, for which a square root could not be taken to calculate lab RSD_ILS (mod). There were twelve negative differences for $[(\text{lab RSD\_ ILS})^2 - (\text{batch RSD\_Reflab})^2)]$. For all twelve differences, lab RSD_ ILS values were less than 0.1, and six were less than 0.01. This kind of result is not unexpected, where the variances are based on models with small sample size and when lab RSD_ ILS values are small. Set DIF=lab RSD_ILS -lab RSD_ILS (mod) when lab RSD_ILS (mod) can be calculated. Ideally DIF values are small, which indicates that when the variability associated with between batch variation is removed, the between laboratory estimates change little. There were four instances among the 102 models where DIF exceeded 0.05. The largest difference was 0.11. This result, together with the fact that the cases for which the reference laboratory between batch RSD estimate exceeded the ILS between laboratory RSD estimate occurred when the between laboratory ILS was less than 0.1, suggests that there seems little indication that between batch variability had large effect for many of the laboratory RSD estimates. Also we recognize that the between batch estimates from the reference laboratory data are overestimates, since the reference laboratory data include that lab's variability, in addition to batch variability over time. Recall that the reference laboratory results from the first spike batches of ppm and ppb were used for the results in Tables 13 and 14. The above analysis indicates that estimated between laboratory RSDs from the inter-laboratory study would not vary much if another reference laboratory spike-batch were used, since the reference laboratory variability was usually much smaller than the between laboratory variability.

Bias across spike batches was also estimated using the reference laboratory data to ensure consistency in spike batch generation over time. Bias was fairly consistent, falling within ±10% of the theoretical value for most analytes and nominal levels for both ppb-range (Table B1, Appendix B) and ppm-range (Table B2, Appendix B). Representative box plots of bias are presented for ethanol (Figure 1 left) and for 2,3-butanedione (Figure 1 right). Excursions outside the ±10% criterion were observed for ethanol, which is notoriously difficult to analyze due to its low molecular weight and polarity, in spike 3 and 4 at 5, 10, and 15 ppb (Figure 1 top left). Additional excursions were observed for ppm-level range for ethanol (Figure 1 bottom left). Ethanol for spike batch 6 and 7 showed a positive bias compared to spike batches 1 to 5 due to the change in generation procedure. For 2,3-Butanedione, bias across spike batches was more stable with many boxes falling within the ±10% of the theoretical value.

Estimates of total RSD presented here are not significantly affected by these shifts in bias among different spike batch generations. Shifts in bias across batches are associated with between-batch variability, and as was stated above, the between-batch variability results in only small increases in the reproducibility RSD estimates for most analytes.

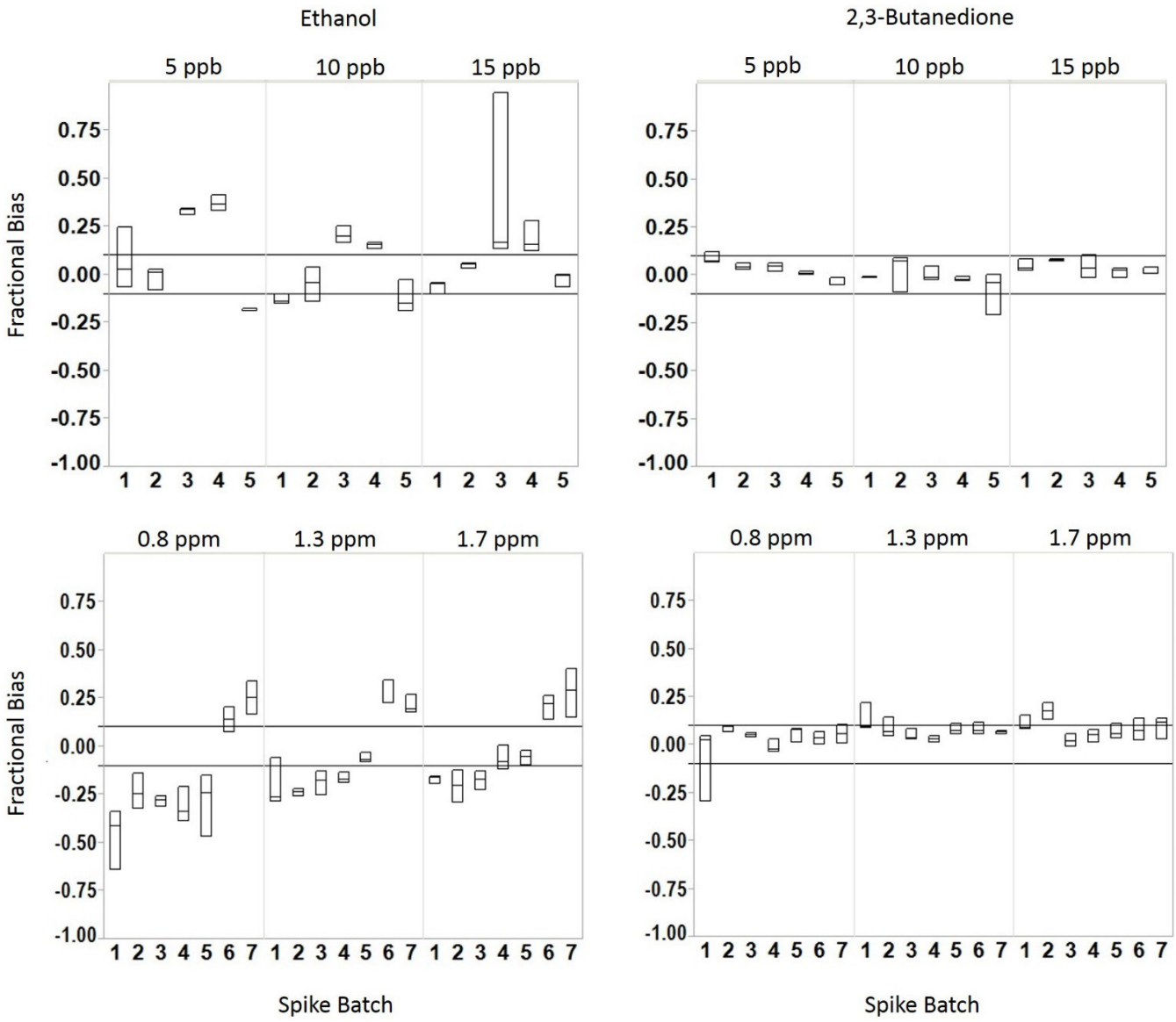

Figure 1. Representative box plots of reference laboratory bias across spike batches and nominal level for ethanol (left) and 2,3-butanedione (right). n=3 per box. Solid line represents +/- 10% bias criterion.

ILS Canister Precision

ILS Precision Estimates

Recall that no effort was made to remove every potential outlier. Only for analyte, nominal combinations with total RSD greater than 0.6 were the results of outlier tests used to remove data, and, for ppm, there were just three analyte, nominal combinations in this range, from each of which the outlying laboratory's data were removed. In this discussion we consider canister variability, whereas in previous outlier discussion we considered only laboratory variability. For instance, for 0.8 ppm in Table 11, only three of seventeen estimates of between-laboratory RSDs exceed within-laboratory RSDs. Laboratory 6 gave a significant result for the Cochran test for outlying variance (from ISO 5725, Table 4) for 12 of the 17 models used to produce the variance estimates for 0.8 ppm data in Table 11. If one canister (974) from laboratory 6 is removed, the results change so that 13 between-laboratory RSDs exceed within-laboratory RSDs (see Table 10 for the laboratory 6

concentrations by canister and Table 11 for the Cochran test calculation). However, the reproducibility RSDs change by no more than 0.025. Note that canister 974 data were not omitted from the calculations shown in Table 11. The discussion above is included in order to show the sensitiveness of the results, not to remove any more data. We also note that there is no way to know whether between-batch variability is introduced during the generation process or by the participating laboratory during analysis.

The ppb-level results in Table 13 show mostly higher between- than within-laboratory RSDs (35/51 or 68.6%), and although the ppm do not, this may be partly due to the presence of some outliers. Also, the ratio of between to within laboratory RSD is quite high for ppb, on average about two.

When analysis of variance is computed separately for each level's reproducibility values as function of analyte and concentration level, neither ppb nor ppm gives results significant at the 5% level.

There is useful information in the outlier analysis. Of the 75 values removed as outliers and not used in the estimates in Tables 13 and 14, all but six came from laboratories 5 and 7. Laboratory 7 produced 57 values, of which 42 were at 5 ppb, 12 were at 15 ppb, and three were at 0.8 ppm. Laboratory 5 produced 12, of which six were at ppb levels (three at 5 ppb and three at 15 ppb), and three at ppm levels. There were no outliers at the 10 ppb level or at the 1.7 ppm level. Thus, almost all outliers were for ppb levels. All outliers were for large magnitude measurements, that is, values larger than the mean. Thus, there is no surprise that the ppb estimates tended to have large between-laboratory RSDS than within-laboratory RSDs. In addition, ppb levels have more total variation than ppm. There are 10 reproducibility RSDs for ppb greater than or equal to 0.5 compared to three for ppm. Furthermore, there are 32 reproducibility RSDs for ppb greater than or equal to 0.3 compared to 11 for ppm. On the other hand, whereas the smallest reproducibility RSD for ppm is approximately 0.19, there are 14 ppb reproducibility RSDs less than or equal to 0.19. Thus, the ppm data have less spread in reproducibility than the ppb. Likewise, there are just two ppm within-laboratory RSDs less than or equal to 0.14 but 27 for ppb. There appear to be four ppm values less than or equal to 0.14 in Table 14, but that is just due to rounding. There are four ppb within-laboratory RSDs 0.3 or larger, compared to three for ppm. Thus, except for the high within-laboratory RSDs, ppb RSDs have a wider spread than ppm.

The reasons for these differences between ppb and ppm are not clear. It does seem that the low levels used for ppb are associated with large positive bias for some laboratories, although that does not occur at 10 ppb, where results look more like ppm level results than like ppb level results. Analytes are more alike at the ppm level than at the ppb level, in the sense that there are many ppb RSDs less than and others more than most ppm RSDs. This may mean that at high levels (ppm), the instructions for the method are followed better by all labs than at lower levels (ppb) or, perhaps more likely, method precision becomes poorer as analyte concentration decreases from ppm to ppb levels.

Also, RSDs for ppb may be influenced by some of the potential outlier laboratories, whose practices are discussed below (laboratories 5, 6, and 7).

In summary, for ppb, estimates for repeatability ranged from 0.04 to 0.55 and estimates for reproducibility ranged from 0.10 to 0.62. For ppm, estimates for repeatability ranged from 0.10 to 0.47 and for reproducibility from 0.19 to 0.58.

For comparison, ASTM D6196 provides some insight about precision estimates from thermal desorption tubes, a complementary sampling and detection technique that provides sensitive estimates of airborne VOC concentrations [14]. They reported mean ISO repeatability estimates between 0.072 and 0.216 for hydrocarbons C3 to C11 from Coker et al. [15] which are compared to canister method ILS results of within-laboratory RSDs from 0.04 to 0.55 with a median of 0.14 for ppb and from 0.1 to 0.47 with a median of 0.19 for ppm. They reported ISO reproducibility estimates between 0.259 to 0.432 compared to canister method ILS results of total

RSDs from 0.1 to 0.62 with a median of 0.37 for ppb and from 0.19 to 0.58 to with a median of 0.23 for ppm. While some of these values are higher than those reported in ASTM D6196, more laboratories were used in this study (nine vs. four).

Table 13. Between- and within-laboratory and total RSD estimates for ppb-level analytes.

Note that "Within RSD" is the same as the repeatability RSD, and "Total RSD" is the same as the reproducibility RSD.

	5 ppb			10 ppb			15 ppb		
Analyte	**Between RSD**	**Within RSD**	**Total RSD**	**Between RSD**	**Within RSD**	**Total RSD**	**Between RSD**	**Within RSD**	**Total RSD**
2,3-Butanedione	0.30	0.10	0.32	0.16	0.23	0.28	0.53	0.18	0.56
2,3-Hexanedione	0.58	0.23	0.62	0.32	0.29	0.43	0.42	0.31	0.52
2,3-Pentanedione	0.53	0.15	0.55	0.28	0.25	0.37	0.49	0.29	0.57
Acetone	0.07	0.10	0.12	0.07	0.55	0.56	0.39	0.18	0.43
Benzene	0.13	0.09	0.16	0.00	0.14	0.14	0.37	0.09	0.38
Trichloromethane	0.14	0.12	0.18	0.06	0.14	0.15	0.45	0.10	0.46
d-Limonene	0.48	0.15	0.51	0.40	0.17	0.43	0.15	0.11	0.19
Ethanol	0.30	0.17	0.35	0.35	0.36	0.50	0.09	0.10	0.13
Ethylbenzene	0.31	0.11	0.33	0.18	0.21	0.28	0.50	0.11	0.51
2-Propanol	0.28	0.32	0.43	0.34	0.14	0.37	0.13	0.08	0.15
Methyl methacrylate	0.43	0.16	0.46	0.14	0.19	0.23	0.40	0.18	0.44
Dichloromethane	0.05	0.10	0.11	0.00	0.16	0.16	0.32	0.11	0.34
Toluene	0.16	0.11	0.19	0.05	0.14	0.15	0.41	0.11	0.42
α-Pinene	0.24	0.12	0.26	0.19	0.25	0.31	0.38	0.09	0.39
m,p-Xylene	0.38	0.11	0.39	0.49	0.21	0.53	0.38	0.11	0.40
Hexane	0.08	0.10	0.13	0.09	0.04	0.10	0.38	0.11	0.40
o-Xylene	0.08	0.12	0.15	0.26	0.24	0.36	0.57	0.09	0.58

Note: Outliers removed prior to generation of RSD estimates.

Table 14. Between- and within- laboratory and total RSD estimates for ppm-level analytes.

Note that "Within RSD" is the same as the repeatability RSD, and "Total RSD" is the same as the reproducibility RSD.

	0.8 ppm			1.3 ppm			1.7 ppm		
Analyte	**Between RSD**	**Within RSD**	**Total RSD**	**Between RSD**	**Within RSD**	**Total RSD**	**Between RSD**	**Within RSD**	**Total RSD**
2,3-Butanedione	0.14	0.18	0.23	0.05	0.19	0.20	0.12	0.15	0.19
2,3-Hexanedione	0.00	0.32	0.32	0.21	0.26	0.33	0.22	0.24	0.32
2,3-Pentanedione	0.29	0.25	0.38	0.15	0.22	0.26	0.18	0.16	0.24
Acetone	0.10	0.17	0.20	0.34	0.47	0.58	0.14	0.15	0.20
Benzene	0.09	0.19	0.21	0.13	0.18	0.22	0.17	0.15	0.22
Trichloromethane	0.04	0.21	0.21	0.15	0.19	0.25	0.14	0.20	0.25
d-Limonene	0.32	0.27	0.41	0.13	0.23	0.26	0.21	0.17	0.27
Ethanol	0.32	0.39	0.51	0.21	0.17	0.27	0.26	0.10	0.28
Ethylbenzene	0.12	0.23	0.26	0.00	0.22	0.22	0.19	0.14	0.23
2-Propanol	0.16	0.29	0.33	0.13	0.17	0.22	0.12	0.15	0.19
Methyl methacrylate	0.15	0.18	0.23	0.07	0.19	0.20	0.13	0.14	0.19
Dichloromethane	0.04	0.19	0.19	0.15	0.17	0.23	0.12	0.18	0.21
Toluene	0.17	0.20	0.26	0.09	0.19	0.21	0.18	0.14	0.23
α-Pinene	0.14	0.22	0.26	0.00	0.23	0.23	0.19	0.16	0.24
m,p-Xylene	0.46	0.24	0.52	0.23	0.23	0.33	0.25	0.18	0.30
Hexane	0.07	0.18	0.19	0.14	0.17	0.22	0.15	0.16	0.22
o-Xylene	0.12	0.24	0.27	0.00	0.23	0.23	0.19	0.16	0.24

Note: Outliers removed prior to generation of RSD estimates.

h- and k-Statistics

k-Statistic for ppb-level within-laboratory variability by analyte shows a majority of the laboratories and analytes were less than the 2.09 criterion (413/459 or 90.0%) (Figure 2, 3, and 4). Most of these excursions above the criterion were laboratory 7 at 5 ppb (Figure 2), laboratory 5 at 10 ppb (Figure 3), and laboratories 8 and 6 at 15 ppb (Figure 4).

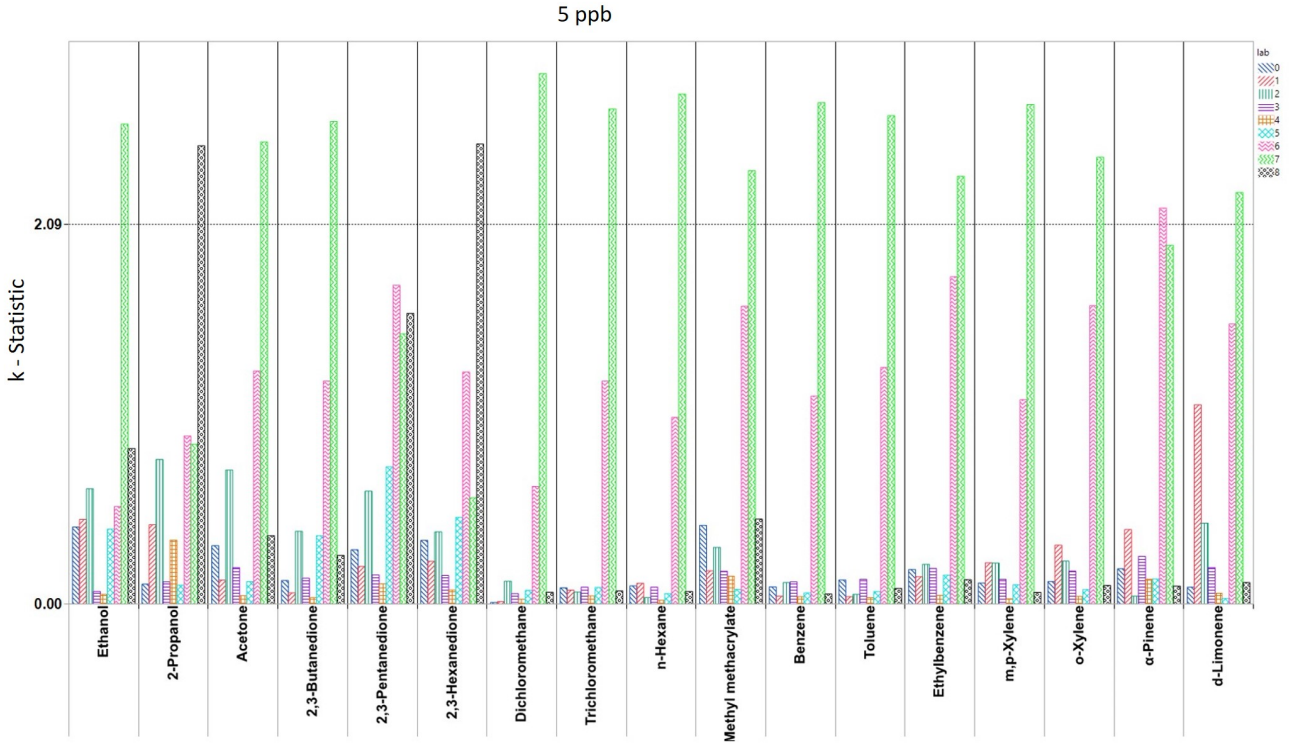

Figure 2. Within-laboratory statistic (k-plot) for 5 ppb nominal level. Dashed line = 2.09 criterion.

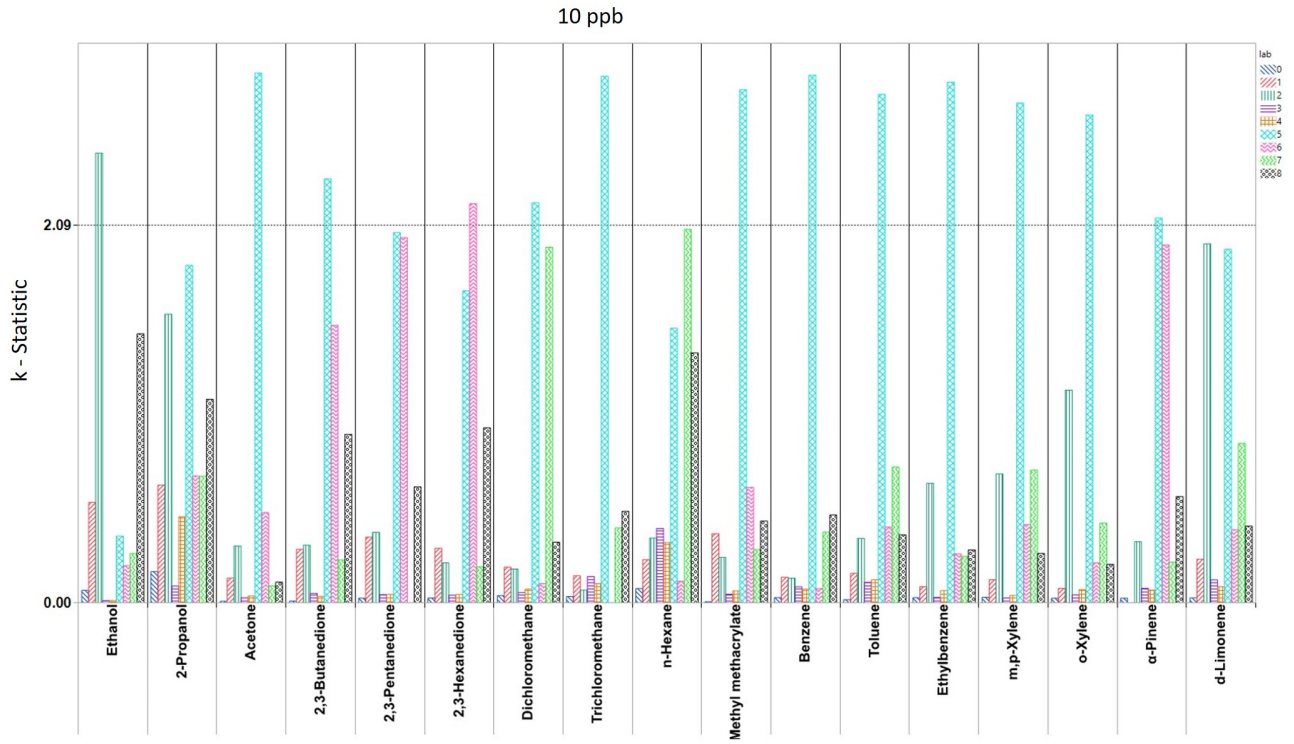

Figure 3. Within-laboratory statistic (k-plot) for 10 ppb nominal level. Dashed line = 2.09 criterion.

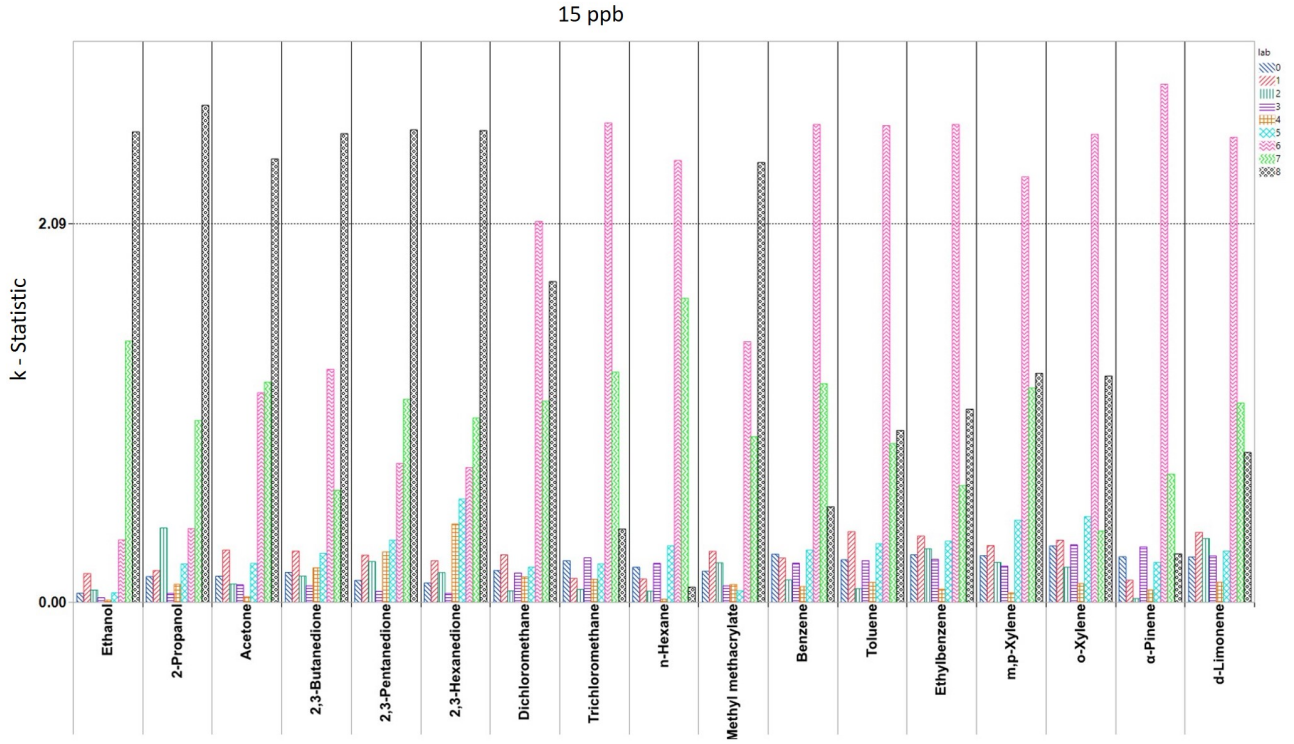

Figure 4. Within-laboratory statistic (k-plot) for 15 ppb nominal level. Dashed line = 2.09 criterion.

k-Statistic for ppm-level within-laboratory variability by analyte shows most laboratories and analytes were less than the 2.09 criterion (428/459 or 93.2%) (Figures 5, 6, and 7). Most of these excursions above the criterion were laboratory 6 at 0.8 ppm (Figure 5), laboratory 5 at 1.3 ppm (Figure 6), and laboratory 6 at 1.7 ppm (Figure 7).

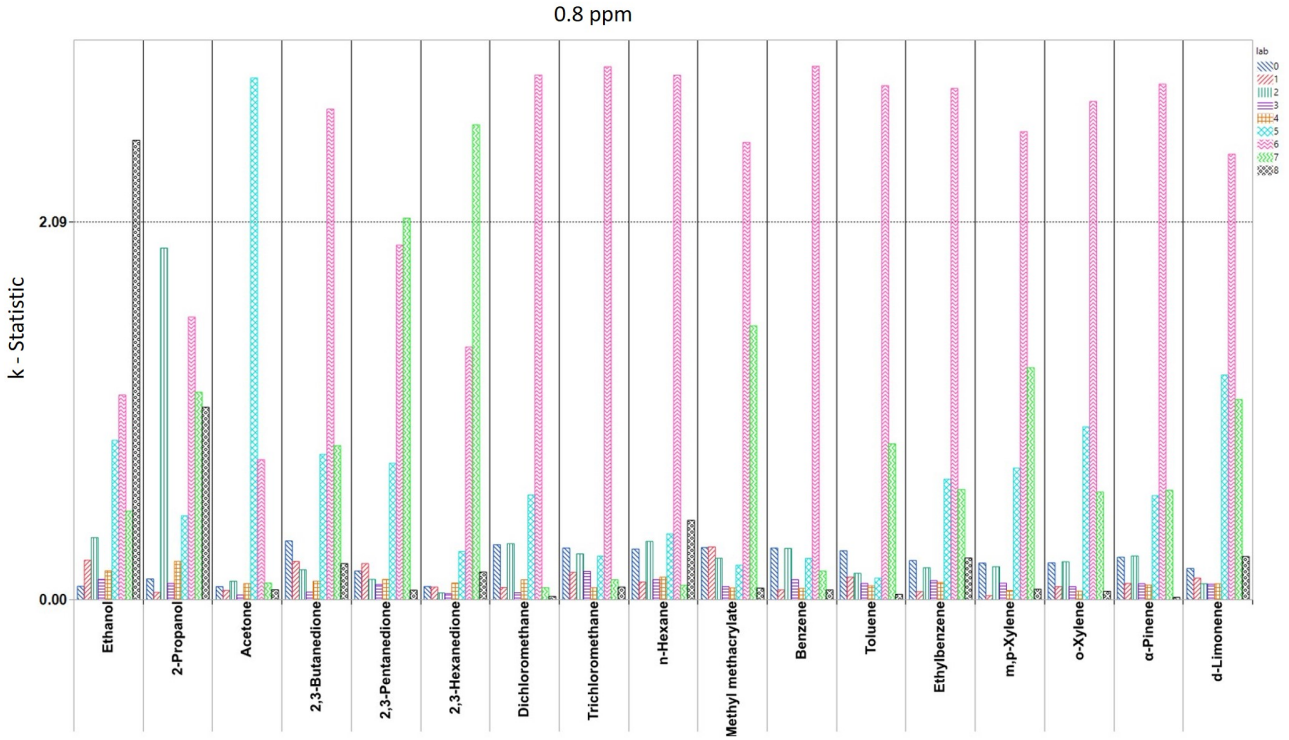

Figure 5. Within-laboratory statistic (k-plot) for 0.8 ppm nominal level. Dashed line = 2.09 criterion.

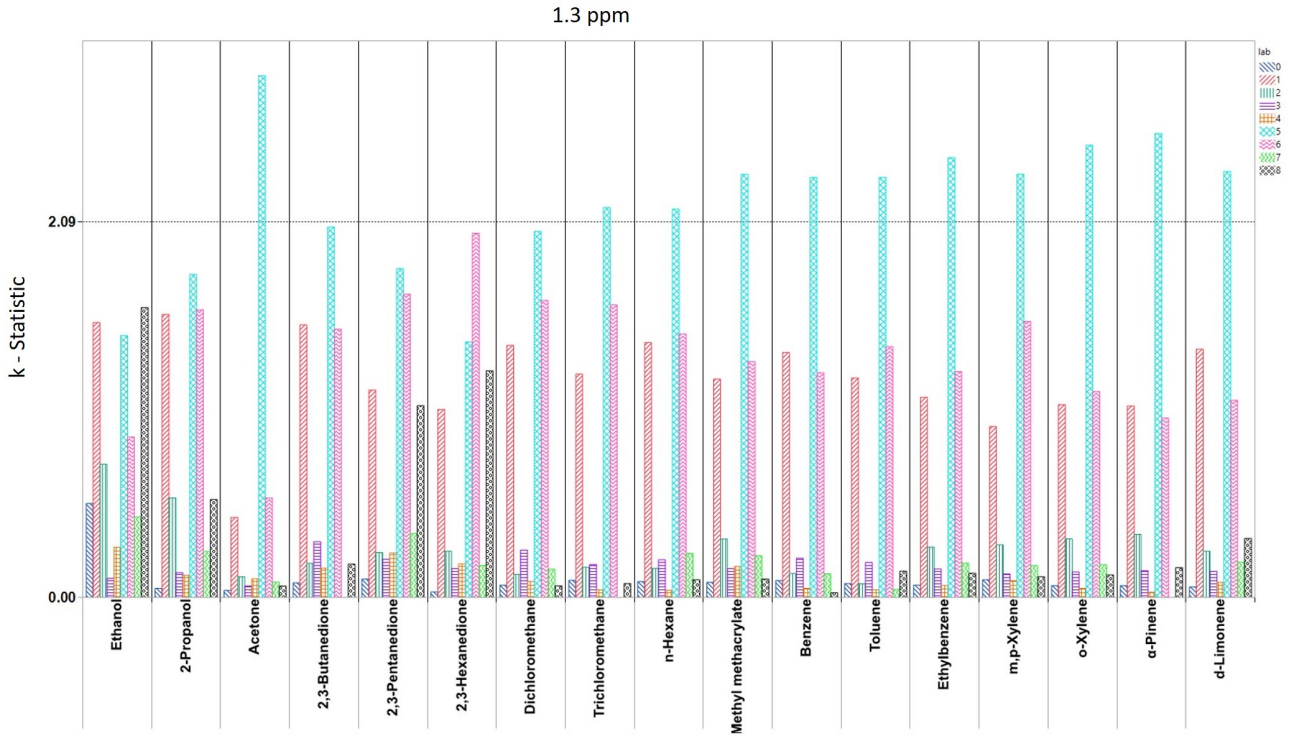

Figure 6. Within-laboratory statistic (k-plot) for 1.3 ppm nominal level. Dashed line = 2.09 criterion.

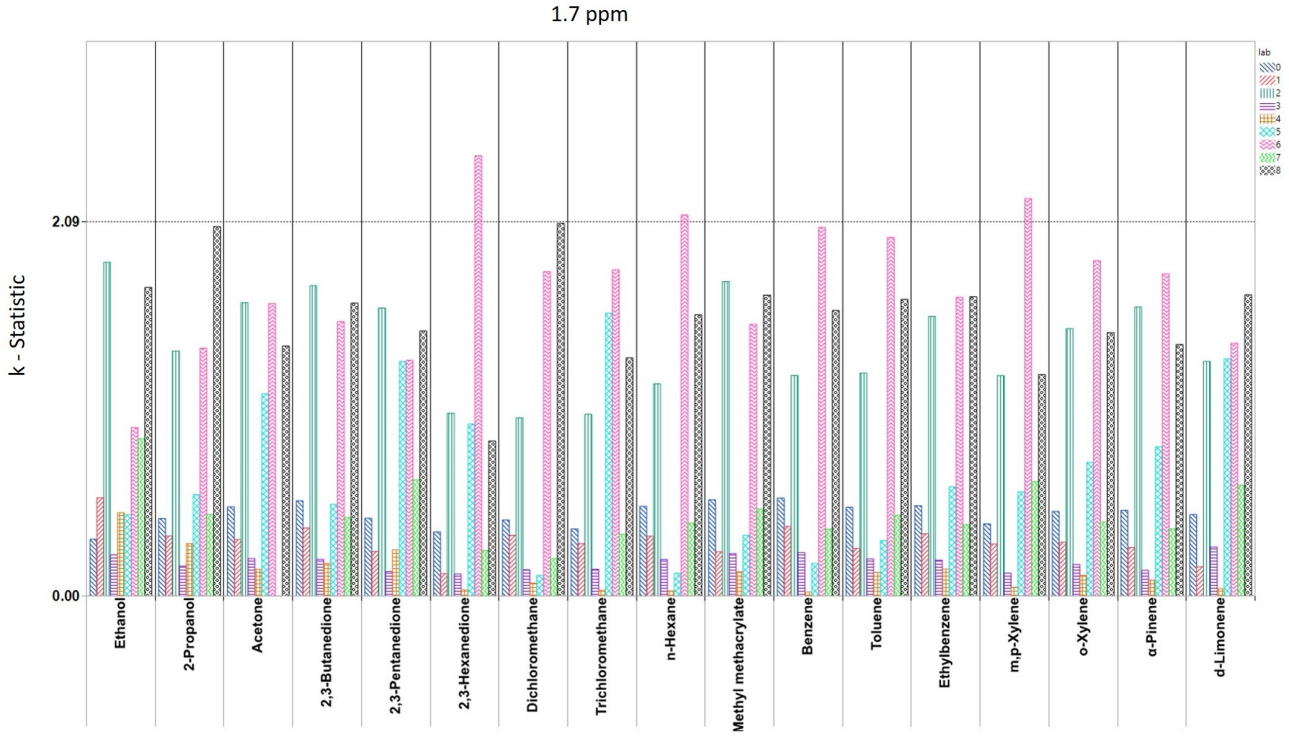

Figure 7. Within-laboratory statistic (k-plot) for 1.7 ppm nominal level. Dashed line = 2.09 criterion.

h-Statistic for ppb-level between-laboratory variability by analyte shows most laboratories and analytes (430/459 combinations or 93.7%) were within the ±2.23 criterion (Figures 8, 9, and 10). Most of the excursions outside the criterion were due to laboratory 7 (25/29 excursions) at 5 ppb (Figure 8), at 10 ppb (Figure 9), and at 15 ppb (Figure 10). The rest were due to laboratory 5 at 10 ppb (Figure 9). A pattern of mostly positive h-values for laboratory 5 and laboratory 7 is opposed to the mostly negative h-values for other laboratories, although some laboratory/analyte combinations do not follow this trend (e.g., laboratory 6 positive h-values for some analytes at 5 ppb but negative at 10 ppb and at 15 ppb).

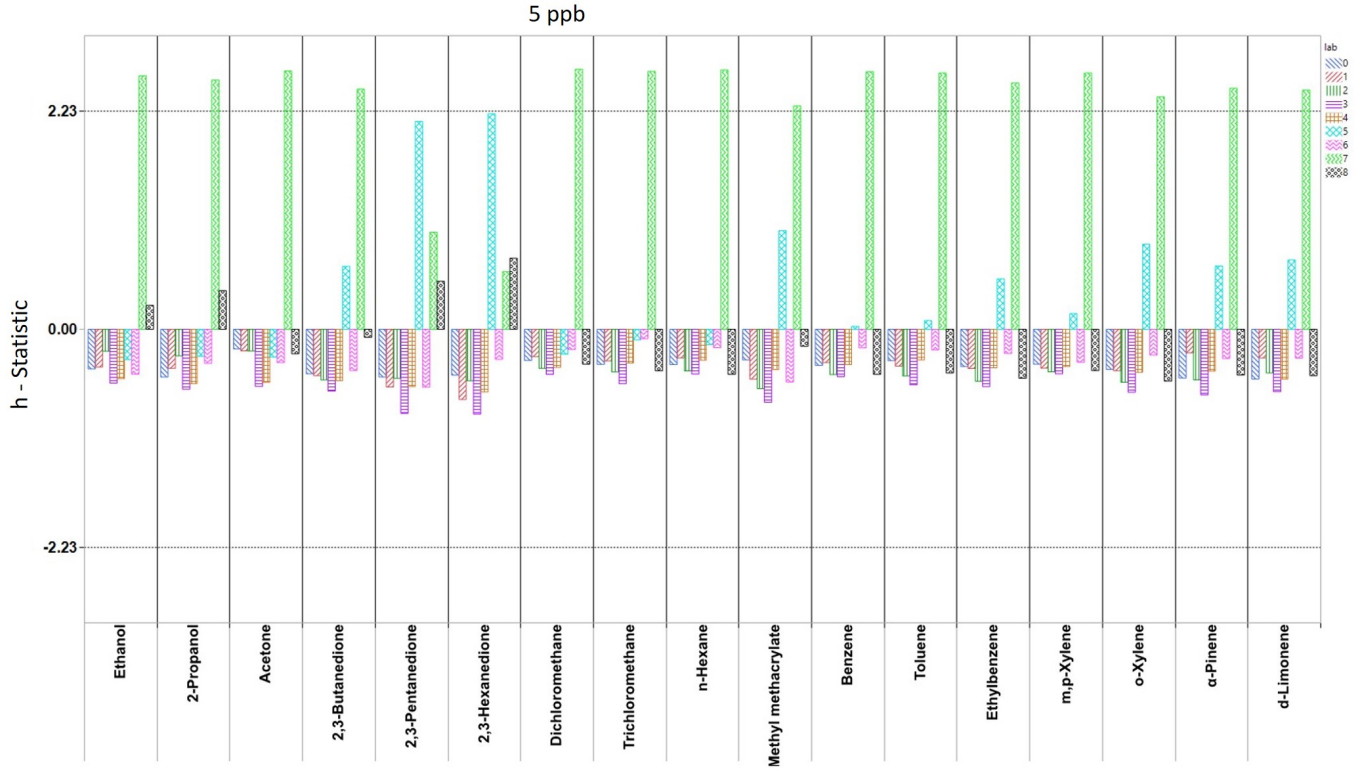

Figure 8. Between-laboratory statistic (h-plot) for 5 ppb nominal level. Dashed line = 2.23 to -2.23 criteria.

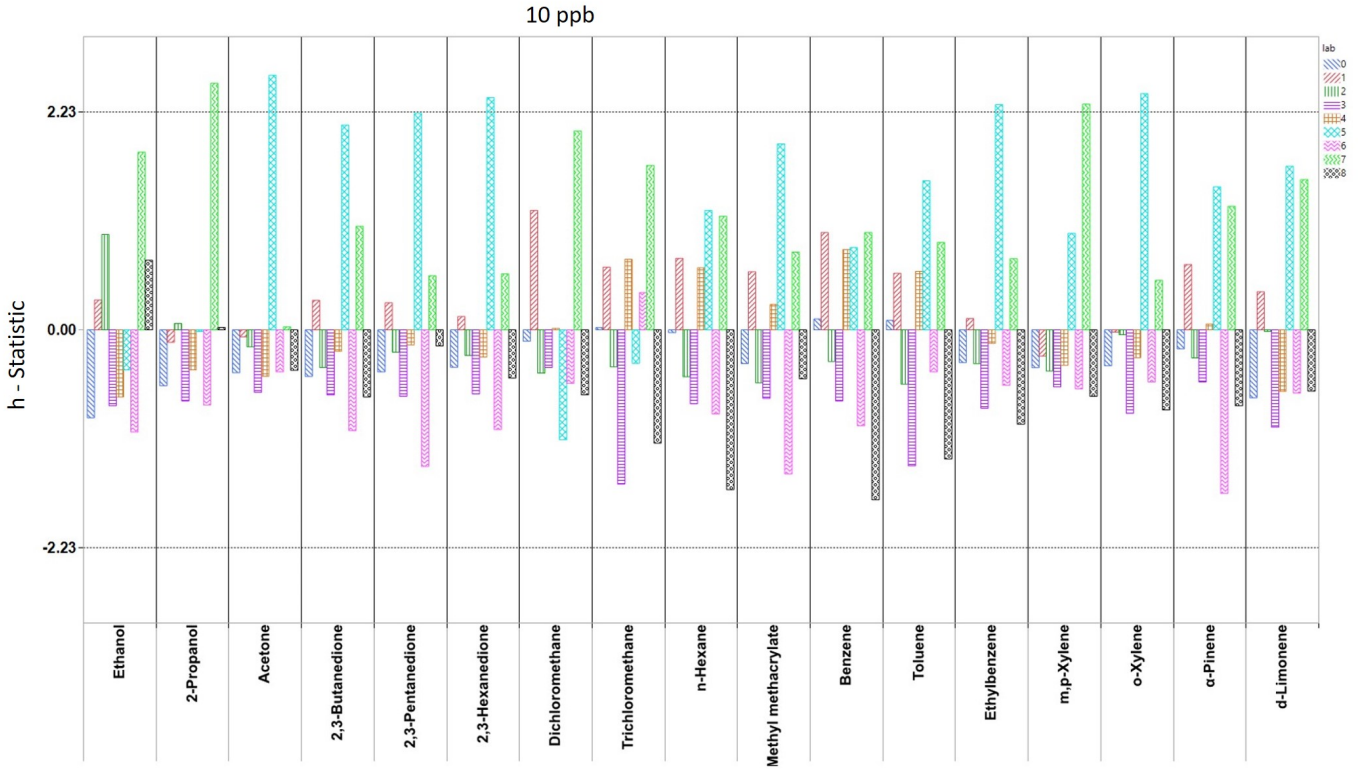

Figure 9. Between-laboratory statistic (h-plot) for 10 ppb nominal level. Dashed line = 2.23 to -2.23 criteria.

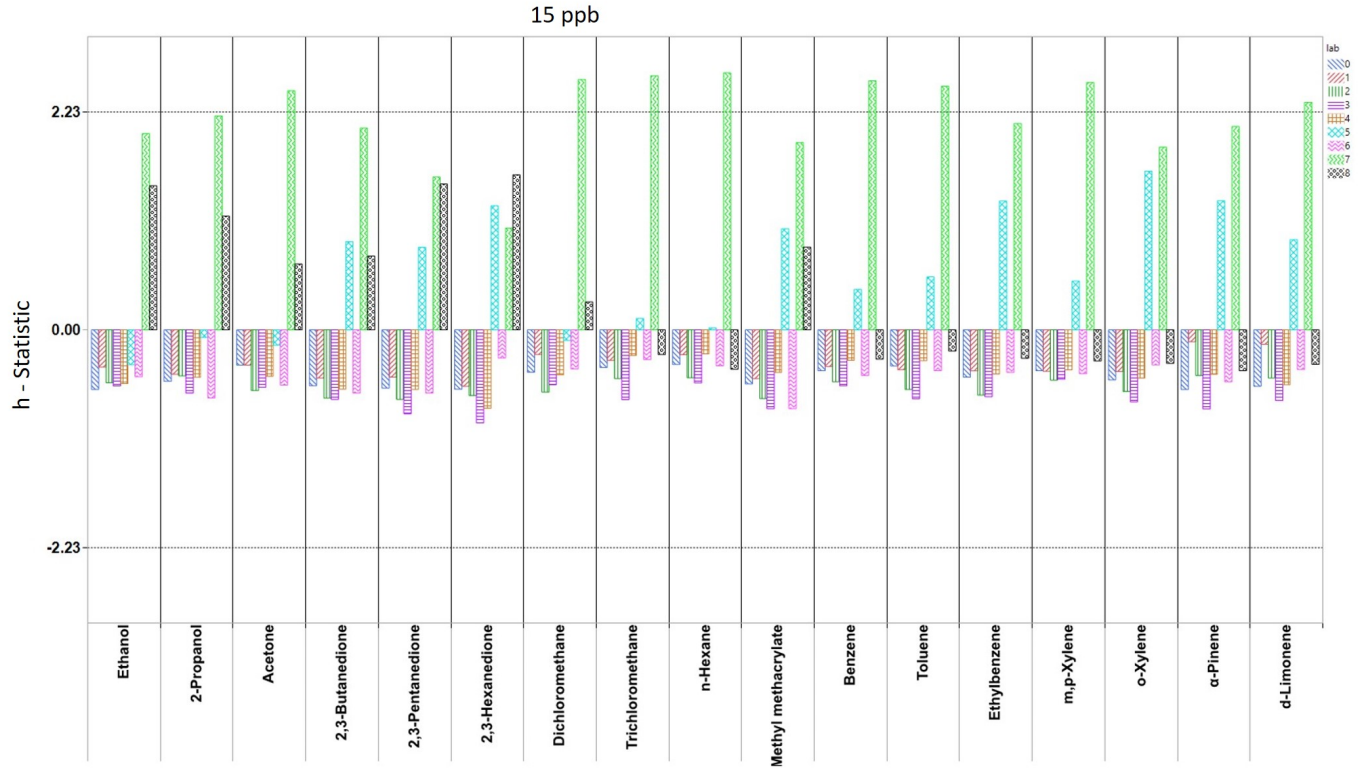

Figure 10. Between-laboratory statistic (h-plot) for 15 ppb nominal level. Dashed line = 2.23 to -2.23 criteria.

h-Statistic for ppm-level between-laboratory variability by analyte shows most laboratories and analytes (450/459 combinations or 98.0%) were within the ±2.23 (Figures 11, 12, and 13). The excursions were limited to laboratory 5 and laboratory 7. A pattern of positive and negative h-values by laboratory with the number of positive values approximately equal to the number of negative laboratories is observed at the ppm-level. This is a normal pattern to inter-laboratory studies and did not require investigation.

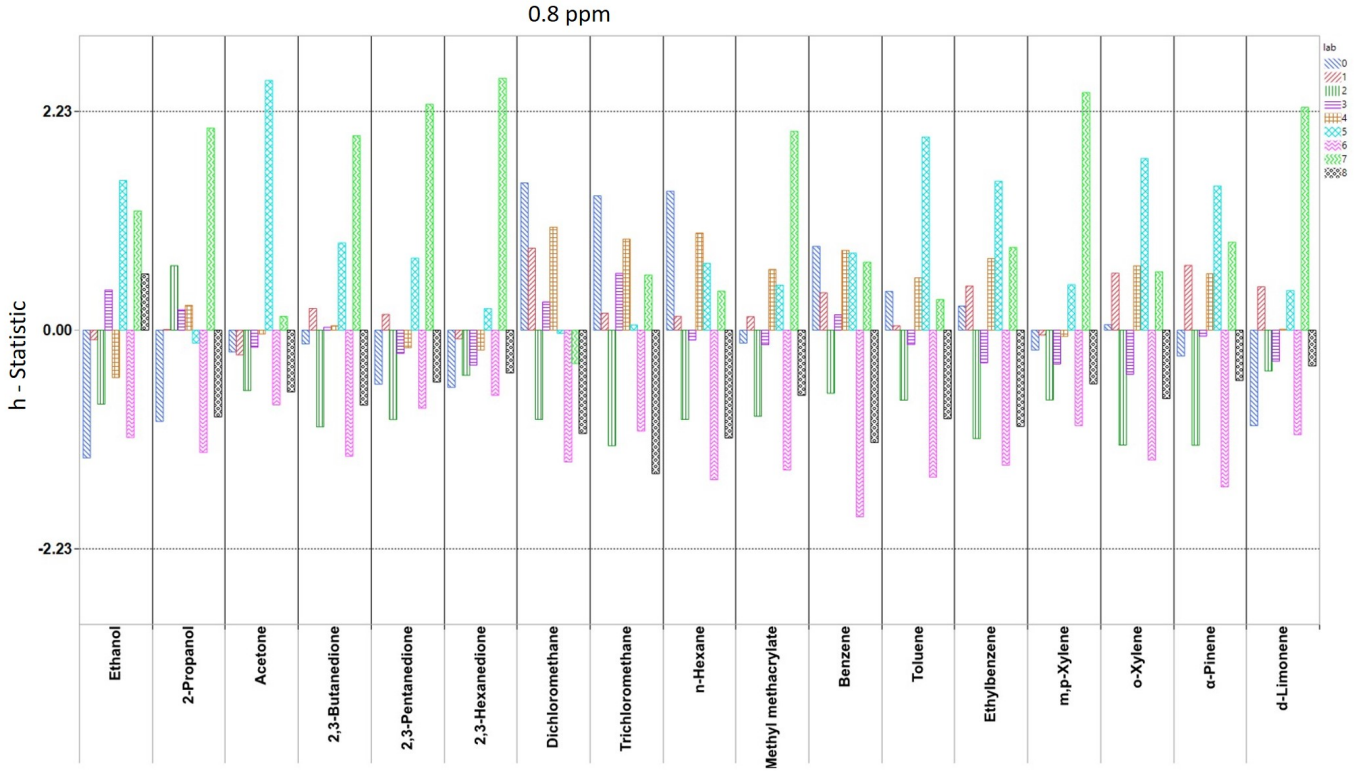

Figure 11. Between-laboratory statistic (h-plot) for 0.8 ppm nominal level. Dashed line = 2.23 to -2.23 criteria.

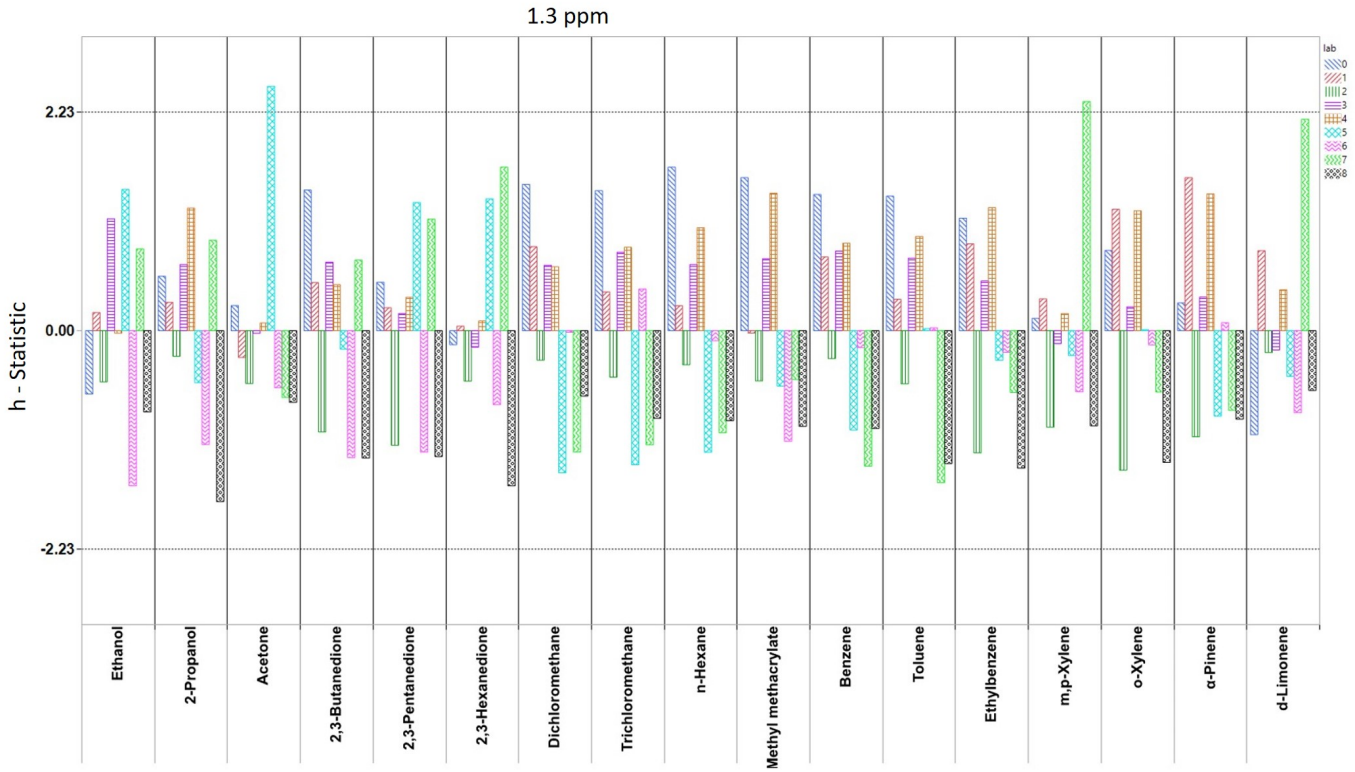

Figure 12. Between-laboratory statistic (h-plot) for 1.3 ppm nominal level. Dashed line = 2.23 to -2.23 criteria.

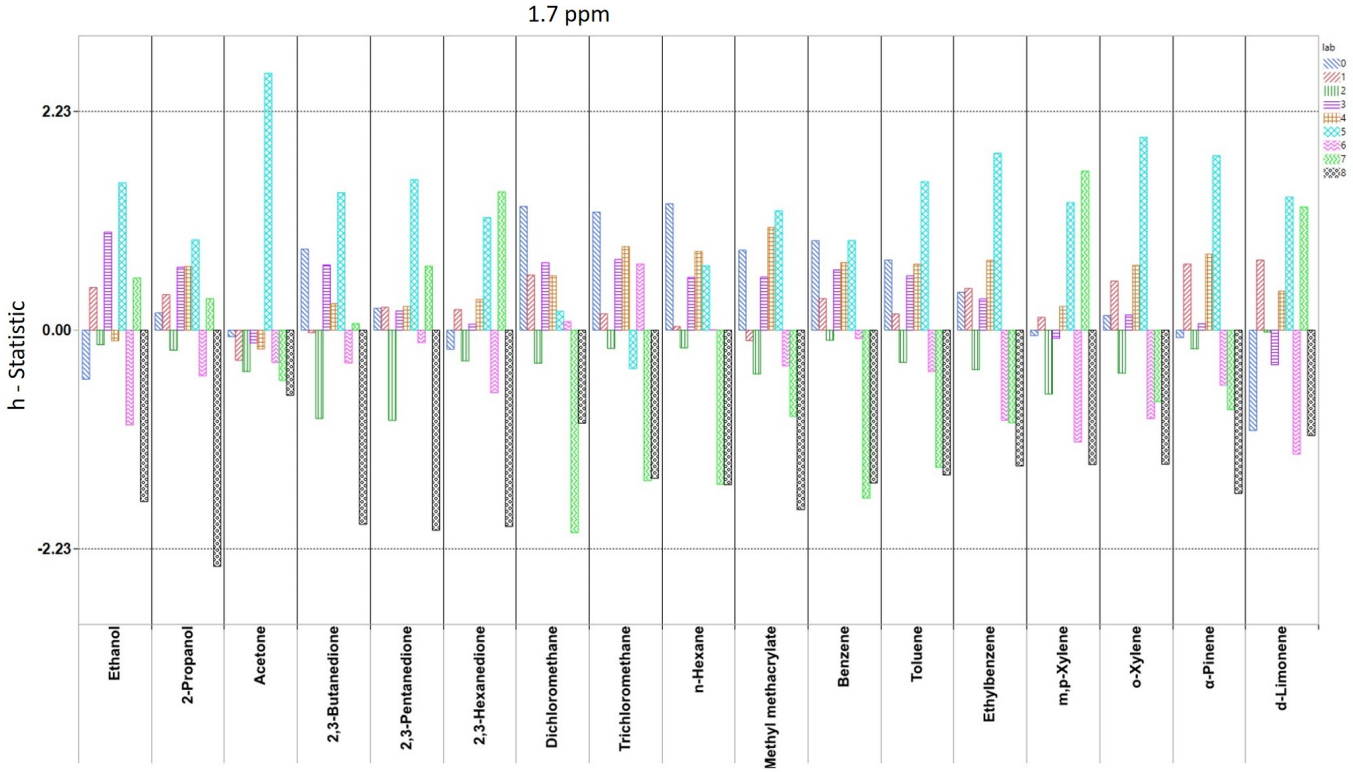

Figure 13. Between-laboratory statistic (h-plot) for 1.7 ppm nominal level. Dashed line = 2.23 to -2.23 criteria.

Laboratories 5, 6, and 7 were investigated based on the h- and k-plots and outlier results (These laboratories contributed to all but six of the 75 deleted values.) For dilution of ppm-level samples, laboratory 5 performed syringe transfers to a tedlar bag. Ideally, a canister-to-canister pressure dilution would take place although in the original draft NMAM provided to the test laboratories syringe transfers from a glass bulb to a canister were discussed for calibration standard preparation. Laboratory 5 performed well on a number of analyte/concentration combinations but some individual canisters and combinations had elevated bias and precision indicative of poor instrument performance (e.g., preconcentrator may have not made an incorrect injection volume or trapping temperatures may not have been stable). Laboratory 6 took 42 days to analyze samples with a calibration to sample analysis duration of 28 days. This time may be too long for the analytical system to maintain stability of the calibration curve. For dilution of ppm-level samples, laboratory 6 performed 10 mL gas transfers using a syringe into a 1-L canister and pressurized to ambient. Laboratory 6 agreed to conduct the inter-laboratory study again with a fresh set of spiked samples. Laboratory 6 repeat data was marginally better than before and used in the current analysis. Laboratory 7 calibrated at ambient pressure but the spike samples were pressurized. This can cause issues with delivery volumes in the preconcentrator system as internal tubing effective volume is greater under pressure. For dilution of ppm-level samples, laboratory 7 performed pressure dilutions using a homemade pressure transducer system. Laboratory 7 also calibrated up to 100 ppb instead of the recommended 20 ppb which can increase variability on the low end of the calibration curve. Since the original draft NMAM method was disseminated to the laboratories, we have found that using a 500 mL injection of our 20 ppb standard can effectively extended the calibration range to 40 ppb, depending on the analyte, without compromising variability. Laboratory 7 declined to repeat the analysis. Reported results

from Laboratory 7 were quite different from theoretical values indicating an incorrect calibration standard preparation at the laboratory or poorly prepared spikes, although reference canisters for this trial did not indicate poor preparation. Large variability in Laboratory 7 data may have been due to preconcentrator system instability and/or a higher than normal dynamic range of 5 to 100 ppb. In particular, 5 ppb results were much higher than other labs, and most of the analytes were identified as outliers at 5 ppb for laboratory 7.

ILS Conclusions

Precision estimates for repeatability ranged from 0.04 to 0.55 at ppb concentrations and from 0.10 to 0.47 for ppm concentrations. Precision estimates for reproducibility ranged from 0.10 to 0.62 at ppb concentrations and from 0.19 to 0.58 at ppm concentrations, depending on analyte and nominal. Plots of h- and k-statistics 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. Precision varied by laboratory with more than half of the laboratories performing well indicating a fairly robust method across laboratories. 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.

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Appendix A: Backup Data for Spiking Experiments, LOD, and Stability

Table A1: PPB-level spiking experiment data

Analyte	Nominal Target Concentration (ppb)	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Mean Bias	CV
ethanol	1	-0.109	-0.157	-0.148	-0.120	-0.184	-0.125	-0.043	-0.105		-0.124	0.042
ethanol	4	0.039	-0.094	-0.092	-0.010	-0.070	-0.039	0.036	-0.086		-0.040	0.056
ethanol	10	-0.221	-0.176	-0.056	-0.058	-0.054	-0.142	-0.153	-0.126	-0.045	-0.115	0.064
2-propanol	1	-0.192	-0.293	-0.194	-0.277	-0.235	-0.132	-0.129	-0.190		-0.205	0.060
2-propanol	4	0.014	-0.192	-0.066	-0.025	-0.169	-0.030	0.067	-0.040		-0.055	0.087
2-propanol	10	-0.234	-0.176	-0.035	-0.054	-0.033	-0.110	-0.141	-0.102	-0.089	-0.108	0.067
acetone	1	-0.038	-0.089	0.000	-0.053	-0.122	-0.019	0.202	-0.027		-0.018	0.097
acetone	4	0.075	-0.079	0.035	0.065	-0.059	0.048	0.081	-0.024		0.018	0.063
acetone	10	-0.138	-0.127	-0.050	-0.070	-0.050	-0.106	-0.138	-0.107	-0.070	-0.095	0.036
dichloromethane	1	0.043	0.065	0.016	0.056	0.052	0.016	0.012	0.032		0.036	0.020
dichloromethane	4	0.094	0.080	0.144	0.122	0.082	0.125	0.131	0.094		0.109	0.024
dichloromethane	10	-0.040	-0.066	-0.066	-0.072	-0.050	-0.053	-0.084	-0.059	-0.067	-0.062	0.013
trichloromethane	1	-0.027	0.004	-0.039	-0.020	0.004	-0.047	-0.060	-0.035		-0.028	0.023
trichloromethane	4	0.070	0.037	0.110	0.101	0.049	0.112	0.088	0.054		0.078	0.029
trichloromethane	10	-0.044	-0.062	-0.069	-0.061	-0.046	-0.065	-0.073	-0.058	-0.061	-0.060	0.010
hexane	1	-0.093	-0.055	-0.101	-0.089	-0.047	-0.112	-0.117	-0.085		-0.087	0.025
hexane	4	0.135	0.115	0.178	0.168	0.110	0.176	0.155	0.122		0.145	0.028
hexane	10	-0.042	-0.063	-0.066	-0.059	-0.064	-0.076	-0.072	-0.068	-0.059	-0.063	0.010
benzene	1	-0.129	-0.103	-0.150	-0.142	-0.091	-0.157	-0.155	-0.150		-0.134	0.025
benzene	4	0.082	0.062	0.125	0.114	0.059	0.118	0.101	0.067		0.091	0.027
benzene	10	-0.024	-0.044	-0.051	-0.035	-0.047	-0.057	-0.051	-0.055	-0.042	-0.045	0.010
toluene	1	-0.182	-0.173	-0.207	-0.213	-0.178	-0.219	-0.219	-0.229		-0.203	0.021
toluene	4	0.089	0.078	0.140	0.139	0.077	0.125	0.120	0.102		0.109	0.026
toluene	10	-0.005	-0.037	-0.035	-0.006	-0.016	-0.035	-0.029	-0.032	-0.029	-0.025	0.013
ethylbenzene	1	-0.202	-0.173	-0.188	-0.178	-0.195	-0.191	-0.181	-0.219		-0.191	0.015
ethylbenzene	4	0.075	0.087	0.101	0.118	0.081	0.081	0.121	0.128		0.099	0.021
ethylbenzene	10	-0.020	-0.061	-0.048	-0.009	-0.042	-0.055	-0.032	-0.047	-0.054	-0.041	0.017

Table A1 (continued): PPB-level spiking experiment data

Analyte	Nominal Target Concentration (ppb)	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Mean Bias	CV
m,p-xylene	1	-0.230	-0.196	-0.209	-0.193	-0.224	-0.220	-0.210	-0.244		-0.216	0.017
m,p-xylene	4	0.041	0.056	0.064	0.091	0.047	0.046	0.092	0.104		0.068	0.024
m,p-xylene	10	-0.031	-0.080	-0.062	-0.014	-0.054	-0.070	-0.043	-0.060	-0.070	-0.054	0.021
o-xylene	1	-0.242	-0.208	-0.217	-0.201	-0.224	-0.228	-0.214	-0.256		-0.224	0.018
o-xylene	4	0.051	0.075	0.077	0.101	0.062	0.060	0.109	0.136		0.084	0.029
o-xylene	10	-0.015	-0.073	-0.052	0.004	-0.040	-0.059	-0.028	-0.047	-0.061	-0.041	0.024
methyl methacrylate	1	-0.256	-0.295	-0.234	-0.314	-0.349	-0.207	-0.230	-0.230		-0.265	0.049
methyl methacrylate	4	0.072	-0.108	0.023	0.070	-0.092	0.035	0.082	0.013		0.012	0.073
methyl methacrylate	10	-0.102	-0.096	-0.012	-0.011	0.005	-0.064	-0.080	-0.064	-0.052	-0.053	0.039
α-pinene	1	-0.186	-0.139	-0.168	-0.141	-0.160	-0.188	-0.161	-0.199		-0.168	0.022
α-pinene	4	0.018	0.081	0.057	0.081	0.052	0.070	0.103	0.145		0.076	0.038
α-pinene	10	-0.013	-0.093	-0.065	-0.006	-0.054	-0.052	-0.028	-0.058	-0.076	-0.049	0.029
d-limonene	1	-0.246	-0.183	-0.150	-0.156	-0.191	-0.150	-0.143	-0.169		-0.173	0.034
d-limonene	4	-0.022	0.104	-0.059	0.021	0.030	0.066	0.116	0.312		0.071	0.114
d-limonene	10	0.011	-0.121	-0.053	0.048	-0.044	-0.063	0.040	-0.042	-0.094	-0.035	0.058

Table A2: PPM-level spiking experiment data

Analyte	Nominal Target Concentration (ppm)	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Mean Bias	CV
ethanol	0.8	0.179	0.143	0.112	0.079	0.112	0.100	0.085	0.138	0.129	0.120	0.031
ethanol	1	0.075	0.140	0.206	0.107	0.176	0.151	0.152	0.152	0.164	0.147	0.038
ethanol	2	-0.002	-0.012	0.020	0.037	0.046	0.014	0.023	0.006		0.017	0.019
2-propanol	0.8	0.143	0.158	0.140	0.130	0.140	0.115	0.064	0.141	0.143	0.130	0.027
2-propanol	1	0.098	0.105	0.146	0.064	0.156	0.132	0.166	0.150	0.162	0.131	0.035
2-propanol	2	-0.039	-0.010	0.022	0.017	0.026	0.017	-0.020	0.030		0.005	0.025
acetone	0.8	0.171	0.136	0.179	0.122	0.130	0.131	0.127	0.167	0.146	0.145	0.021
acetone	1	0.081	0.120	0.144	0.080	0.132	0.132	0.100	0.108	0.120	0.113	0.023
acetone	2	-0.030	-0.007	0.008	0.003	0.018	0.008	0.005	0.010		0.002	0.015
dichloromethane	0.8	-0.003	-0.014	-0.005	-0.015	-0.018	-0.043	-0.021	-0.004	-0.015	-0.015	0.012
dichloromethane	1	-0.082	-0.101	-0.042	-0.017	-0.021	-0.021	0.048	-0.011	0.042	-0.023	0.049
dichloromethane	2	-0.144	-0.085	-0.075	-0.081	-0.014	-0.019	-0.038	-0.010		-0.058	0.046
trichloromethane	0.8	0.161	0.138	0.133	0.136	0.146	0.108	0.117	0.145	0.124	0.134	0.016
trichloromethane	1	0.057	0.039	0.047	0.031	0.035	0.035	0.044	0.019	0.039	0.038	0.011
trichloromethane	2	-0.029	-0.011	0.004	0.004	0.008	-0.001	0.001	0.001		-0.003	0.012
hexane	0.8	0.136	0.125	0.119	0.123	0.132	0.107	0.104	0.133	0.123	0.123	0.011
hexane	1	0.078	0.060	0.085	0.060	0.064	0.072	0.073	0.057	0.085	0.070	0.011
hexane	2	-0.046	-0.017	-0.007	0.009	0.002	-0.002	-0.004	-0.004		-0.009	0.017
benzene	0.8	0.089	0.104	0.099	0.076	0.086	0.061	0.071	0.100	0.076	0.085	0.015
benzene	1	0.102	0.092	0.092	0.067	0.079	0.079	0.081	0.072	0.092	0.084	0.011
benzene	2	0.013	0.014	0.030	0.035	0.022	0.019	0.026	0.010		0.021	0.009
toluene	0.8	0.063	0.064	0.048	0.051	0.036	0.023	0.032	0.085	0.038	0.049	0.019
toluene	1	0.072	0.070	0.078	0.053	0.065	0.048	0.058	0.050	0.070	0.063	0.011
toluene	2	0.056	0.046	0.056	0.078	0.054	0.044	0.063	0.035		0.054	0.013
ethylbenzene	0.8	0.092	0.093	0.064	0.079	0.064	0.077	0.073	0.114	0.055	0.079	0.018
ethylbenzene	1	0.042	0.032	0.049	0.016	0.044	-0.005	0.038	0.013	0.032	0.029	0.018
ethylbenzene	2	0.026	0.011	0.015	0.049	0.041	0.049	0.051	0.034		0.034	0.016

Table A2 (continued): PPM-level spiking experiment data

Analyte	Nominal Target Concentration (ppm)	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Mean Bias	CV
m,p-xylene	0.8	0.090	0.104	0.074	0.090	0.061	0.074	0.071	0.125	0.053	0.082	0.022
m,p-xylene	1	0.027	0.001	0.026	0.001	0.021	-0.021	0.014	-0.002	0.009	0.008	0.015
m,p-xylene	2	0.013	-0.002	0.007	0.030	0.034	0.052	0.049	0.027		0.026	0.019
o-xylene	0.8	0.090	0.092	0.061	0.090	0.061	0.074	0.071	0.125	0.065	0.081	0.021
o-xylene	1	0.043	0.034	0.059	0.026	0.062	0.004	0.039	0.031	0.043	0.038	0.017
o-xylene	2	0.041	0.015	0.019	0.058	0.051	0.058	0.066	0.038		0.043	0.019
methyl methacrylate	0.8	0.089	0.066	0.049	0.077	0.062	0.037	0.009	0.074	0.040	0.056	0.025
methyl methacrylate	1	0.081	0.087	0.071	0.046	0.075	0.066	0.076	0.068	0.087	0.073	0.013
methyl methacrylate	2	0.034	0.031	0.051	0.051	0.044	0.040	0.053	0.037		0.043	0.009
α-pinene	0.8	0.106	0.121	0.078	0.106	0.078	0.115	0.100	0.153	0.081	0.104	0.024
α-pinene	1	0.060	0.050	0.084	0.017	0.071	0.005	0.056	0.048	0.050	0.049	0.024
α-pinene	2	0.055	0.018	0.027	0.055	0.054	0.066	0.069	0.047		0.049	0.018
d-limonene	0.8	0.186	0.188	0.132	0.199	0.119	0.220	0.179	0.256	0.186	0.185	0.041
d-limonene	1	0.131	0.172	0.197	0.089	0.224	0.067	0.152	0.185	0.155	0.152	0.050
d-limonene	2	0.099	-0.006	0.004	0.060	0.058	0.094	0.079	0.063		0.056	0.039

Table A3: PPB-level limit of detection data, 2012

Analyte	Nominal Target Concentration (ppb)	Measured Concentration (ppb)	Theoretical Concentration (ppb)	Bias
ethanol	0.03	0.115	0.033	2.495
ethanol	0.07	0.140	0.066	1.137
ethanol	0.5	0.595	0.519	0.146
ethanol	0.7	0.570	0.689	-0.172
ethanol	1	1.075	1.033	0.041
2-propanol	0.03	0.060	0.033	0.807
2-propanol	0.07	0.085	0.066	0.286
2-propanol	0.5	0.615	0.524	0.174
2-propanol	0.7	0.600	0.695	-0.137
2-propanol	1	1.225	1.042	0.175
acetone	0.03	0.210	0.034	5.269
acetone	0.07	0.235	0.067	2.523
acetone	0.5	0.720	0.528	0.364
acetone	0.7	0.705	0.701	0.006
acetone	1	1.335	1.051	0.271
dichloromethane	0.03	0.140	0.032	3.321
dichloromethane	0.07	0.165	0.064	1.562
dichloromethane	0.5	0.620	0.510	0.216
dichloromethane	0.7	0.665	0.677	-0.017
dichloromethane	1	1.305	1.015	0.286
trichloromethane	0.03	0.020	0.033	-0.388
trichloromethane	0.07	0.055	0.065	-0.155
trichloromethane	0.5	0.500	0.516	-0.030
trichloromethane	0.7	0.560	0.684	-0.181
trichloromethane	1	1.045	1.026	0.019
hexane	0.03	0.020	0.033	-0.396
hexane	0.07	0.050	0.066	-0.241
hexane	0.5	0.495	0.522	-0.051
hexane	0.7	0.540	0.692	-0.220
hexane	1	1.025	1.038	-0.012
benzene	0.03	0.030	0.033	-0.080
benzene	0.07	0.050	0.065	-0.230
benzene	0.5	0.485	0.514	-0.057
benzene	0.7	0.540	0.682	-0.208
benzene	1	1.005	1.023	-0.018

Table A3 (continued): PPB-level limit of detection data, 2012

Analyte	Nominal Target Concentration (ppb)	Measured Concentration (ppb)	Theoretical Concentration (ppb)	Bias
toluene	0.03	0.030	0.033	-0.094
toluene	0.07	0.055	0.066	-0.164
toluene	0.5	0.500	0.521	-0.040
toluene	0.7	0.565	0.691	-0.182
toluene	1	1.025	1.037	-0.011
ethylbenzene	0.03	0.035	0.033	0.064
ethylbenzene	0.07	0.060	0.066	-0.084
ethylbenzene	0.5	0.525	0.519	0.012
ethylbenzene	0.7	0.575	0.688	-0.165
ethylbenzene	1	1.060	1.033	0.027
m,p-xylene	0.03	0.050	0.033	0.534
m,p-xylene	0.07	0.060	0.065	-0.076
m,p-xylene	0.5	0.510	0.514	-0.008
m,p-xylene	0.7	0.555	0.682	-0.186
m,p-xylene	1	1.030	1.023	0.007
o-xylene	0.03	0.045	0.033	0.380
o-xylene	0.07	0.060	0.065	-0.076
o-xylene	0.5	0.520	0.514	0.011
o-xylene	0.7	0.550	0.682	-0.194
o-xylene	1	1.040	1.023	0.017
methyl methacrylate	0.03	0.035	0.033	0.061
methyl methacrylate	0.07	0.060	0.066	-0.087
methyl methacrylate	0.5	0.535	0.520	0.028
methyl methacrylate	0.7	0.560	0.690	-0.189
methyl methacrylate	1	1.085	1.035	0.048

Table A3 (continued): PPB-level limit of detection data, 2012

Analyte	Nominal Target Concentration (ppb)	Measured Concentration (ppb)	Theoretical Concentration (ppb)	Bias
α-pinene	0.03	0.030	0.033	-0.088
α-pinene	0.07	0.050	0.065	-0.235
α-pinene	0.5	0.515	0.518	-0.006
α-pinene	0.7	0.555	0.687	-0.192
α-pinene	1	1.065	1.031	0.033
d-limonene	0.03	0.060	0.033	0.835
d-limonene	0.07	0.050	0.065	-0.232
d-limonene	0.5	0.525	0.516	0.018
d-limonene	0.7	0.520	0.684	-0.240
d-limonene	1	1.080	1.026	0.052

Table A4: PPM-level limit of detection data

Analyte	Nominal Target Concentration (ppb)	Measured Concentration (ppb)	Theoretical Concentration (ppb)	Bias
ethanol	2	2.010	1.945	0.034
ethanol	1.3	1.220	1.305	-0.065
ethanol	0.8	0.810	0.878	-0.077
ethanol	0.4	0.445	0.441	0.008
ethanol	0.2	0.210	0.221	-0.049
ethanol	0.1	0.130	0.111	0.172
2-propanol	2	2.065	1.962	0.052
2-propanol	1.3	1.240	1.317	-0.058
2-propanol	0.8	0.820	0.886	-0.074
2-propanol	0.4	0.450	0.445	0.010
2-propanol	0.2	0.215	0.223	-0.035
2-propanol	0.1	0.120	0.112	0.072
acetone	2	1.945	1.978	-0.017
acetone	1.3	1.140	1.327	-0.141
acetone	0.8	0.785	0.893	-0.121
acetone	0.4	0.450	0.449	0.002
acetone	0.2	0.230	0.225	0.024
acetone	0.1	0.140	0.113	0.240
dichloromethane	2	1.875	1.911	-0.019
dichloromethane	1.3	1.040	1.282	-0.189
dichloromethane	0.8	0.740	0.863	-0.142
dichloromethane	0.4	0.400	0.434	-0.078
dichloromethane	0.2	0.230	0.217	0.060
dichloromethane	0.1	0.150	0.109	0.376
trichloromethane	2	2.085	1.932	0.079
trichloromethane	1.3	1.195	1.297	-0.078
trichloromethane	0.8	0.800	0.872	-0.083
trichloromethane	0.4	0.455	0.439	0.038
trichloromethane	0.2	0.215	0.219	-0.018
trichloromethane	0.1	0.120	0.110	0.091
hexane	2	2.300	1.955	0.177
hexane	1.3	1.390	1.311	0.060
hexane	0.8	0.875	0.882	-0.008
hexane	0.4	0.440	0.444	-0.008
hexane	0.2	0.190	0.222	-0.144
hexane	0.1	0.100	0.111	-0.099

Table A4 (continued): PPM-level limit of detection data

Analyte	Nominal Target Concentration (ppb)	Measured Concentration (ppb)	Theoretical Concentration (ppb)	Bias
benzene	2	2.235	1.926	0.160
benzene	1.3	1.365	1.293	0.056
benzene	0.8	0.865	0.870	-0.005
benzene	0.4	0.440	0.437	0.007
benzene	0.2	0.190	0.219	-0.132
benzene	0.1	0.100	0.109	-0.083
toluene	2	2.530	1.948	0.299
toluene	1.3	1.470	1.308	0.124
toluene	0.8	0.930	0.878	0.059
toluene	0.4	0.450	0.441	0.020
toluene	0.2	0.190	0.222	-0.144
toluene	0.1	0.100	0.111	-0.099
ethylbenzene	2	2.520	1.941	0.298
ethylbenzene	1.3	1.450	1.303	0.113
ethylbenzene	0.8	0.910	0.874	0.041
ethylbenzene	0.4	0.450	0.439	0.025
ethylbenzene	0.2	0.190	0.221	-0.140
ethylbenzene	0.1	0.100	0.110	-0.091
m,p-xylene	2	2.480	1.923	0.290
m,p-xylene	1.3	1.420	1.291	0.100
m,p-xylene	0.8	0.890	0.866	0.028
m,p-xylene	0.4	0.440	0.435	0.011
m,p-xylene	0.2	0.190	0.219	-0.132
m,p-xylene	0.1	0.100	0.110	-0.091
o-xylene	1.3	1.460	1.291	0.131
o-xylene	0.8	0.910	0.866	0.051
o-xylene	0.4	0.440	0.435	0.011
o-xylene	0.2	0.185	0.219	-0.155
o-xylene	0.1	0.100	0.110	-0.091
methyl methacrylate	2	2.580	1.946	0.326
methyl methacrylate	1.3	1.540	1.306	0.179
methyl methacrylate	0.8	0.950	0.877	0.083
methyl methacrylate	0.4	0.460	0.440	0.045
methyl methacrylate	0.2	0.195	0.221	-0.118
methyl methacrylate	0.1	0.090	0.111	-0.189

Table A4 (continued): PPM-level limit of detection data

Analyte	Nominal Target Concentration (ppb)	Measured Concentration (ppb)	Theoretical Concentration (ppb)	Bias
α-pinene	2	2.680	1.938	0.383
α-pinene	1.3	1.550	1.301	0.191
α-pinene	0.8	0.940	0.873	0.077
α-pinene	0.4	0.450	0.438	0.027
α-pinene	0.2	0.185	0.220	-0.159
α-pinene	0.1	0.090	0.110	-0.182
d-limonene	2	2.880	1.930	0.492
d-limonene	1.3	1.690	1.295	0.305
d-limonene	0.8	0.890	0.869	0.024
d-limonene	0.4	0.440	0.437	0.007
d-limonene	0.2	0.170	0.220	-0.227
d-limonene	0.1	0.090	0.110	-0.182

Table A5: PPB-level limit of detection data, 2017

Analyte	Nominal Target Concentration (ppb)	Measured Concentration (ppb)	Theoretical Concentration (ppb)	Bias
ethanol	0.1	0.106	0.11	-0.033
ethanol	0.25	0.204	0.26	-0.214
ethanol	0.5	0.247	0.51	-0.516
ethanol	1	0.536	1.03	-0.480
ethanol	2	2.729	2.05	0.331
ethanol	3	1.490	3.09	-0.518
ethanol	6	2.627	6.08	-0.568
2-propanol	0.1	0.095	0.11	-0.135
2-propanol	0.25	0.195	0.27	-0.279
2-propanol	0.5	0.323	0.55	-0.412
2-propanol	1	0.830	1.1	-0.246
2-propanol	2	1.940	2.19	-0.114
2-propanol	3	2.479	3.3	-0.249
2-propanol	6	5.179	6.5	-0.203
acetone	0.1	0.138	0.12	0.150
acetone	0.25	0.234	0.28	-0.165
acetone	0.5	0.464	0.56	-0.171
acetone	1	1.053	1.13	-0.068
acetone	2	2.294	2.25	0.019
acetone	3	3.027	3.39	-0.107
acetone	6	6.125	6.68	-0.083
2,3-butanedione	0.1	0.000	0.11	-1.000
2,3-butanedione	0.25	0.184	0.26	-0.294
2,3-butanedione	0.5	0.380	0.52	-0.269
2,3-butanedione	1	0.924	1.05	-0.120
2,3-butanedione	2	1.837	2.09	-0.121
2,3-butanedione	3	2.836	3.15	-0.100
2,3-butanedione	6	6.047	6.2	-0.025
2,3-pentanedione	0.1	0.000	0.09	-1.000
2,3-pentanedione	0.25	0.124	0.23	-0.461
2,3-pentanedione	0.5	0.354	0.46	-0.230
2,3-pentanedione	1	0.810	0.92	-0.119
2,3-pentanedione	2	1.649	1.83	-0.099
2,3-pentanedione	3	2.735	2.76	-0.009
2,3-pentanedione	6	5.239	5.43	-0.035

Table A5 (continued): PPB-level limit of detection data, 2017

Analyte	Nominal Target Concentration (ppb)	Measured Concentration (ppb)	Theoretical Concentration (ppb)	Bias
2,3-hexanedione	0.1	0.072	0.09	-0.197
2,3-hexanedione	0.25	0.158	0.22	-0.281
2,3-hexanedione	0.5	0.285	0.45	-0.366
2,3-hexanedione	1	0.629	0.9	-0.301
2,3-hexanedione	2	1.410	1.79	-0.212
2,3-hexanedione	3	2.216	2.7	-0.179
2,3-hexanedione	6	4.961	5.32	-0.067
dichloromethane	0.1	0.008	0.11	-0.932
dichloromethane	0.25	0.212	0.26	-0.183
dichloromethane	0.5	0.371	0.52	-0.288
dichloromethane	1	0.937	1.04	-0.099
dichloromethane	2	1.864	2.07	-0.100
dichloromethane	3	2.963	3.12	-0.050
dichloromethane	6	5.753	6.14	-0.063
trichloromethane	0.1	0.000	0.11	-1.000
trichloromethane	0.25	0.170	0.27	-0.370
trichloromethane	0.5	0.369	0.54	-0.317
trichloromethane	1	0.907	1.08	-0.161
trichloromethane	2	1.917	2.15	-0.108
trichloromethane	3	2.889	3.24	-0.108
trichloromethane	6	5.725	6.38	-0.103
hexane	0.1	0.065	0.11	-0.410
hexane	0.25	0.193	0.27	-0.287
hexane	0.5	0.407	0.54	-0.246
hexane	1	0.908	1.09	-0.167
hexane	2	1.877	2.17	-0.135
hexane	3	2.928	3.27	-0.105
hexane	6	5.980	6.44	-0.071
benzene	0.1	0.070	0.11	-0.363
benzene	0.25	0.209	0.27	-0.227
benzene	0.5	0.425	0.54	-0.213
benzene	1	0.897	1.08	-0.169
benzene	2	1.846	2.15	-0.141
benzene	3	2.992	3.24	-0.077
benzene	6	5.977	6.38	-0.063

Table A5 (continued): PPB-level limit of detection data, 2017

Analyte	Nominal Target Concentration (ppb)	Measured Concentration (ppb)	Theoretical Concentration (ppb)	Bias
toluene	0.1	0.115	0.11	0.045
toluene	0.25	0.248	0.27	-0.081
toluene	0.5	0.411	0.53	-0.224
toluene	1	0.866	1.07	-0.190
toluene	2	1.780	2.13	-0.165
toluene	3	2.856	3.21	-0.110
toluene	6	5.976	6.32	-0.054
ethylbenzene	0.1	0.099	0.11	-0.096
ethylbenzene	0.25	0.239	0.26	-0.079
ethylbenzene	0.5	0.412	0.52	-0.207
ethylbenzene	1	0.846	1.05	-0.195
ethylbenzene	2	1.768	2.09	-0.154
ethylbenzene	3	2.844	3.15	-0.097
ethylbenzene	6	5.930	6.2	-0.044
m,p-xylene	0.1	0.101	0.11	-0.080
m,p-xylene	0.25	0.249	0.27	-0.076
m,p-xylene	0.5	0.415	0.55	-0.246
m,p-xylene	1	0.897	1.1	-0.185
m,p-xylene	2	1.832	2.19	-0.164
m,p-xylene	3	3.070	3.3	-0.070
m,p-xylene	6	6.311	6.5	-0.029
o-xylene	0.1	0.082	0.11	-0.253
o-xylene	0.25	0.203	0.26	-0.221
o-xylene	0.5	0.369	0.52	-0.290
o-xylene	1	0.852	1.05	-0.188
o-xylene	2	1.766	2.09	-0.155
o-xylene	3	2.938	3.15	-0.067
o-xylene	6	5.967	6.2	-0.038
methyl methacrylate	0.1	0.103	0.1	0.026
methyl methacrylate	0.25	0.204	0.25	-0.183
methyl methacrylate	0.5	0.345	0.51	-0.323
methyl methacrylate	1	0.783	1.02	-0.233
methyl methacrylate	2	1.601	2.03	-0.211
methyl methacrylate	3	2.538	3.06	-0.171
methyl methacrylate	6	5.634	6.03	-0.066

Table A5 (continued): PPB-level limit of detection data, 2017

Analyte	Nominal Target Concentration (ppb)	Measured Concentration (ppb)	Theoretical Concentration (ppb)	Bias
α-Pinene	0.1	0.143	0.11	0.301
α-Pinene	0.25	0.245	0.26	-0.057
α-Pinene	0.5	0.392	0.52	-0.246
α-Pinene	1	0.767	1.05	-0.269
α-Pinene	2	1.602	2.09	-0.233
α-Pinene	3	2.657	3.15	-0.157
α-Pinene	6	5.742	6.2	-0.074
d-limonene	0.1	0.191	0.11	0.733
d-limonene	0.25	0.263	0.26	0.012
d-limonene	0.5	0.367	0.52	-0.293
d-limonene	1	0.670	1.04	-0.356
d-limonene	2	1.336	2.07	-0.355
d-limonene	3	2.346	3.12	-0.248
d-limonene	6	5.393	6.14	-0.122

Table A6: PPB-level storage stability study, 30 day

Analyte	Mean Concentration Day 0 (ppb) n= 12	Mean Concentration Day 30 (ppb) n= 12	CV Day 0	CV Day 30	Bias Day 30
ethanol	5.44	5.40	12.6	27.3	-0.006
2-propanol	5.52	5.87	11.2	24.7	0.064
acetone	5.83	5.98	10.9	21.1	0.025
dichloromethane	5.91	5.66	3.3	4.1	-0.041
trichloromethane	5.88	5.90	2.7	2.7	0.003
hexane	5.97	6.15	2.1	2.5	0.031
benzene	5.92	6.02	2.2	3.7	0.016
toluene	6.17	6.08	2.9	7.3	-0.014
ethylbenzene	5.75	5.94	4.5	8.1	0.033
m,p-xylene	5.49	5.65	6.8	8.5	0.029
o-xylene	5.56	5.76	7.3	9.1	0.038
methyl methacrylate	6.09	5.70	7.1	13.5	-0.064
α-pinene	5.79	5.24	5.2	16.6	-0.095
d-limonene	5.65	5.93	14.9	13.8	0.051

Table A7: PPM-level storage stability study, 30 day

Analyte	Mean Concentration Day 0 (ppm) n= 12	Mean Concentration Day 21 (ppm) n=3	Mean Concentration Day 30 (ppm) n=3	CV Day 0	CV Day 21	CV Day 30	Bias Day 21	Bias Day 30
ethanol	0.771	0.797	0.700	4.0	16.7	8.9	0.034	-0.092
2-propanol	0.783	0.770	0.760	3.9	3.4	7.0	-0.016	-0.029
acetone	0.759	0.910	0.747	3.4	33.3	3.9	0.199	-0.016
dichloromethane	0.763	0.677	0.727	8.9	23.9	7.9	-0.113	-0.047
trichloromethane	0.673	0.660	0.660	0.9	2.6	3.0	-0.019	-0.019
hexane	0.713	0.707	0.713	1.2	2.2	1.6	-0.008	0.001
benzene	0.658	0.723	0.707	3.4	4.4	0.8	0.099	0.073
toluene	0.639	0.703	0.680	4.5	5.9	0.0	0.100	0.064
ethylbenzene	0.628	0.663	0.633	2.9	1.7	3.3	0.056	0.008
m,p-xylene	0.609	0.633	0.597	3.2	2.4	5.9	0.040	-0.021
o-xylene	0.625	0.650	0.623	3.2	2.7	3.3	0.040	-0.003
methyl methacrylate	0.644	0.693	0.653	3.8	5.8	4.7	0.076	0.014
α-pinene	0.638	0.677	0.527	3.4	1.7	50.5	0.061	-0.174
d-limonene	0.703	0.680	0.507	7.1	5.3	54.1	-0.032	-0.279

Table A8: PPB-level storage stability study, 58 day

Analyte	Mean Concentration Day 0 (ppb) n= 12	Mean Concentration Day 58 (ppb) n= 12	CV Day 0	CV Day 58	Bias Day 58
ethanol	9.17	10.68	2.8	3.3	16.50
2-propanol	9.84	11.45	2.8	14.2	16.10
acetone	10.27	11.41	2.3	6.8	11.17
2,3-butanedione	9.94	10.35	2.0	7.7	4.06
2,3-pentanedione	10.17	10.44	1.5	6.7	2.70
2,3 hexanedione	10.59	10.30	1.8	8.5	-2.88
dichloromethane	9.85	9.87	1.2	2.8	0.22
trichloromethane	9.98	10.30	1.0	3.6	3.13
hexane	10.41	10.78	1.2	4.6	3.55
benzene	9.98	10.34	1.2	3.5	3.58
toluene	10.58	10.75	1.2	2.6	1.57
ethylbenzene	10.51	10.45	1.4	3.4	-0.57
m,p-xylene	10.82	9.94	1.2	22.4	-8.13
o-xylene	10.47	10.11	1.1	5.1	-3.45
methyl methacrylate	10.07	10.22	1.2	3.7	1.46
α-pinene	10.38	10.03	0.7	5.1	-3.34
d-limonene	10.37	10.18	1.3	9.6	-1.87

Appendix B: Spike Batch Bias

Table B1: Reference laboratory PPB-range spike batch bias (mean and one standard deviation) across nominal level

Identifier		5 ppb			10 ppb			15 ppb		
Analyte	**Spike Batch**	**N**	**Mean**	**SD**	**N**	**Mean**	**SD**	**N**	**Mean**	**SD**
ethanol	1	3	0.070	0.159	3	-0.131	0.025	3	-0.064	0.034
ethanol	2	3	-0.015	0.057	3	-0.049	0.089	3	0.048	0.016
ethanol	3	3	0.331	0.017	3	0.205	0.044	3	0.416	0.460
ethanol	4	3	0.370	0.040	3	0.153	0.016	3	0.187	0.081
ethanol	5	3	-0.179	0.006	3	-0.121	0.083	3	-0.024	0.037
2-propanol	1	3	0.131	0.037	3	0.023	0.024	3	0.063	0.048
2-propanol	2	3	0.078	0.042	3	0.008	0.193	3	0.107	0.053
2-propanol	3	3	0.101	0.058	3	0.027	0.034	3	0.123	0.123
2-propanol	4	3	0.055	0.022	3	0.087	0.037	3	0.050	0.036
2-propanol	5	3	-0.021	0.019	3	-0.055	0.186	3	0.052	0.057
acetone	1	3	0.283	0.058	3	0.057	0.004	3	0.073	0.028
acetone	2	3	0.182	0.024	3	0.075	0.112	3	0.095	0.012
acetone	3	3	0.046	0.016	3	0.013	0.036	3	0.086	0.135
acetone	4	3	0.064	0.010	3	-0.005	0.010	3	0.009	0.029
acetone	5	3	0.006	0.025	3	-0.063	0.090	3	0.019	0.027
2,3-butanedione	1	3	0.086	0.029	3	-0.012	0.002	3	0.047	0.031
2,3-butanedione	2	3	0.045	0.017	3	0.024	0.100	3	0.077	0.004
2,3-butanedione	3	3	0.043	0.022	3	0.004	0.038	3	0.044	0.060
2,3-butanedione	4	3	0.010	0.009	3	-0.020	0.012	3	0.016	0.027
2,3-butanedione	5	3	-0.026	0.021	3	-0.082	0.109	3	0.020	0.020
2,3-pentanedione	1	3	0.097	0.048	3	-0.025	0.006	3	0.064	0.037
2,3-pentanedione	2	3	0.012	0.013	3	-0.058	0.217	3	0.080	0.006
2,3-pentanedione	3	3	0.095	0.006	3	0.003	0.051	3	0.046	0.079
2,3-pentanedione	4	3	-0.019	0.008	3	-0.032	0.015	3	0.007	0.022
2,3-pentanedione	5	3	-0.050	0.019	3	-0.304	0.451	3	-0.015	0.037
2,3-hexanedione	1	3	0.130	0.089	3	0.004	0.008	3	0.093	0.036
2,3-hexanedione	2	3	0.017	0.016	3	-0.107	0.347	3	0.105	0.013
2,3-hexanedione	3	3	0.143	0.036	3	0.000	0.059	3	0.032	0.083
2,3-hexanedione	4	3	-0.016	0.009	3	-0.042	0.015	3	-0.014	0.025
2,3-hexanedione	5	3	-0.041	0.016	3	-0.325	0.516	3	-0.030	0.002

Table B1 (continued): Reference laboratory PPB-range spike batch bias (mean and one standard deviation) across nominal level

Identifier		5 ppb			10 ppb			15 ppb		
Analyte	**Spike Batch**	**N**	**Mean**	**SD**	**N**	**Mean**	**SD**	**N**	**Mean**	**SD**
dichloromethane	1	3	0.107	0.003	3	-0.004	0.006	3	0.017	0.021
dichloromethane	2	3	0.089	0.023	3	0.057	0.005	3	0.049	0.006
dichloromethane	3	3	-0.014	0.024	3	-0.021	0.023	3	-0.009	0.039
dichloromethane	4	3	-0.009	0.009	3	-0.031	0.012	3	-0.022	0.021
dichloromethane	5	3	-0.019	0.012	3	0.005	0.006	3	0.008	0.006
trichloromethane	1	3	0.127	0.025	3	0.074	0.005	3	0.083	0.025
trichloromethane	2	3	0.122	0.027	3	0.091	0.006	3	0.068	0.004
trichloromethane	3	3	-0.018	0.025	3	-0.023	0.020	3	-0.016	0.025
trichloromethane	4	3	-0.017	0.006	3	-0.030	0.014	3	-0.024	0.020
trichloromethane	5	3	-0.017	0.015	3	-0.010	0.010	3	-0.005	0.002
hexane	1	3	0.037	0.029	3	0.004	0.004	3	0.016	0.022
hexane	2	3	0.054	0.024	3	0.071	0.006	3	0.063	0.007
hexane	3	3	-0.042	0.016	3	-0.016	0.011	3	0.005	0.025
hexane	4	3	-0.041	0.006	3	-0.026	0.012	3	0.000	0.018
hexane	5	3	-0.040	0.016	3	0.005	0.006	3	0.016	0.005
methyl methacrylate	1	3	0.122	0.074	3	-0.009	0.001	3	0.048	0.033
methyl methacrylate	2	3	-0.025	0.014	3	-0.059	0.180	3	0.063	0.003
methyl methacrylate	3	3	-0.041	0.015	3	-0.010	0.044	3	0.037	0.071
methyl methacrylate	4	3	-0.052	0.004	3	-0.031	0.017	3	0.008	0.021
methyl methacrylate	5	3	-0.056	0.012	3	-0.122	0.102	3	-0.053	0.004
benzene	1	3	0.052	0.022	3	0.005	0.004	3	0.018	0.024
benzene	2	3	0.040	0.022	3	0.048	0.010	3	0.047	0.005
benzene	3	3	-0.010	0.022	3	-0.015	0.017	3	-0.006	0.025
benzene	4	3	-0.015	0.004	3	-0.022	0.013	3	-0.014	0.019
benzene	5	3	-0.021	0.006	3	-0.029	0.013	3	-0.006	0.014
toluene	1	3	0.079	0.032	3	0.011	0.002	3	0.035	0.026
toluene	2	3	0.024	0.021	3	0.049	0.020	3	0.072	0.004
toluene	3	3	-0.020	0.026	3	-0.005	0.043	3	0.002	0.040
toluene	4	3	-0.031	0.009	3	-0.026	0.015	3	-0.010	0.020
toluene	5	3	-0.045	0.008	3	-0.034	0.009	3	-0.035	0.004
ethylbenzene	1	3	0.088	0.035	3	0.013	0.006	3	0.033	0.030
ethylbenzene	2	3	0.045	0.022	3	0.062	0.035	3	0.085	0.002
ethylbenzene	3	3	-0.003	0.019	3	-0.009	0.022	3	0.011	0.027
ethylbenzene	4	3	-0.030	0.004	3	-0.018	0.014	3	0.007	0.022
ethylbenzene	5	3	-0.069	0.005	3	-0.039	0.006	3	-0.031	0.003

Table B1 (continued): Reference laboratory PPB-range spike batch bias (mean and one standard deviation) across nominal level

Identifier		5 ppb			10 ppb			15 ppb		
Analyte	Spike Batch	N	Mean	SD	N	Mean	SD	N	Mean	SD
m,p-xylene	1	3	0.081	0.031	3	0.007	0.006	3	0.029	0.031
m,p-xylene	2	3	0.048	0.021	3	0.056	0.041	3	0.084	0.002
m,p-xylene	3	3	0.020	0.016	3	0.002	0.025	3	0.017	0.039
m,p-xylene	4	3	-0.012	0.005	3	-0.013	0.014	3	0.002	0.023
m,p-xylene	5	3	-0.053	0.008	3	-0.035	0.011	3	-0.034	0.006
o-xylene	1	3	0.075	0.025	3	0.015	0.006	3	0.029	0.029
o-xylene	2	3	0.049	0.018	3	0.073	0.030	3	0.087	0.003
o-xylene	3	3	-0.018	0.014	3	-0.039	0.012	3	-0.010	0.048
o-xylene	4	3	-0.049	0.002	3	-0.045	0.015	3	-0.029	0.026
o-xylene	5	3	-0.060	0.005	3	-0.041	0.016	3	-0.030	0.004
α-pinene	1	3	0.033	0.030	3	0.008	0.006	3	0.010	0.024
α-pinene	2	3	0.049	0.026	3	0.080	0.004	3	0.080	0.004
α-pinene	3	3	-0.029	0.030	3	-0.053	0.007	3	-0.014	0.052
α-pinene	4	3	-0.072	0.007	3	-0.050	0.015	3	-0.013	0.057
α-pinene	5	3	-0.070	0.007	3	-0.097	0.117	3	-0.027	0.007
d-limonene	1	3	0.031	0.022	3	0.016	0.005	3	0.034	0.027
d-limonene	2	3	-0.007	0.023	3	0.057	0.032	3	0.092	0.006
d-limonene	3	3	-0.089	0.039	3	-0.081	0.047	3	0.004	0.086
d-limonene	4	3	-0.154	0.015	3	-0.092	0.027	3	-0.040	0.033
d-limonene	5	3	-0.077	0.006	3	-0.065	0.022	3	-0.039	0.007

Table B2: Reference laboratory PPM-range spike batch bias (mean and one standard deviation) across nominal level

Identifier		0.8 ppm			1.3 ppm			1.7 ppm		
Analyte	Spike Batch	N	Mean	SD	N	Mean	SD	N	Mean	SD
ethanol	1	3	-0.465	0.157	3	-0.204	0.125	3	-0.172	0.021
ethanol	2	3	-0.235	0.092	3	-0.238	0.021	2	-0.206	0.116
ethanol	3	3	-0.285	0.027	3	-0.187	0.061	3	-0.175	0.051
ethanol	4	3	-0.312	0.093	3	-0.166	0.029	3	-0.065	0.062
ethanol	5	3	-0.286	0.164	3	-0.060	0.023	3	-0.058	0.037
ethanol	6	2	0.140	0.088	3	0.266	0.068	3	0.210	0.063
ethanol	7	2	0.252	0.122	3	0.214	0.050	3	0.281	0.128
2-propanol	1	3	-0.259	0.211	3	-0.006	0.110	3	-0.044	0.085
2-propanol	2	3	-0.054	0.006	3	-0.047	0.044	2	0.022	0.084
2-propanol	3	3	-0.136	0.003	3	-0.066	0.055	3	-0.138	0.055
2-propanol	4	3	-0.149	0.085	3	-0.105	0.017	3	-0.032	0.064
2-propanol	5	3	-0.108	0.056	3	-0.047	0.027	3	-0.029	0.017
2-propanol	6	2	0.065	0.142	3	0.081	0.123	3	-0.017	0.046
2-propanol	7	2	0.039	0.029	3	0.082	0.048	3	0.038	0.091
acetone	1	3	-0.109	0.188	3	0.112	0.082	3	0.076	0.039
acetone	2	3	0.084	0.034	3	0.062	0.052	2	0.127	0.078
acetone	3	3	-0.003	0.037	3	-0.002	0.004	3	-0.030	0.039
acetone	4	3	-0.049	0.057	3	-0.011	0.019	3	0.008	0.028
acetone	5	3	0.001	0.097	3	0.038	0.023	3	0.031	0.029
acetone	6	2	0.017	0.018	3	0.046	0.044	3	0.038	0.047
acetone	7	2	0.069	0.075	3	0.030	0.004	3	0.057	0.063
2,3-butanedione	1	3	-0.075	0.190	3	0.134	0.073	3	0.110	0.039
2,3-butanedione	2	3	0.086	0.018	3	0.085	0.051	2	0.175	0.060
2,3-butanedione	3	3	0.051	0.008	3	0.050	0.031	3	0.020	0.032
2,3-butanedione	4	3	-0.009	0.036	3	0.030	0.015	3	0.048	0.034
2,3-butanedione	5	3	0.059	0.041	3	0.080	0.026	3	0.067	0.037
2,3-butanedione	6	2	0.034	0.044	3	0.081	0.030	3	0.079	0.055
2,3-butanedione	7	2	0.057	0.070	3	0.066	0.009	3	0.096	0.056
2,3-pentanedione	1	3	-0.171	0.220	3	0.088	0.095	3	0.060	0.049
2,3-pentanedione	2	3	-0.007	0.020	3	0.022	0.025	2	0.133	0.073
2,3-pentanedione	3	3	0.003	0.008	3	0.055	0.063	3	0.004	0.027
2,3-pentanedione	4	3	-0.054	0.040	3	0.024	0.038	3	0.047	0.033
2,3-pentanedione	5	3	0.055	0.015	3	0.086	0.024	3	0.069	0.048
2,3-pentanedione	6	2	-0.001	0.091	3	0.039	0.033	3	0.030	0.052
2,3-pentanedione	7	2	-0.010	0.056	3	0.027	0.035	3	0.048	0.062

Table B2 (continued): Reference laboratory PPM-range spike batch bias (mean and one standard deviation) across nominal level

Identifier		0.8 ppm			1.3 ppm			1.7 ppm		
Analyte	Spike Batch	N	Mean	SD	N	Mean	SD	N	Mean	SD
2,3-hexanedione	1	3	-0.264	0.243	3	-0.013	0.089	3	-0.053	0.062
2,3-hexanedione	2	3	-0.089	0.012	3	-0.076	0.013	2	0.047	0.035
2,3-hexanedione	3	3	-0.071	0.014	3	0.004	0.058	3	-0.051	0.035
2,3-hexanedione	4	3	-0.116	0.024	3	-0.030	0.057	3	0.004	0.029
2,3-hexanedione	5	3	0.015	0.021	3	0.058	0.039	3	0.035	0.032
2,3-hexanedione	6	2	0.039	0.229	3	-0.001	0.019	3	-0.033	0.049
2,3-hexanedione	7	2	-0.027	0.081	3	-0.011	0.047	3	-0.011	0.062
dichloromethane	1	3	0.057	0.130	3	0.141	0.049	3	0.122	0.020
dichloromethane	2	3	0.149	0.024	3	0.098	0.063	2	0.179	0.045
dichloromethane	3	3	0.066	0.026	3	0.036	0.024	3	0.018	0.026
dichloromethane	4	3	0.028	0.030	3	0.023	0.020	3	0.026	0.034
dichloromethane	5	3	0.084	0.029	3	0.066	0.040	3	0.043	0.011
dichloromethane	6	2	0.063	0.004	3	0.078	0.015	3	0.103	0.067
dichloromethane	7	2	0.081	0.069	3	0.068	0.002	3	0.092	0.032
trichloromethane	1	3	0.166	0.143	3	0.245	0.026	3	0.223	0.017
trichloromethane	2	3	0.252	0.032	3	0.190	0.060	2	0.238	0.018
trichloromethane	3	3	0.095	0.016	3	0.036	0.019	3	0.014	0.033
trichloromethane	4	3	0.057	0.024	3	0.008	0.015	3	0.010	0.024
trichloromethane	5	3	0.100	0.041	3	0.041	0.019	3	0.037	0.035
trichloromethane	6	2	0.053	0.014	3	0.082	0.017	3	0.100	0.070
trichloromethane	7	2	0.075	0.078	3	0.067	0.005	3	0.090	0.033
hexane	1	3	0.083	0.143	3	0.178	0.019	3	0.170	0.015
hexane	2	3	0.169	0.031	3	0.134	0.059	2	0.176	0.001
hexane	3	3	0.041	0.022	3	0.029	0.019	3	0.017	0.034
hexane	4	3	0.031	0.027	3	0.002	0.022	3	0.013	0.021
hexane	5	3	0.069	0.022	3	0.039	0.019	3	0.028	0.017
hexane	6	2	0.051	0.009	3	0.103	0.019	3	0.135	0.069
hexane	7	2	0.081	0.083	3	0.092	0.005	3	0.122	0.034
methyl methacrylate	1	3	-0.119	0.192	3	0.088	0.078	3	0.059	0.042
methyl methacrylate	2	3	0.029	0.014	3	0.023	0.031	2	0.125	0.059
methyl methacrylate	3	3	-0.030	0.007	3	0.038	0.060	3	-0.006	0.030
methyl methacrylate	4	3	-0.057	0.032	3	0.003	0.039	3	0.032	0.027
methyl methacrylate	5	3	0.041	0.025	3	0.066	0.026	3	0.058	0.020
methyl methacrylate	6	2	0.033	0.099	3	0.040	0.026	3	0.050	0.061
methyl methacrylate	7	2	-0.005	0.058	3	0.024	0.029	3	0.049	0.062

Table B2 (continued): Reference laboratory PPM-range spike batch bias (mean and one standard deviation) across nominal level

Identifier		0.8 ppm			1.3 ppm			1.7 ppm		
Analyte	Spike Batch	N	Mean	SD	N	Mean	SD	N	Mean	SD
benzene	1	3	0.032	0.137	3	0.129	0.031	3	0.117	0.017
benzene	2	3	0.119	0.027	3	0.082	0.056	2	0.143	0.022
benzene	3	3	0.060	0.034	3	0.028	0.019	3	0.012	0.030
benzene	4	3	0.038	0.029	3	0.003	0.009	3	0.014	0.024
benzene	5	3	0.071	0.019	3	0.039	0.020	3	0.029	0.013
benzene	6	2	0.057	0.001	3	0.079	0.019	3	0.097	0.068
benzene	7	2	0.077	0.074	3	0.070	0.006	3	0.089	0.037
toluene	1	3	0.006	0.142	3	0.108	0.052	3	0.084	0.026
toluene	2	3	0.092	0.021	3	0.051	0.048	2	0.124	0.043
toluene	3	3	0.053	0.025	3	0.023	0.027	3	-0.006	0.022
toluene	4	3	0.027	0.032	3	-0.006	0.011	3	-0.001	0.024
toluene	5	3	0.077	0.013	3	0.042	0.022	3	0.028	0.023
toluene	6	2	0.039	0.017	3	0.070	0.019	3	0.088	0.075
toluene	7	2	0.072	0.096	3	0.045	0.008	3	0.077	0.040
ethylbenzene	1	3	-0.058	0.137	3	0.034	0.062	3	0.007	0.031
ethylbenzene	2	3	0.036	0.019	3	-0.018	0.030	2	0.043	0.054
ethylbenzene	3	3	-0.049	0.011	3	-0.050	0.035	3	-0.082	0.013
ethylbenzene	4	3	-0.057	0.043	3	-0.080	0.015	3	-0.076	0.019
ethylbenzene	5	3	0.010	0.019	3	-0.022	0.029	3	-0.039	0.029
ethylbenzene	6	2	0.025	0.022	3	0.053	0.021	3	0.065	0.071
ethylbenzene	7	2	0.016	0.056	3	0.034	0.008	3	0.074	0.055
m,p-xylene	1	3	-0.093	0.135	3	0.006	0.067	3	-0.027	0.037
m,p-xylene	2	3	0.010	0.020	3	-0.048	0.031	2	0.018	0.055
m,p-xylene	3	3	-0.060	0.013	3	-0.064	0.034	3	-0.101	0.010
m,p-xylene	4	3	-0.068	0.041	3	-0.093	0.022	3	-0.091	0.020
m,p-xylene	5	3	0.003	0.018	3	-0.031	0.033	3	-0.055	0.033
m,p-xylene	6	2	0.047	0.054	3	0.038	0.020	3	0.044	0.066
m,p-xylene	7	2	0.012	0.051	3	0.021	0.012	3	0.056	0.040
o-xylene	1	3	-0.099	0.137	3	-0.008	0.067	3	-0.043	0.040
o-xylene	2	3	0.004	0.018	3	-0.062	0.029	2	-0.001	0.050
o-xylene	3	3	-0.086	0.013	3	-0.091	0.035	3	-0.129	0.009
o-xylene	4	3	-0.089	0.041	3	-0.120	0.015	3	-0.123	0.019
o-xylene	5	3	-0.019	0.019	3	-0.060	0.027	3	-0.083	0.038
o-xylene	6	2	-0.013	0.012	3	-0.004	0.012	3	0.003	0.065
o-xylene	7	2	-0.039	0.042	3	-0.026	0.017	3	0.027	0.061

Table B2 (continued): Reference laboratory PPM-range spike batch bias (mean and one standard deviation) across nominal level

Identifier		0.8 ppm			1.3 ppm			1.7 ppm		
Analyte	Spike Batch	N	Mean	SD	N	Mean	SD	N	Mean	SD
α-pinene	1	3	-0.100	0.138	3	-0.036	0.054	3	-0.056	0.038
α-pinene	2	3	-0.020	0.012	3	-0.084	0.026	2	-0.060	0.028
α-pinene	3	3	-0.114	0.010	3	-0.129	0.043	3	-0.151	0.015
α-pinene	4	3	-0.104	0.044	3	-0.154	0.002	3	-0.156	0.015
α-pinene	5	3	-0.058	0.024	3	-0.109	0.012	3	-0.110	0.041
α-pinene	6	2	-0.030	0.044	3	0.016	0.027	3	0.039	0.071
α-pinene	7	2	-0.040	0.056	3	-0.024	0.009	3	0.031	0.061
d-limonene	1	3	-0.337	0.135	3	-0.216	0.090	3	-0.249	0.060
d-limonene	2	3	-0.215	0.014	3	-0.266	0.017	2	-0.205	0.059
d-limonene	3	3	-0.292	0.039	3	-0.280	0.062	3	-0.307	0.013
d-limonene	4	3	-0.270	0.043	3	-0.303	0.028	3	-0.302	0.011
d-limonene	5	3	-0.219	0.012	3	-0.239	0.029	3	-0.254	0.043
d-limonene	6	2	-0.085	0.061	3	-0.027	0.119	3	-0.104	0.041
d-limonene	7	2	-0.195	0.030	3	-0.125	0.068	3	-0.139	0.107