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Sample integrity evaluation and EPA method 325B interlaboratory comparison for select volatile organic compounds collected diffusively on Carbopack X sorbent tubes

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Abstract

A sample integrity evaluation and an interlaboratory comparison were conducted in application of U.S. Environmental Protection Agency (EPA) Methods 325A and 325B for diffusively monitoring benzene and other selected volatile organic compounds (VOCs) using Carbopack X sorbent tubes. To evaluate sample integrity, VOC samples were refrigerated for up to 240 days and analyzed using thermal desorption/gas chromatography-mass spectrometry at the EPA Office of Research and Development laboratory in Research Triangle Park, NC, USA. For the interlaboratory comparison, three commercial analytical laboratories were asked to follow Method 325B when analyzing samples of VOCs that were collected in field and laboratory settings for EPA studies. Overall results indicate that the selected VOCs collected diffusively on sorbent tubes generally were stable for 6 months or longer when samples were refrigerated. This suggests the specified maximum 30-day storage time of VOCs collected diffusively on Carbopack X passive samplers

Appendix A. Supplementary data

The following is the supplementary data related to this article:
Online data.

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and analyzed using Method 325B might be able to be relaxed. Interlaboratory comparison results were in agreement for the challenge samples collected diffusively in an exposure chamber in the laboratory, with most measurements within $\pm 25\%$ of the theoretical concentration. Statistically significant differences among laboratories for ambient challenge samples were small, less than 1 part per billion by volume (ppbv). Results from all laboratories exhibited good precision and generally agreed well with each other.

Keywords

EPA Method 325; Benzene; 1,3-Butadiene; Refinery fenceline rule; Sample integrity evaluation; Carbopack X sorbent tubes

1. Introduction

The U.S. Environmental Protection Agency (EPA) has recognized the need to refine regional emission inventories based on its revised emission control requirements in EPA's New Source Performance Standards for the oil and natural gas sector (U.S. EPA, 2015a). To meet this need, EPA Methods 325A and 325B were established as part of the performance standards to monitor fenceline benzene originating from fugitive and area sources within petroleum refineries U.S. EPA, 2015b, U.S. EPA, 2015c. These methods most commonly employ diffusive tube samplers that use Carbopack X or alternative sorbents for collection (325A) and subsequent determination of benzene using thermal desorption/gas chromatography-mass spectrometry (TD/GC-MS) analytical techniques (325B).

During the rulemaking process for the New Source Performance Standards for the oil and natural gas sector, field and laboratory studies were conducted to inform the efforts of laboratories preparing to meet the sampling and analytical requirements of Methods 325A and 325B. Several recently published studies discussing field efforts (Thoma et al., 2016, Eisele et al., 2016, Mukerjee et al., 2016) included the determination of a number of volatile organic compounds (VOCs) in addition to benzene, the target compound in Methods 325A and 325B. To complement the discussions of field activities, the work reported here details the results of a sample integrity study for benzene and selected VOCs (1,3-butadiene, toluene, tetrachloroethene, ethylbenzene, *m,p*-xylene, styrene, and *o*-xylene) collected diffusively on Carbopack X sorbent tubes. This paper also reports results from an interlaboratory comparison study in which ambient and laboratory-prepared VOC challenge samples were collected on Carbopack X sorbent tubes.

Results from previous sample integrity studies for selected VOCs collected on Carbopack X sorbent tubes have been reported for periods of up to 37 days for 1,3-butadiene (Martin et al., 2005); for 28 days for a set of eight VOCs including benzene, toluene, and *m*-xylene (Martin et al., 2010); for periods of up to 75 days for benzene and 1,3-butadiene (Footer et al., 2015, Eastern Research Group, 2015); and for periods of up to one year for benzene (Caurant et al., 2010). Martin et al. (2005) noted that storage stability results for 1,3-butadiene were better for samples that were refrigerated. As Methods 325A and 325B focus on the collection and determination of benzene, for which maximum hold times are specified, these methods do not specify refrigeration of samples collected on sorbent tubes.

The EPA VOC laboratory,¹ however, has historically refrigerated Carbopack X tubes samples at 6 °C after they are prepared or received in the laboratory because a number of target compounds other than benzene, including 1,3-butadiene, are monitored by the laboratory. The sample integrity study results reported in this paper expand both the list of compounds that have been evaluated and the holding times for selected VOCs collected diffusively on Carbopack X sorbent tubes. These data will be beneficial to laboratories that conduct ambient air monitoring studies using Carbopack X tubes, many of which are challenged by 30-day sample holding times.

For the interlaboratory comparison study, three commercial analytical laboratories were asked to follow Method 325B when analyzing samples of VOCs that were collected diffusively on Carbopack X tubes in ambient and laboratory settings. The results of these analyses and the EPA laboratory analyses were then evaluated and compared statistically to determine the reliability of the method when using different calibration standard types (liquid and gaseous) and standard preparation techniques (active and diffusive).

2. Methods

2.1. Sampling media and calibration standard preparation

The diffusive tube samplers were 40/60 mesh Carbopack X sorbent packed in industry-standard passivated stainless steel tubes that were 89 mm in length with an outer diameter of 6.4 mm (current part number 28 686-U, Supelco FLM Carbopack X deactivated TD tube for fence line monitoring, preconditioned and fitted with 0.25-in. brass Swagelok fittings with one-piece PTFE ferrules; Millipore Sigma-Aldrich Co. LLC, St. Louis, MO, USA). Upon receipt in the laboratory, all tubes were conditioned for a minimum of 5 h at 350 °C while purging with 75 ml/min (min) of research-grade helium (99.9999% purity; Airgas, Morrisville, NC, USA). The tubes were then blanked on the analytical system to assess background levels of VOCs on the tubes. Prior to sample collection in the field or laboratory, the tubes were conditioned for 1 h at 350 °C using a 20-tube conditioner (model TC-20, Markes International, Cincinnati, OH, USA). After conditioning, the tubes were refrigerated at 6 °C until use.

Mixtures of VOCs were prepared dynamically in an exposure chamber at a nominal concentration of 2 parts per billion by volume (ppbv) using a high-pressure cylinder containing 1 ppm per compound in nitrogen of a 43-component EPA Method TO-14A (U.S. Environmental Protection Agency (U.S. EPA), 1999a) gas mixture (Linde Spectra, Stewartville, NJ, USA) that was diluted with purified air (737–10 air generator, Aadco Instruments, Cleves, OH, USA) using Tylan mass flow controllers. The mixtures were humidified to 50% relative humidity and allowed to equilibrate for a minimum of 5 h in the exposure chamber prior to sample collection. Samples of the calibration mixture subsequently were collected diffusively for 24 h at room temperature on sets of six to 15 Carbopack X sorbent tubes fitted with diffusive sampling caps (part number L407–0207; PerkinElmer, Shelton, CT, USA). An Entech 7200 VOC concentrator (Entech Instruments, Simi Valley, CA, USA) interfaced to an Agilent 7890 GC-flame ionization detection system (Agilent Technologies, Santa Clara, CA, USA) was used to monitor the exposure chamber contents periodically to verify that the VOCs were at the expected concentrations and that

the concentrations remained consistent during the exposures. All gas flows were measured following each exposure, and precise dilution ratios and theoretical calibration concentrations were calculated. Some of the diffusively loaded tubes were used as daily check standards, whereas other tubes were used as laboratory and field controls for field studies (Eisele et al., 2016, Mukerjee et al., 2016, Thoma et al., 2015, Thoma et al., 2016).

The laboratory-prepared challenge tubes that were sent to the commercial laboratories for the interlaboratory comparison were prepared in the same manner. Extra, unused tubes loaded with VOC standards at the 2 ppbv concentration level that were remaining from various field studies and laboratory studies were held and analyzed for the sample integrity study (designated “unpaired lab” tubes for statistical analysis). Conditioned tubes, laboratory control samples, and tubes held for evaluating sample integrity (“unpaired” tubes) remained refrigerated until time for analysis; field controls were shipped to the field for the various studies along with field blanks and tubes to be used for collection of field samples using a cooler (without ice) to provide a measure of thermal stability and physical protection.

2.2. Field sample collection

Tubes deployed in the field were mounted vertically with the sampling end down in a protective sampling shelter using a convenient snap-in aluminum holder described elsewhere (Eisele et al., 2016, Mukerjee et al., 2016, Thoma et al., 2015, Thoma et al., 2016). Field personnel deployed the field controls by placing them side-by-side with the sampling tubes without removal of the brass storage end caps, whereas tubes used for sample collection were fitted with diffusive sampling caps at the time of deployment. For collection of the ambient samples used in the interlaboratory comparison, six diffusive sampling tubes were placed in a single sampling shelter that was located beside a sampling shelter for collection of the field study samples. The sampling shelters were attached to a previously installed mounting fixture on fence or ground stakes, light poles, or electronic/mechanical billboards with no obvious VOC sources in the immediate area. After a nominal 2-week exposure period, the tubes were retrieved and capped as appropriate, the details of sample collection were recorded in a chain of custody document, and the tubes were packaged and returned to the laboratory for analysis. Upon receipt in the laboratory, tubes were refrigerated at 6 °C until analysis.

2.3. Analytical procedures

Samples were analyzed in the EPA laboratory by TD/GC-MS using a PerkinElmer TurboMatrix ATD interfaced to an Agilent 6890 GC/5975 inert mass selective detector. The TurboMatrix ATD was equipped with an SVI focusing trap (custom product; PerkinElmer, Shelton, CT, USA) to capture the VOCs that were desorbed from the Carboxpack X diffusive sampling tubes. The TurboMatrix ATD operating conditions were set as follows: 8 psig head pressure; 4 min reverse dry purge with helium at 16 ml/min and 27 °C; 10 min tube desorption using 30 ml/min helium at 350 °C; and a 5 min trap desorption at 350 °C with a 10:1 outlet split. Upon desorption from the focusing trap, the VOCs were transferred to an Rxi-1ms 60 m × 0.32 mm × 1 µm capillary GC column (part number 1335; Restek, Bellefonte, PA, USA) for gas chromatographic separation of analytes. The GC oven program was set at 35 °C with a 5 min hold followed by a ramp of 6 °C/min to 210 °C with a final

hold of 0.83 min for a total GC analysis time of 35 min. The MS was operated in selected ion monitoring (SIM) mode for optimum sensitivity, and an external standard calibration with a quadratic curve fit was used for data reduction. Following sample analysis, tubes were conditioned on the Markes tube conditioner for 1 h in preparation for reuse. Additional details on the development of the EPA Office of Research and Development's Carbopack X tube sampling methodology are presented elsewhere (McClenny et al., 2005, McClenny et al., 2006), as are earlier field studies in which this methodology was used (Mukerjee et al., 2009, Thoma et al., 2011).

The EPA laboratory reported VOC concentrations in ppbv. Due to inherent benzene background on Carbopack X tubes, the concentration values reported by the EPA laboratory for benzene were corrected using background subtraction techniques. The three commercial analytical laboratories used EPA Method 325B (U.S. EPA, 2015c) to analyze the VOC samples that were collected diffusively on Carbopack X tubes. Mass concentrations reported by the commercial laboratories were converted to ppbv by a fifth coordinating laboratory (Eastern Research Group, 2015) using uptake rates (McClenny et al., 2005). These uptake rates were in agreement with uptake rates previously reported by other researchers who evaluated 1,3-butadiene, benzene, toluene and *o*-xylene using entirely independent calibration standards, test chambers and procedures (Martin et al., 2003, Martin et al., 2005).

2.4. Sample integrity evaluation

The sample integrity of 1,3-butadiene, benzene, toluene, tetrachloroethene, ethylbenzene, *m,p*-xylene, styrene, and *o*-xylene collected diffusively on Carbopack X tubes held for periods ranging from 11 to 240 days prior to analysis was investigated in two steps to assess the effect of storage time on percent recovery. To potentially maximize the number of data points for statistical analysis, it was first necessary to determine if field deployment affected recovery as a function of storage time. Thus, field study quality control (QC) samples were evaluated to determine if they should be included in the statistical analyses along with the samples stored solely in the laboratory.

Sets of QC samples for the field studies were prepared in batches in the laboratory as described in Section 2.1. These batches subsequently were divided such that some of the samples (usually two) were retained in the laboratory as lab controls, while others were deployed capped and unexposed in the field as field controls. In general, lab controls were held until the corresponding field controls were returned to the EPA laboratory, and when possible these were analyzed in the same sample sequence. As a result, the lab control/field control sample sets were analyzed after different storage times. The nominal concentration level for the lab controls and field controls was 2 ppbv; however, the actual concentrations were theoretically calculated for each tube batch based on the concentration in the calibration mixture and the flow rate of the standard gas and the diluent air. For each tube, the percent recovery of target VOCs was calculated as $(\text{measured/theoretical}) \times 100\%$. The lab control/field control comparison results, discussed in section 3.1, demonstrated the field control data could be included in the sample integrity evaluation.

Data from lab controls, field controls, and unpaired lab tubes (analyzed at different times after preparation) were combined into a single data set, yielding a data set of 213 observations (212 for benzene) with a range of storage times from 11 to 240 days. Linear regressions of percent recovery on storage time were performed for each VOC separately using these combined data.

2.5. Interlaboratory comparison

A two-part study was designed to evaluate how well laboratories compared with each other in analysis of 1,3-butadiene, benzene, toluene, ethylbenzene, *m,p*-xylene, styrene, and *o*-xylene collected on Carbopack X sorbent tubes using the analytical methodology described in Method 325B. Four laboratories—three commercial laboratories (designated A, B, and C) and the EPA laboratory (designated D)—participated in this comparison study. A fifth independent laboratory served as the coordinator for this study. This laboratory selected the three commercial laboratories from an initial pool of nine commercial laboratories that had experience in determining VOCs collected on sorbent tubes using thermal desorption techniques (Eastern Research Group, 2015). The four participating laboratories reported data to the coordinating laboratory which subsequently combined all the measurements into a single database used for the statistical analyses.

In the first phase, tubes were deployed in four EPA Regions at collocated sites for 14-day sampling periods such that a total of 19 sample sets were collected in various parts of the country at various times of the year over the course of the field study (Thoma et al., 2016, Eisele et al., 2016, Mukerjee et al., 2016). For each of the 19 sample sets, the number of samples for analysis were distributed to the three commercial laboratories such that one laboratory analyzed three samples from a set of six intercomparison samples to allow for an assessment of precision, while each of the other two commercial laboratories analyzed one sample from the set to facilitate the interlaboratory comparison. As a result, each of the three commercial laboratories analyzed either seven (Lab C) or six (Labs A and B) intercomparison sample sets in which multiple tubes were available to a particular laboratory. The EPA laboratory analyzed one sample from each intercomparison set since this laboratory was already analyzing field study samples in duplicate from the collocated field study sampling shelters. In one case, however, the EPA laboratory analyzed two samples from an intercomparison set in which a field operator deployed seven sampling tubes in the intercomparison shelter rather than six.

In the second phase of the study, conditioned tubes were diffusively loaded over a 24-hr period in an exposure chamber at the EPA laboratory with nominal concentrations of 3 ppbv and 20 ppbv of the VOCs, and tubes from these sample batches were sent to the commercial laboratories for analysis. Samples from these batches were also analyzed in the EPA laboratory. Each of the four laboratories analyzed six diffusively loaded samples: three at the lower challenge level and three at the higher challenge level. In addition, all laboratories analyzed nine tubes that were laboratory blanks.

To examine whether laboratories were reporting similar values for the laboratory-prepared challenge samples, the mean values from the laboratories were compared in a pairwise fashion using *t*-tests. In cases where a significant difference among the variances was found

at the 10% level, Satterthwaite's adjustment to the degrees of freedom was used. To guard against false positives (i.e., incorrectly declaring two laboratories to be different), Hommel's procedure was used to adjust the p -values from the individual tests for each compound at each challenge level.

To investigate potential laboratory differences with respect to the analysis of ambient samples, an unbalanced analysis of variance (ANOVA) was used, and the least squares means were compared with the Tukey-Kramer procedure guarding against false positives. The ANOVA contained three factors: laboratory, region, and batch. As potential laboratory differences were the subject of interest, the use of least squares means allowed laboratory comparisons to be made unencumbered by batch or regional effects.

Precision was compared among the laboratories using both the ambient duplicate samples and the lower- and higher-level laboratory-prepared challenge samples. To ensure that the precision comparisons were reliable, the coefficient of variation (CV, also called relative standard deviation), expressed as a percentage, was used as the measure of precision. This accounted for any region and batch effects observed in the ambient sample concentrations and the two different concentrations in the challenge samples. The exact Wilcoxon rank sum test was used to compare the laboratories with Hodges-Lehmann estimates indicating the magnitude of the precision differences. The CV is not normally distributed, and these nonparametric approaches were used for the precision comparisons to accommodate this. Due to the small sample sizes, the exact (as opposed to the asymptotic) version of the Wilcoxon test (Hollander and Wolfe, 1999) was used.

Since the four laboratories reported VOC concentrations that were below the detection limit (BDL) differently, concentrations reported as BDL were set to half the method detection limit (the average of bounds of zero and the detection limit) prior to any summarization or analyses (Mukerjee et al., 2009, Mukerjee et al., 2016, Eisele et al., 2016). All statistical analyses were performed in SAS[®] Version 9.3 (SAS, 2012). For all analyses, two significant digits were used for the concentrations.

3. Results

3.1. Sample integrity evaluation

Samples were analyzed over a range of tube storage times from 11 to 240 days. (Fourteen samples with storage times greater than 240 days, ranging from 272 to 862 days, were excluded from the analysis since there were so few data points in this range.) In addition, visual inspection of data plots indicated two apparent outliers across all compounds that were dropped: 10.1 and 7.4 standard deviations removed from the benzene and toluenemeans, respectively (see Fig. 1).

The first part of the sample integrity evaluation investigated the possibility that deployment of field controls might affect percent recovery. For each VOC, the percent recovery for the lab controls was regressed against storage time in days. Each compound had 61 data points except benzene, which had only 60. Sample storage times ranged between 11 and 227 days in this part of the evaluation. Complete regression results are reported in Table S1 of the

supporting material. An effect of storage time was only seen for 1,3-butadiene (1% significance level) and benzene (5% significance level). Even for these two VOCs, the estimated regression slopes indicated minimal decreases in percent recovery through time. For example, the largest estimate of a loss of 0.106%/day for 1,3-butadiene implied a recovery reduction of approximately 6% due to storage after 60 days (although the intercept estimate for this VOC showed a bias to low recovery). Intercepts, except for 1,3-butadiene, were all estimated to be near 100%.

To account for a potential batch effect, mean values of the percent recovery for the lab controls were calculated for each batch. The lab control mean value for each batch was then subtracted from the field control recoveries for those tubes from the same batch. For each compound, these differences were then regressed against storage time. Each compound had 125 data points available for these regressions, with storage times ranging from 18 to 227 days. Table S2 of the supporting material presents the results. No effect was seen for storage time (at the 5% significance level) on these field control recoveries adjusted for the lab control batch. All intercepts were near zero, and none were different from zero at the 5% significance level. Confidence intervals for the slopes from these regressions indicated no differences at the 5% significance level among the estimated slopes for the lab control and field control adjusted recoveries for any of the VOCs. These results suggest that field deployment does not affect percent recovery as a function of storage time and that these data could be used in the sample integrity evaluation.

Results of linear regressions of percent recovery on storage time are presented in Table 1. The overall regression model was significant in all cases ($p < 0.0001$). Examination of diagnostics indicated no troublesome departures from the basic regression assumptions. The slopes were significantly different from zero for five compounds ($p < 0.10$). For three compounds, slopes were not significantly different from zero, implying no change over the 240 days of storage. Although some slopes were significantly different from zero, they were small in all cases. Except for 1,3-butadiene (slope = -0.08), all slopes were $< 0.04\%/day$, which translates into a 14.6% change within a one-year period. These changes are within the audit accuracy of 30% specified in EPA Compendium Method TO-17, "Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes (U.S. EPA, 1999b). Except for 1,3-butadiene, estimates of the intercepts were near 100%, indicating no overall bias. (*Note:* Since EPA has not developed a guidance document that addresses the determination of VOCs in ambient air using diffusive sample collection with sorbents, the performance of these studies is measured against performance criteria specified in EPA Compendium Method TO-17, a similar sorbent sampling method.

While data for the regressions extended to 240 days (approximately 8 months), it is useful to consider the predicted recovery levels after shorter periods of storage. Table 2 presents predicted values and the associated 95% confidence intervals for the mean at 30 days (~1 month), 90 days (~3 months), and 180 days (~6 months). Results indicate that these VOCs are quite stable for storage times of up to 6 months. In the case of 1,3-butadiene, which is by far the poorest performer of the compound set, the predicted recovery is 80% at 90 days and 73% at 180 days. The predicted recovery of the remaining compounds is 95% or greater at 180 days.

3.2. Interlaboratory comparison

3.2.1. Laboratory blanks—Each laboratory reported concentrations as BDL for all target VOCs for the blank tubes. Thus, no differences were observed among the laboratories for the blank analyses.

3.2.2. Laboratory-prepared challenge samples—Results for statistical analysis of the laboratory-prepared challenge samples are reported separately for the lower and higher concentrations. To assess how close each laboratory was to being “on target,” *t*-tests were done to compare the measured mean value to the theoretical challenge concentration. Results from this testing are summarized in Table 3. Note that some of the cells contain a superscript S, indicating that the laboratory obtained exactly (to two significant digits) the same value on each of three measurements; no formal tests were done in these situations.

The measurements reported for both the higher- and lower-level laboratory-prepared challenge samples were $\pm 25\%$ of the theoretical concentration (with one exception), with most results $\pm 20\%$ of the theoretical concentration. These results meet the audit accuracy value of $\pm 30\%$ that is specified in EPA Method TO-17 (U.S. EPA, 1999b).

Results of *t*-tests to assess whether laboratories were reporting similar values for the laboratory-prepared challenge samples are given in Table 4, Table 5. Although two significant digits were used in the analyses, the tables report no more than two decimal places for readability and ease of comparison.

For the lower-level laboratory-prepared challenge samples (Table 4), Lab B tended to be higher than the other laboratories. Conversely, Labs A, C, and D generally agreed with each other. The vast majority of laboratory differences were estimated to be < 1 ppbv. Although small differences might be expected given the low concentrations (see Table 3), this observation is still notable.

In contrast to the lower-level laboratory-prepared challenge samples, results for the higher-level (Table 5) samples exhibited many statistically significant differences among laboratories across all the species. In most cases the differences were > 1 ppbv; however, it is again important to remember that most results were within $\pm 25\%$ of the theoretical concentration, which meets the audit accuracy criteria of $\pm 30\%$ specified in EPA Method TO-17 (U.S. EPA, 1999b).

3.2.3. Ambient samples—Differences between laboratories with respect to the ambient samples were assessed using an unbalanced ANOVA with three factors: laboratory, region, and batch. Highly statistically significant (1% level) effects were found for each factor for all species with the following exceptions: Region and batch effects were only significant at the 10% level for 1,3-butadiene; a laboratory effect was significant for benzene at the 5% level; and no batch effect was seen for styrene. Differences between laboratories were evaluated by comparing least squares means from the ANOVA (Table 6). Least squares means remove the effects of the other factors. Thus, laboratory comparisons were made without possibly being compromised by any region or batch effects. Although two

significant digits were used in the analyses, the table reports no more than two decimal places for readability and ease of comparison.

It is important to note that for the interlaboratory comparisons, 1,3-butadiene concentrations were reported as BDL in nearly every ambient air sample. As presented in Table 6, Labs A, C, and D were generally in agreement, with exceptions for a few VOCs. Lab B differed from Labs C and D for all the VOCs except benzene. However, it is worth noting that the differences in all cases were small, with each being <1 ppbv.

3.2.4. Analytical precision—Coefficients of variation, expressed as a percentage, were used to measure precision among the laboratories using both the ambient duplicate sampling and the lower- and higher-level laboratory-prepared challenge samples. Table 7 presents the median CVs, all of which were 10%. Duplicate precision within $\pm 20\%$ is the criterion specified in EPA Compendium Method TO-17 (U.S. EPA, 1999b), and these results are well within that range.

Table 8 presents the results of the exact Wilcoxon rank sum tests and the Hodges-Lehmann estimates of differences between the laboratories. Few significant differences are seen in Table 8, indicating the laboratories generally exhibited comparable precision. (Note that no adjustments were made for multiple comparisons or potential false positives in this testing.) Further emphasizing the agreement in precision among laboratories, 31 of the 42 entries in Table 8 are < 5%, and the maximum difference estimated is 10%.

One caveat needs to be mentioned regarding the results for 1,3-butadiene and styrene in Table 7, Table 8. Because of the large numbers of BDLs reported from duplicate samples, results for the precision comparisons for these two VOCs should be viewed with caution.

4. Discussion and conclusions

EPA Method 325B states that VOCs from air samples collected on sorbent tubes should be analyzed within 30 days. However, the results presented here indicate that the VOCs benzene, toluene, tetrachloroethene, ethylbenzene, *m*, *p*-xylene, styrene, and *o*-xylene are stable when collected on Carbopack X sorbent tubes and refrigerated for periods of up to 6 months or longer. Percent recovery was biased low for 1,3-butadiene over this period, and a slight negative bias was seen for the other VOCs except benzene, which was not biased. Multiple sample integrity studies for benzene collected on Carbopack X over extended time periods (3 months and longer) have been reported previously (Martin et al., 2010, Footer et al., 2015, Eastern Research Group, 2015, Caurant et al., 2010), but sample integrity studies for the other seven compounds over extended time periods of 3 months and longer have not been reported.

VOC samples collected on Carbopack X tubes for the determination of benzene do not necessarily require refrigeration. The EPA VOC laboratory, however, routinely refrigerates samples since 1,3-butadiene is a compound of interest for the laboratory, and Martin et al. (2005) noted that sample integrity results for 1,3-butadiene were better for samples that were refrigerated than those stored at room temperature. Future studies on the sample integrity of VOCs collected on Carbopack X tubes and subsequently stored at room temperature for

periods of 3–6 months would be of value to the community of users who are employing Method 325B or similar diffusive sampling methods.

For the comparison of different laboratories analyzing selected VOCs collected on Carpack X sorbent tubes, all laboratories reported levels below the detection limit for each compound for laboratory blanks, which suggests that the laboratories were not reporting biased numbers, at least for these low levels. For laboratory-prepared challenge samples, the laboratories were generally on target with their measurements ($\pm 25\%$) as compared to the theoretical concentrations of VOCs that were diffusively loaded on the Carpack X sorbent tubes. For lower-level challenge samples at 3 ppbv, the laboratories were generally in agreement with each other, and any observed differences were small (< 1 ppbv). At the higher challenge level of 20 ppbv, most of the observed laboratory differences were > 1 ppbv, yet the reported concentrations generally were within $\pm 25\%$ of the theoretical concentration. When using collocated ambient samples to compare laboratories, any statistically significant differences were found to be small, < 1 ppbv. All laboratories exhibited excellent precision, well within the performance criterion of $\pm 20\%$ specified in EPA Compendium Method TO-17, and were generally in agreement with each other.

The results of these interlaboratory comparison studies, for both the laboratory-prepared challenge samples and the ambient samples, suggest that Method 325B can be employed reliably by commercial laboratories using Carpack X sorbent tubes. Furthermore, it should be noted that different sources and types of calibration standards (liquid and gaseous) and different loading techniques for preparing calibration standards (active and diffusive) were employed by the laboratories and that uptake rates were used for three of the laboratories to convert mass to a ppbv concentration. The good agreement of the four laboratories in determining ambient-level concentrations of VOCs collected diffusively on Carpack X sorbent tubes indicates that high-quality data can be generated for concentrations of VOCs in ambient air when laboratories employ EPA Method 325B.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

- Caurant A, Lal_ere B, Schbath M-C, Stumpf C, Sutour C, Mace T, Quisefi J-P, Doussin J-F, Vaslin-Reimann S, 2010 A new certified reference material for benzene measurement in air on a sorbent tube: development and proficiencytesting. *Anal. Bioanal. Chem* 398, 2265e2277. [PubMed: 20835870]
- Eastern Research Group, 2015 Evaluation of VOC Passive Sorbent Tube Technology Performance Eastern Research Group, Morrisville, NC.

- Eisele AP, Mukerjee S, Smith LA, Thoma ED, Whitaker DA, Oliver KD, Wu T, Colon M, Alston L, Cousett TA, Miller MC, Smith DM, Stallings C, 2016 Volatile organic compounds at two oil and natural gas production well pads in Colorado and Texas using passive samplers. *J. Air Waste Manag. Assoc* 66, 412e419. [PubMed: 26771215]
- Footer T, Van Enwyck L, Krnavek L, Dayton D, 2015 Passive sorbent tube performance evaluation for ambient and source monitoring of benzene and 1,3-butadiene. In: *Proceedings of the 108th Annual Conference of the Air & Waste Management Association*, June 23e26, 2015, Raleigh, North Carolina.
- Hollander M, Wolfe DA, 1999 *Nonparametric Statistical Methods*, second ed, 35 Wiley, New York, p. 125.
- Martin NA, Marlow DJ, Henderson MH, Goody BA, Quincey PE, 2003 Studies using the sorbent Carpack X for measuring environmental benzene with Perkin-Elmer-type pumped and diffusive samplers. *Atmos. Environ* 37, 871e879.
- Martin NA, Duckworth P, Henderson MH, Swann NRW, Granshaw ST, Lipscombe RP, Goody BA, 2005 Measurements of environmental 1,3-butadiene with pumped and diffusive samplers using the sorbent Carpack X. *Atmos. Environ* 39, 1069e1077.
- Martin NA, Leming EJ, Henderson MH, Lipscombe RP, Black JK, Jarvis SD, 2010 Verification of diffusive and pumped samplers for volatile organic compounds using a controlled atmosphere test facility. *Atmos. Environ* 44, 3378e3385.
- McClenny WA, Oliver KD, Jacumin HH, Jr., Daughtrey EH, Jr., Whitaker DA, 2005 24 h diffusive sampling of toxic VOCs in air onto Carpack X solid adsorbent followed by thermal desorption/GC/MS analysis in laboratory studies. *J. Environ. Monit* 7, 248e256. [PubMed: 15735783]
- McClenny WA, Jacumin HH, Jr., Oliver KD, Daughtrey EH, Jr., Whitaker DA, 2006 Comparison of 24 h averaged VOC monitoring results for residential indoor and outdoor air using Carpack X-filled diffusive samplers and active sampling: a pilot study. *J. Environ. Monit* 8, 263e269. [PubMed: 16470258]
- Mukerjee S, Oliver KD, Seila RL, Jacumin HH, Jr., Croghan C, Daughtrey EH, Jr., Neas LM, Smith LA, 2009 Field comparison of passive air samplers with reference monitors for ambient volatile organic compounds and nitrogen dioxide under week-long integrals. *J. Environ. Monit* 11, 220e227. [PubMed: 19137161]
- Mukerjee S, Smith LA, Thoma ED, Oliver KD, Whitaker DA, Wu T, Colon M, Alston L, Cousett TA, Stallings C, 2016 Spatial analysis of volatile organic compounds in South Philadelphia using passive samplers. *J. Air Waste Manag. Assoc* 66, 492e498. [PubMed: 26828464]
- SAS, 2012 *SAS OnlineDoc® 9.3*. SAS Institute Inc., Cary, NC.
- Thoma ED, Miller MC, Chung KC, Parsons NL, Shine BC, 2011 Facility fence line monitoring using passive samplers. *J. AirWaste Manag. Assoc* 61, 834e842.
- Thoma ED, Jiao W, Brantley H, Wu T, Squier B, Mitchell B, Oliver K, Whitaker D, Mukerjee S, Colon M, Alston L, Gross-Davis CA, Schmidt H, Landy R, DeWees J, Merrill R, Escobar E, Amin MS, Modrak M, 2015 South Philadelphia passive sampler and sensor study: interim report. In: *Proceedings of the 108th Annual Conference of the Air & Waste Management Association*, June 23e26, 2015, Raleigh, North Carolina.
- Thoma ED, Brantley HL, Oliver KD, Whitaker DA, Mukerjee S, Mitchell B, Wu T, Squier B, Escobar E, Cousett TA, Gross-Davis CA, Schmidt H, Sosna D, Weiss H, 2016 South Philadelphia passive sampler and sensor study. *J. Air Waste Manag. Assoc* 66, 959e970 <http://dx.doi.org/10.1080/10962247.2016.1184724>. [PubMed: 27192142]
- U.S. Environmental Protection Agency (U.S. EPA), 1999a *Compendium Method TO-14A: Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography* In *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, second ed. EPA/625/R-96/010b Available at: <https://www3.epa.gov/ttnamti1/files/ambient/airtox/to-14ar.pdf> (Accessed 25 August, 2016).
- U.S. EPA, 1999b *Compendium Method TO-17: Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes* In *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, second ed. EPA/625/R-96/010b

Available at: <https://www3.epa.gov/ttnamti1/files/ambient/airtox/to-17r.pdf> (Accessed 25 August, 2016).

- U.S. EPA, 2015a Petroleum Refinery Sector Risk and Technology Review and New Source Performance Standards e Final Rule. Federal Register 40 CFR Part 63, ID: EPA-HQ-OAR-2010-0682-0700. <https://www.regulations.gov> (Accessed 10 November, 2016).
- U.S. EPA, 2015b Method 325A: Volatile Organic Compounds from Fugitive and Area Sources: Sampler Deployment and VOC Sample Collection. 40 CFR Part 63, Subpart UUU [EPA-HQ-OAR-2010-0682; FRL-9720-4], RIN 2060-AQ75, Petroleum Refinery Sector Risk and Technology Review and New Source Performance Standards. Available at: <http://www3.epa.gov/ttn/emc/promgate/m-325a.pdf> (Accessed 25 August, 2016).
- U.S. EPA, 2015c Method 325B-volatile Organic Compounds from Fugitive and Area Sources: Sampler Preparation and Analysis. 40 CFR Part 63, Subpart UUU [EPAHQ-OAR-2010-0682; FRL-9720-4], RIN 2060-AQ75, Petroleum Refinery Sector Risk and Technology Review and New Source Performance Standards. Available at: <http://www3.epa.gov/ttn/emc/promgate/m-325b.pdf> (Accessed 25 August, 2016).

Fig. 1.

Percent recovery of all measurements for each of the compounds. The points in red were eliminated for the analysis; red numbers indicate the distance from the mean in terms of the number of standard deviations.

Table 1.

Results of storage stability regressions.

Compound	Intercept (%)	Test for Intercept = 100%? <i>p</i> -value	Slope (%/day)	Slope <i>p</i> -value	R ² (%)	CV (%)
1,3-Butadiene	87.7	<0.0001	-0.081	<0.0001	13	14
Benzene	99.7	0.7955	-0.028	0.0399	2	11
Toluene	97.5	0.0161	0.033	0.0019	4	9
Tetrachloroethene	96.9	<0.0001	0.039	0.0003	6	6
Ethylbenzene	96.7	0.0011	0.021	0.0521	2	9
<i>m,p</i> -Xylene	96.6	0.0012	0.016	0.1571	1	9
Styrene	96.6	0.0080	0.011	0.4137	0.3	11
<i>o</i> -Xylene	96.9	0.0026	0.016	0.1425	1	9

Table 2.

Predicted recoveries and 95% confidence intervals for recovery (%) after 30, 90, and 180 days.

Compound	Predicted recovery (%)	Upper confidence limit (mean)	Lower confidence limit (mean)
1,3-Butadiene			
30 days	85	87	83
90 days	80	82	79
180 days	73	76	70
Benzene			
30 days	99	101	97
90 days	97	98	96
180 days	95	98	92
Toluene			
30 days	98	100	97
90 days	101	102	99
180 days	104	106	101
Tetrachloroethene			
30 days	98	99	97
90 days	100	100	99
180 days	102	104	100
Ethylbenzene			
30 days	97	99	96
90 days	98	100	97
180 days	100	103	98
<i>m,p</i>-Xylene			
30 days	97	99	96
90 days	98	99	97
180 days	99	102	97
Styrene			
30 days	97	99	95
90 days	98	99	96
180 days	99	102	95
<i>o</i>-Xylene			
30 days	97	99	96
90 days	98	100	97
180 days	100	102	97

Table 3.

Mean measured and target challenge concentrations (ppbv).

Compound	Lower challenge sample (n = 3)					Higher challenge sample (n = 3)				
	Target	Lab A	Lab B	Lab C	Lab D	Target	Lab A	Lab B	Lab C	Lab D
1,3-Butadiene	2.9	2.3 ^a	2.9	2.2 ^b	2.4 ^a	20	19	22 ^S	16 ^a	17 ^b
Benzene	2.9	2.4 ^b	3.1 ^c	3.0	2.7	20	17 ^S	21	18	21
Toluene	2.9	2.7 ^S	3.5 ^S	3.0	2.8 ^c	20	19 ^S	25 ^S	21 ^S	20 ^S
Ethylbenzene	2.9	2.9	3.4 ^b	2.9	2.8	20	22 ^a	25 ^S	21 ^c	19 ^S
<i>m,p</i> -Xylene	5.8	6.6 ^S	6.6 ^S	5.8	5.4	40	49 ^S	49 ^S	41	37 ^c
Styrene	2.9	3.6 ^S	3.0	2.8	2.6	20	27 ^a	24 ^S	20	18 ^c
<i>o</i> -Xylene	2.9	3.1 ^a	3.2 ^S	2.8	2.7	20	23 ^a	24 ^b	20	19 ^c

Notes:

^aMean different from target at 5% level.^bMean different from target at 1% level.^cMean different from target at 10% level.^SAll measured values were the same to two significant digits; no formal test was done.

Table 4.

Lower-level challenge sample concentration differences. For each laboratory comparison shown, the differences of means (ppbv) are given as Lab X – Lab Y (e.g., A – B).

Compound	A vs. B	A vs. C	A vs. D	B vs. C	B vs. D	C vs. D
1,3-Butadiene	−0.57 ^a	0.13	−0.13	0.70 ^b	0.43 ^c	−0.27
Benzene	−0.67 ^b	−0.53 ^b	−0.30	0.13	0.37 ^c	0.23
Toluene	−0.80 ^b	−0.30 ^c	−0.07	0.50 ^a	0.73 ^a	0.23 ^c
Ethylbenzene	−0.43 ^b	0.00	0.13	0.43 ^a	0.57 ^b	0.13
<i>m,p</i> -Xylene	0.00 ^S	0.80	1.2	0.80	1.2	0.37
Styrene	0.60 ^a	0.80 ^a	1.0	0.20	0.43	0.23
<i>o</i> -Xylene	−0.13	0.30 ^c	0.33	0.43 ^c	0.47	0.03

Notes:

^aSignificant at the 5% level.

^bSignificant at the 1% level.

^cSignificant at the 10% level.

^STo two significant digits, both laboratories measured the same value all three times; no formal test was done.

Table 5.

Higher level challenge sample concentration differences. For each laboratory comparison shown, the differences of means (ppbv) are given as Lab X – Lab Y (e.g., A – B).

Compound	A vs. B	A vs. C	A vs. D	B vs. C	B vs. D	C vs. D
1,3-Butadiene	-3.0 ^a	3.0 ^a	2.3 ^a	6.0 ^b	5.3 ^b	-0.67
Benzene	-3.7 ^b	-1.3	-3.7	2.3	0.00	-2.3
Toluene	-6.0 ^R	-2.0 ^R	-1.0 ^R	4.0 ^R	5.0 ^R	1.0 ^R
Ethylbenzene	-2.7 ^b	1.0	3.3 ^b	3.7 ^b	6.0 ^c	2.3 ^b
<i>m,p</i> -Xylene	0.00 ^S	8.3 ^b	12 ^b	8.3 ^b	12 ^b	3.3 ^b
Styrene	3.3	7.7 ^b	9.3 ^c	4.3 ^a	6.0 ^b	1.7
<i>o</i> -Xylene	-1.3	3.3 ^a	4.3 ^b	4.7 ^b	5.7 ^c	1.0

Notes:

^aSignificant at the 10% level.

^bSignificant at the 5% level.

^cSignificant at the 1% level.

^RThe laboratories reported different values, but within each laboratory, the same value was reported all three times to two significant digits; no formal test was done.

^STo two significant digits, both laboratories measured the same value all three times; no formal test was done.

Table 6.

Laboratory comparisons based on the ambient sampling. For each laboratory comparison shown, the differences of means (ppbv) are given as Lab X – Lab Y (e.g., A – B).

Compound	A vs. B	A vs. C	A vs. D	B vs. C	B vs. D	C vs. D
1,3-Butadiene	−0.01 ^a	0.01 ^b	0.03 ^b	0.02 ^b	0.04 ^b	0.02 ^b
Benzene	−0.24 ^c	−0.17	−0.04	0.07	0.21	0.14
Toluene	−0.38 ^a	−0.03	0.36 ^c	0.36 ^c	0.75 ^b	0.39 ^a
Ethylbenzene	−0.04 ^b	−0.01	−0.00	0.04 ^b	0.04 ^b	0.00
<i>m,p</i> -Xylene	−0.14 ^c	0.04	0.10	0.18 ^a	0.24 ^b	0.06
Styrene	−0.04 ^b	−0.01 ^b	−0.00	0.04 ^b	0.04 ^b	0.01 ^b
<i>o</i> -Xylene	−0.06 ^b	−0.01	−0.00	0.04 ^b	0.06 ^b	0.01

Notes:

^aSignificant at the 5% level.

^bSignificant at the 1% level.

^cSignificant at the 10% level.

Table 7.

Median laboratory CVs (%) based on duplicate and challenge samples.

Compound	Lab A	Lab B	Lab C	Lab D
1,3-Butadiene	0.00	0.00	0.00	6.3
Benzene	6.6	3.0	4.2	5.6
Toluene	1.3	5.0	4.0	2.1
Ethylbenzene	0.98	2.3	0.00	3.6
<i>m,p</i> -Xylene	0.00	3.9	5.0	10
Styrene	0.00	0.00	0.00	5.6
<i>o</i> -Xylene	0.00	7.4	6.1	7.6

Table 8.

Laboratory comparisons of precision based on duplicate and challenge samples. For each laboratory comparison shown, the Hodges-Lehmann estimates (ppbv) are given as Lab X – Lab Y (e.g., A – B).

Compound	A vs. B	A vs. C	A vs. D	B vs. C	B vs. D	C vs. D
1,3-Butadiene	0.00	0.00	-6.3 ^a	0.00	-6.3 ^a	-6.3 ^a
Benzene	2.4	1.2	1.5	-1.2 ^b	-2.4 ^b	-1.0
Toluene	-3.8	-3.7	-0.00	1.4	3.3	3.3
Ethylbenzene	-0.23	0.00	-2.6	0.37	-0.00	-3.6
<i>m,p</i> -Xylene	-3.7	-3.7	-10	-0.52	-1.5	-5.5
Styrene	0.00	0.00	-5.6	0.00	-5.6	-5.6 ^b
<i>o</i> -Xylene	-6.1 ^a	-5.9 ^a	-7.6 ^a	0.95	-1.0	-1.7

^aSignificant at the 5% level.

^bSignificant at the 10% level.