March 13, 2026

Transmitted via e-mail to: jigallaghe@pa.gov

Jillian Gallagher
Air Quality Program Manager
Department of Environmental Protection, Southeast Regional Office
2 East Main Street
Norristown, PA 19401

RE: Response to Comments and Addendum to the Fenceline Perimeter Air Monitoring Plan
MIPC Chelsea Facility
PADEP Facility ID No. 634737
920 Cherry Tree Road, Aston, PA 19014
Bethel Township, Upper Chichester Township, Aston Township, Delaware County
Langan Project No. 220240201

Dear Ms. Gallagher:

On behalf of MIPC, LLC (MIPC), Langan Engineering and Environmental Services, LLC (Langan) is submitting the below responses to comments received from the Department of Environmental Protection (the Department or DEP) by letter dated January 29, 2026 regarding the DEP's review of the fenceline perimeter air monitoring plan submitted on January 13, 2026 in accordance with DEP's December 23, 2025 administrative order (order).

The DEP Air Quality Program team, MIPC, and Langan met on March 3, 2026 to discuss the Department's comments, review air monitoring data to date, and discuss proposed alternatives to the procedures and methods outlined in the existing fenceline perimeter air monitoring plan. This letter presents a formal response to DEP's comments in their January 29, 2026 letter and proposes an alternative, 14-day air monitoring plan for the Department's review and consideration.

Additionally, DEP, MIPC, and Langan discussed pausing air monitoring during weekend days (i.e., Saturday and Sunday) when active gasoline recovery activities are not occurring. Eliminating 24-hour sampling during the weekends is justified based on the results from over 190 samples collected since perimeter air monitoring began at the end of December 2025. During our discussion on March 3, 2026, the Department agreed to review MIPC's request to pause TO-15 air monitoring on Saturdays and Sundays when neither active site characterization activities (e.g., drilling, well installation) nor gasoline recovery (via Vacuum Enhanced Fluid Recovery or VEFR) are occurring.

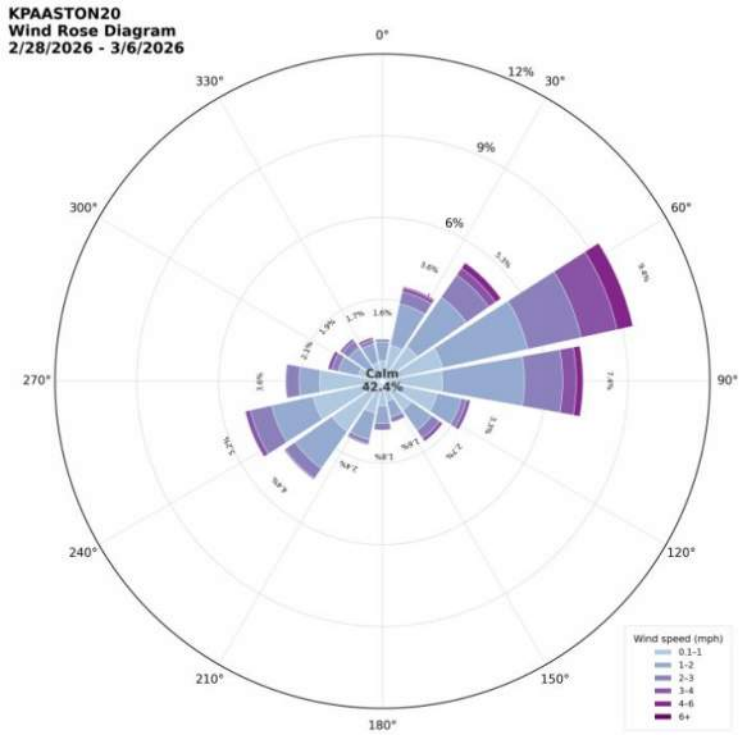
RESPONSE TO DEPARTMENT COMMENTS & ADDENDUM TO PERIMETER AIR MONITORING PLAN

Per the January 29, 2026 letter from the Department to MIPC, DEP offered the following comments; responses from MIPC/Langan follow each of the Department's comments in italicized text:

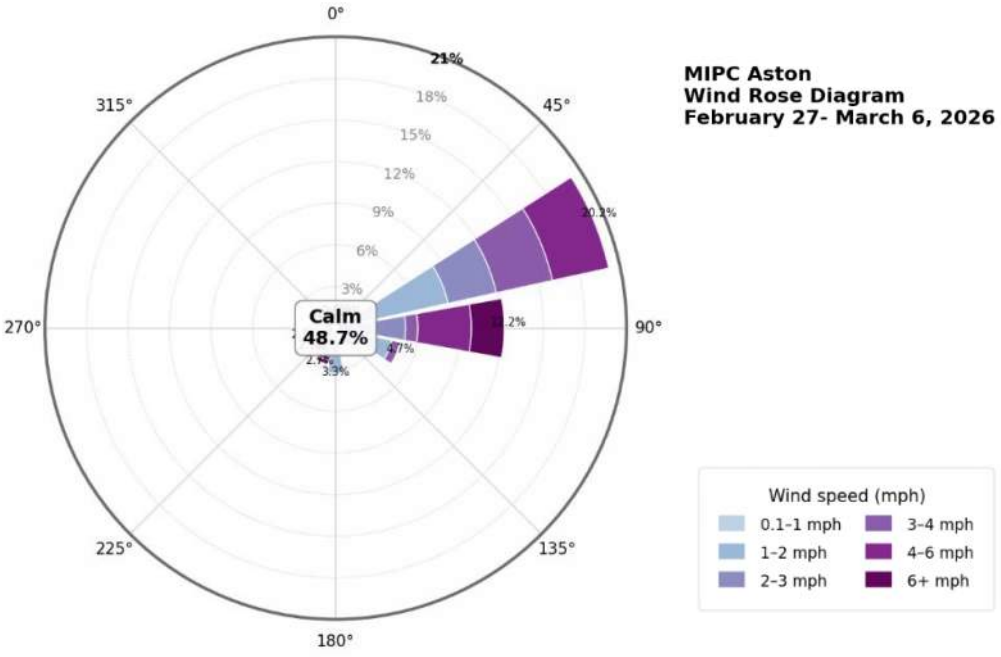
- **Section 3.1:** Please provide a wind rose to support the selection of the sampling location. Sites AA-2, 3, and 4 are very close to trees or shrubs as shown in Figure 2, which could cause obstruction for airflow. Samplers should meet certain siting criteria. For example, sampling unit inlet should be > 10 meters from the drip line of the nearest tree. Refer to NATTS Technical Assistance Document (Section 7.1). https://www.epa.gov/system/files/documents/2022-08/NATTS-TAD-Revision-4-Final-July-2022-508.pdf.

  MIPC/Langan response: *Air monitoring locations were sited in areas deemed most suitable for collecting samples representative of the primary work area and to be protective of residents. Site topography and prevailing wind direction were also considered when selecting air monitoring locations. Overall, stations AA-1 and AA-2 are located beyond 10 meters from tree overhang. Stations AA-3 and AA-4 are located along the western fenceline in the core work area and in the prevailing downwind direction of the core work area, respectively. Air monitoring locations in these important areas are constrained because of the presence of mature trees and smaller shrub vegetation along the western fenceline and the MIPC site access road to the east. Additional information, including a figure and photographs, regarding siting the monitoring locations is presented at the end of this response.*

  Prevailing wind direction from both onsite and offsite weather stations is from the east-northeast. A wind rose was used to support selection of the sampling locations. Wind direction, speed, and gusts are variable; therefore, a single wind rose would not be representative of local weather conditions. However, wind roses generated using both onsite and offsite weather data are provided to DEP weekly in progress reports. The most recent wind rose diagrams from the 11th Weekly Progress Report are re-presented below, and additional weather information follows.



Wind rose diagram for the first week of March using data from offsite weather station KPAASTON20



Wind rose diagram for the first week of March using data from onsite weather station MIPC Aston

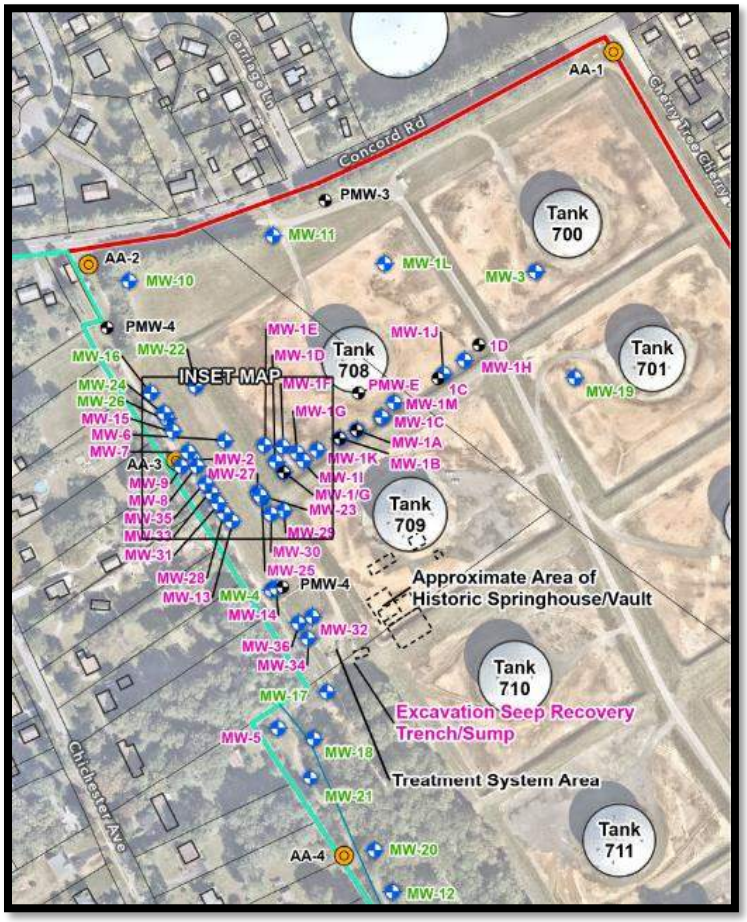
Since the Weekly Progress Report No. 7 dated February 10, 2026 and onwards, Langan has been providing weather data, including wind rose diagrams, from both the offsite, public weather station, KPAASTON20, located about 0.75 miles northeast of MIPC in Aston, PA and from an on-site private weather station, MIPC Aston, located at the southwest corner of the site until March 3, 2026 when it was moved to the northern boundary of the site. A weather station has been installed at the site for site specific data evaluation purposes including temperature, barometric pressure, precipitation, wind speed, and wind direction. Data for both weather stations is available from January 1, 2026 and onwards.

Langan has evaluated wind speed and direction from January 1, 2026 through February 26, 2026 and presented the data collected in Weekly Progress Reports since the submittal of Report No. 7. Langan will continue to provide weather data and perimeter air sampling data (including wind rose diagrams) in subsequent weekly progress reports, as requested.

Both the on-site weather station and public KPAASTON20 station frequently measure calm to no winds as depicted on wind rose diagrams indicating components of wind speeds commonly below 6 mph. For public station KPAASTON20, daily wind direction patterns frequently alternate between NE/ENE and WSW flow. Comparatively, the onsite weather station has displayed different prevailing wind directions, typically alternating from the N/NNW and secondarily to the E. At the on-site station, these prevailing wind directions have remained generally consistent throughout the entire monitoring period.

Initially, the on-site weather station was placed for power and WIFI access, but as of March 3, 2026, the on-site weather station has been relocated to the northern part of the site proximate to the potential source area.

The approach in siting the sampling locations considers both the potential remediation source area and the potential residential receptors. The locations are shown on the inset figure below and on attached Figure 1. Each summa canister and flow controller is outfitted with a specialized goose neck / shepherd's hook intake to attempt to prevent debris or rain from entering the sample train. Monitoring Stations AA-3 and -4 are located on the fence line within the active gasoline release investigation/ recovery area (near station AA-3), and further along the fence line perimeter to the south (AA-4). The western – southwestern perimeter area is forested with an active access road and active remedial efforts in the vicinity, including drilling, single well and multi-well vacuum enhanced recovery, continuous operation of and gasoline product collection/treatment by the water treatment unit (WTU), active installation maintenance of erosion and sediment control measures, and driving activity.



Monitoring locations AA-1 through AA-4 relative to LNAPL recovery operations, which have been focused in the MW-2 and water treatment system areas to date.

Monitor stations AA-1 and AA-2 are located beyond 10 meters from tree overhang, as shown in the photographs below.

Photo of monitoring location AA-1, located near the intersection of Concord and Cherry Tree Roads.

Photo of monitoring location AA-2, located at the northwest corner of the site.

As shown in the photo below, monitoring location AA-3 is placed along the fence line central to the core of on-site gasoline removal/recovery and investigation activities. Its location has limited overhead interferences and is at least 6.5 feet away from nearby shrub vegetation located off-site beyond the fence line.

Photo of monitoring location AA-3 (Summa canisters connected to fence on right) relative to LNAPL recovery operations (vacuum enhanced fluids recovery, VEFR).

Regarding monitoring location AA-4, it is on the western perimeter fence in a forested area with trees present to the north and south along the perimeter fence (see photo below) and an active access road and drilling investigation activities nearby to the east. Monitoring station AA-4 is at least 7 feet and as far away as practical from the nearest tree vegetation with limited overhead interferences.

Photo of monitoring location AA-4 relative to trees, which are present along the western fenceline in this area.

The locations of stations AA-3 and AA-4 are chosen to be near the activities likely to be primary sources of gasoline emissions and at fence line locations proximate to offsite receptors.

- **Section 3.3:** The final pressure in the canister is critical for determining if the sample is valid. Please document equipment QA/QC checks and acceptance criteria for the canister sampling. For data QA/QC, collection of collocated and duplicate field samples is recommended.

  MIPC/Langan response: *As a standard practice, the final pressure readings are recorded for each canister on the laboratory chain-of-custody and field sheets. The automatic sampling devices are programmed to end sampling when the Summa canister pressure reaches approximately - 5 inches of mercury. If the observed final pressure is zero or close to zero (atmospheric), the information is recorded as a qualified sample and sent to the laboratory for verification and sample analysis. The flow rate for that Nutech sampling device is adjusted accordingly, or, if appropriate,*

the automatic sampling device is returned to the supplier and a new device is deployed.

To supplement data QA/QC, a collocated duplicate field sample will be collected and analyzed at a frequency of one for every twenty samples collected.

- **Section 3.4:** Please provide the lab SOP for VOC canister analysis and data verification.

  MIPC/Langan response: *Attached (Attachment 1) please find from Alpha Analytical, LLC, a subsidiary of Pace Analytical, the SOP for VOCs in Ambient Air by TO-15, published October 4, 2024.*

- **Section 3.5:** Data validation is an important step in assessing the quality of the sampling data. It's unclear how data will be reviewed or what data acceptance criteria will be applied. A detailed data review procedure including quality control measures and acceptance criteria should be documented.

  MIPC/Langan response: *Air samples are analyzed in accordance with EPA Method TO-15 per the PA-certified laboratory's SOP, which is included as Attachment 1. Langan reviews the Case Narrative summaries for each air sampling laboratory analytical report for non-conformance issues. If Laboratory Batch, Sample Specific % recovery or RPD values are outside the listed Acceptance Criteria for a PADEP-defined unleaded gasoline VOC, that data package is submitted to Langan's data validation team for completion of a Data Usability Assessment (DUA). Langan's Data Usability Assessments (a first tier data review, equivalent to USEPA's Level 2A validation), is based on completeness and compliance checks of sample-related QC results and recoveries where applicable, including: sample receipt documentation; analytical holding times; sample preservation; blank results (both laboratory- and field-derived); surrogate recoveries; MS/MSD recoveries and RPDs values; field duplicate RPDs, laboratory duplicate RPDs, and LCS/LCSD recoveries and RPDs.*

  If Langan determines that a Data Usability Assessment(s) is warranted for a data package, a copy of the data usability assessment(s) will be included as an attachment to weekly reports moving forward.

- **Section 3.6:** Based on DEP's understanding that remedial activities are expected to take more than a year from the initial discovery, DEP recommends using EPA's risk-based chronic screening levels for resident air (Regional Screening Levels (RSLs) | US EPA), with an HQ=1 for noncancer risks and a cancer risk benchmark of 1 in 100,000 using the more conservative number between the Carcinogenic and Noncarcinogenic Screening Levels ("SL"). If using the Carcinogenic SL, multiply by 10 to achieve a risk benchmark of 1 cancer case/100,000 people exposed.

  MIPC/Langan response*: Since the Weekly Progress Report No. 6 dated February 3, 2026 and onwards, results for gasoline-related constituents have been additionally*

compared to EPA's risk-based chronic screening levels (RSLs) for resident air (target hazard quotient of 1.0, target cancer risk of 1 in 100,000) using the more conservative number between the carcinogenic and noncarcinogenic screening levels, as recommended by DEP.

MIPC uses the EPA chronic RSL for resident air as an initial screening value and not a compliance point. If the RSL is exceeded, it prompts MIPC's further investigation into the nature of site activities on that day and the assessment of needs for any controls or response measures, if warranted. To supplement the continual evaluation of air monitoring results, MIPC has created a customized daily site observation and monitoring checklist to record daily odor checks, as well as applicable observations and work activities. MIPC and Langan site workers are also equipped with hand-held instruments (photoionization detectors (PIDs) to monitor total VOCs and also PIDs specifically calibrated for benzene) to monitor air quality within active work zones for worker health and safety, as well as perimeter sweeps along the nearby fenceline perimeter. PID readings collected periodically within the work zone and along the fenceline perimeter are recorded in our dedicated project field books.

MIPC/Langan also compare the benzene results to two additional screening criteria for data analysis: the EPA Fenceline Action Level for Refineries of 9.0 micrograms per cubic meter (ug/m3), and the PADEP Non-Residential Indoor Air screening value of 16 ug/m3.

Going forward, in accordance with a request from Jillian Gallagher of the Department's Bureau of Air Quality during the meeting on March 3, 2026, MIPC will adopt the EPA Fenceline Action Level for Refineries of 9.0 ug/m3 as a threshold that, if exceeded, will require notification to the Department Bureau of Air Quality within 24 hours of confirming the data.

- Please indicate the location of LNAPL recovery operations in Figure 2. If this is currently unknown, please provide a tentative/interim recovery location.

***MIPC/Langan response**: Figure 1, attached, depicts the area of active investigations and remedial response measures that were initiated upon discovery of the gasoline release on or about August 18, 2025. Response measures and activities have been enhanced/expanded since that time. Initial gasoline recovery efforts involved continuous vacuum truck extraction, and a temporary water treatment system has been operating since September 2025, as indicated on Figure 1 as "Treatment System Area". Since December 8, 2025, Langan and its subcontractor (Republic Services, Inc. through January 9, 2026 and Evergreen starting January 12, 2026) have been performing Vacuum Enhanced Fluid Recovery (VEFR) focused on the wells that are located west of Tank 708 and along the western property boundary, primarily surrounding well MW-2 (see Figure 1). On January 13, 2026, to supplement the WTU system efforts, an LNAPL recovery trench/sump was constructed as an added interim remedial measure immediately north (up-gradient) of the existing WTU, as indicated*

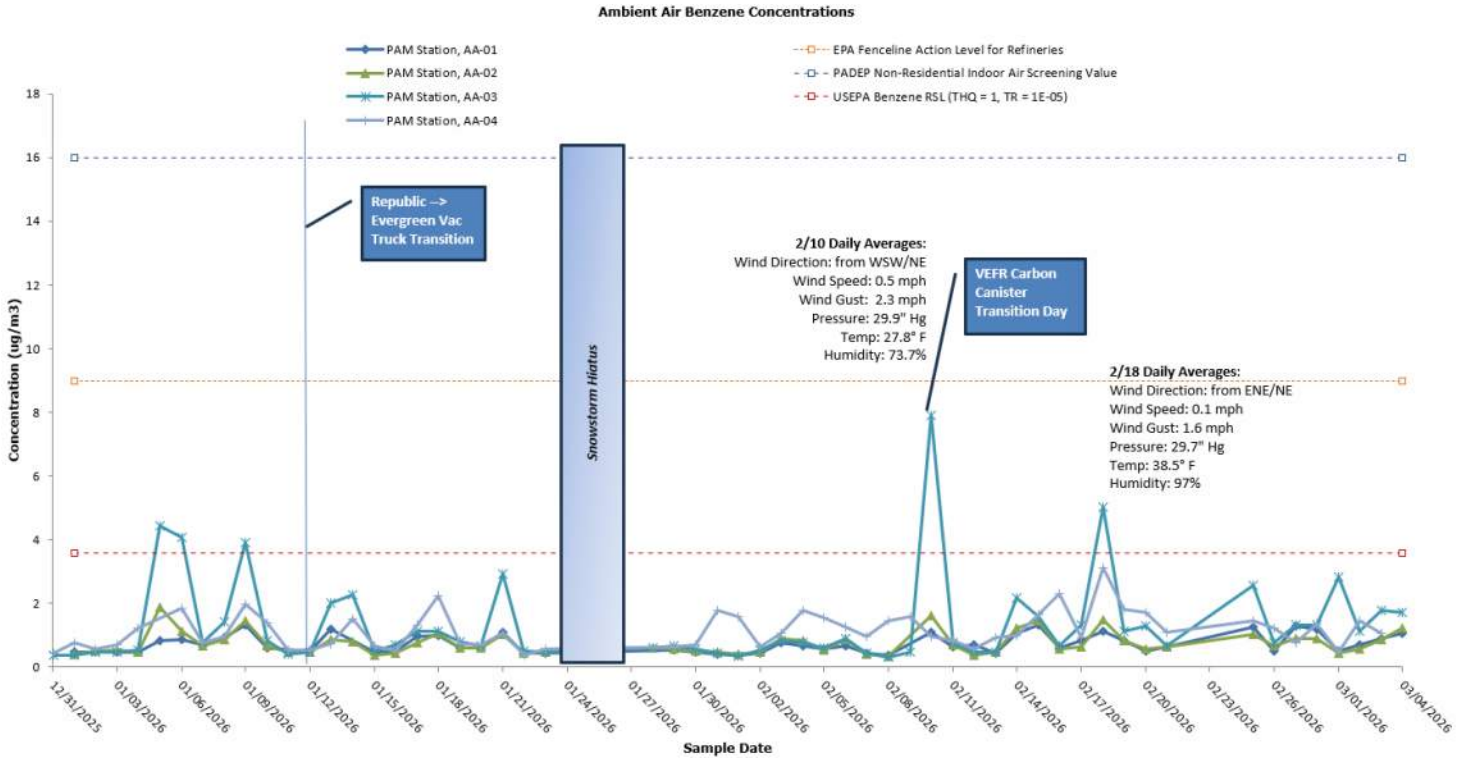
on Figure 1 as "Excavation Seep Recovery Trench/Sump". Multi-well extraction using a manifold system began on January 23, 2026. Perimeter Air Monitoring Sample Location AA-3 is located immediately adjacent to all of these interim and active measures, investigations, and LNAPL recovery efforts in this area along the western perimeter fenceline. Collectively these activities will continue as we progress toward selecting, designing, and constructing longer-term fixed and mobile treatment systems that will have treatment and emission controls and will be supported by Requests for Determination reviewed and approved by the Department.

PROPOSED PATH FORWARD

In summary, the perimeter fenceline air monitoring data collected over the past 60+ days since its start on December 30, 2025, meets the requirements and objectives of this prescribed air monitoring program for MIPC remedial response measures and investigation toward site cleanup:

- Establish fenceline ambient air sampling locations and sample collection procedures to capture release-area specific VOC levels along the westerly site fence line to assess potential sensitive receptors and to establish baseline conditions;
- Establish project screening values for evaluating perimeter VOC levels and response actions, as warranted;
- Prescribe the protocols to be followed if VOC levels approach or exceed the tiered project screening levels; and
- Establish recordkeeping, data review, and reporting procedures.

Since the Weekly Progress Report No. 7 dated February 10, 2026, Langan has evaluated concentrations of benzene because it poses the greatest potential carcinogenic risk of the main gasoline constituents. The inset figure below, also included in Attachment 2, provides a trend chart analysis of benzene concentrations reported for each daily sample at each of the four monitoring stations since December 30, 2025.



The above summary of benzene analytical results for the four air monitoring stations has been annotated to support interpretation of the data and to also highlight certain insights on activities that may be associated with the few results (only five samples in total) that had benzene concentrations above the EPA resident air RSL. Importantly, none of the results for the more than 190 air samples collected and analyzed to date have exceeded the EPA Fenceline Action Level for Refineries of 9.0 ug/m3 nor the PADEP Non-Residential Indoor Air screening value of 16 ug/m3. Key facts noted in the review and interpretation of the benzene data for the air monitoring program to date are summarized below.

- Benzene is the only gasoline compound of concern that has been temporarily measured exceeding the EPA RSL, and only five of the more than 190 samples analyzed by TO-15 had benzene results that exceeded the EPA resident air RSL.
- Monitoring station AA-3 is the only location where temporary measurements of benzene occurred (in those five instances) at concentrations above the EPA RSL; none of the other three monitoring stations have detected benzene above the EPA RSL value. Monitoring station AA-3 is close to the core of various on-site remedial measures and investigation activities that are occurring daily.
- As annotated in the chart above for benzene, the first three of five total instances where benzene concentrations in air were above the EPA RSL are believed to be attributed to a change in vac truck air control systems being used and the improved manner in which the Evergreen vac truck systems manage and control remediation emissions. Since that change to the Evergreen truck system, we have not measured potential concerns or

benzene levels of potential concern that are attributable to the Vac truck system emissions/controls.

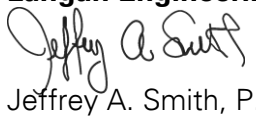
- The benzene result reported for February 10, 2026 was investigated and as noted in the data summary chart, it is postulated that the change from small to larger carbon treatment canisters occurred on that day as the likely contributing factor for the benzene result.
- The benzene result reported for February 18, 2026 was investigated but MIPC has not identified a specific activity on-site that might be related to that result at station AA-3 on that day.
- Overall, air monitoring data over 60+ days indicate that stable air quality conditions prevail across the perimeter fenceline monitoring stations deployed on-site.
- MIPC and Langan have developed and are implementing daily documentation/monitoring checks and record keeping toward evaluating daily operations and retrospectively conduct investigations and response measures, if warranted based on air monitoring results.

Based on the monitoring completed to date and the evaluation of existing perimeter air-monitoring results (190+ samples over more than 60 days), these air monitoring data support the transition to an alternative passive monitoring approach. Langan/MIPC recommends adopting a 14-day fenceline monitoring program under EPA Method 325A/B that aligns with EPA- fenceline air monitoring program. For review and consideration by the Department, Langan has prepared a proposed monitoring plan based on the EPA refinery fence-line monitoring framework described in Methods 325A and 325B, adapted for implementation at the investigation and remediation areas at the Tank 708 release aera.

Provided in Attachment 3, the procedures described in the alternative 14-day average air monitoring plan follow the intent of Method 325A sampler deployment requirements and Method 325B analytical requirements for benzene monitoring using passive diffusive sorbent tubes. For now, Langan and MIPC will continue with the TO-15 sampling program as documented herein and in the PAMP until the Department completes its review of the alternative sampling approach.

If you should have any questions or comments, please feel free to contact Jeffrey Smith directly at 215-694-7549.

Sincerely,
Langan Engineering and Environmental Services, LLC



Jeffrey A. Smith, P.G.
Senior Associate

Robert S. (Rory) Johnston, PE, GE, BCEE
Managing Principal

Enclosures:

Figure 1 – Site Plan with Air Monitoring Locations and Investigation/Recovery Areas

Attachment 1 – Pace Analytical Lab SOP for Method TO-15

Attachment 2 – Benzene Air Monitoring Trend Chart

Attachment 3 – Alternative Passive Air Monitoring Plan (Method 325)

cc: C. David Brown, P.G. Alex M. Langan, Simon Mullen, Lisa Strobridge – PADEP Southeast Regional Office
Township Managers - Aston Township, Bethel Township (+ Ray Stiles), Upper Chichester Township
Elizabeth Clapp, Melissa Turchi, Jeffrey Brockett, Adam Gattuso, Regan Howell, Sharon Watkins – MIPC, LLC
Margaret Hill - Blank Rome, LLP
Cortney Savidge, CHMM, John Loeffel – Langan

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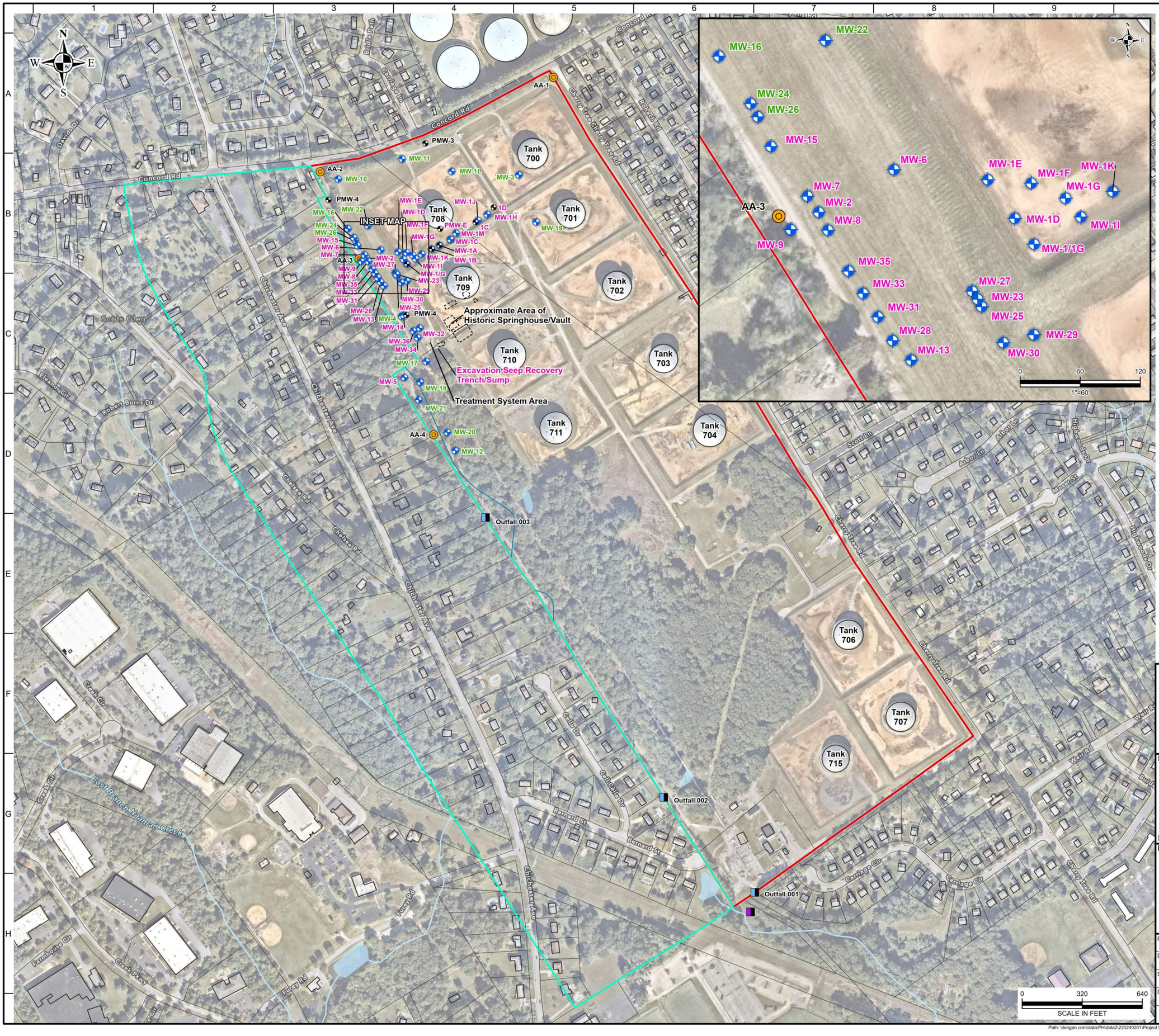
FIGURES



Legend

- Approximate Soil Boring Location
- Approximate Monitoring Well Location
- Air Monitoring Station Location
- Stormwater Outfall Approximate Location
- Approximate Location of Routine MIPC Surface Water Inspection
- Approximate Onsite Portion of Bezer's Run (subject to routine MIPC surface water inspection)
- Historic Site Feature
- 1000-Foot Buffer along Western Property Boundary (Properties Targeted for Semiannual Private Well Testing if not Connected to Public Water (Access Dependent))
- Site Boundary
- Structure
- Lake/Pond
- Stream

Notes:
Green Sample ID – No LNAPL Encountered in Well/Boring
Pink Sample ID – LNAPL Encountered in Well/Boring

1. All site feature locations are approximate.
2. Imagery provided through Langan's subscription to Nearmap.com. Flown 10/9/2025.
3. Parcel boundaries are provided by the Delaware County Office of Data and Mapping Innovation (ODMI).
4. Monitoring well and soil boring locations per survey data provided by Envirosure.
5. Streams and waterbodies are provided by the National Hydrography Dataset (NHD).
6. Structure outlines provided by the Federal Emergency Management Agency (FEMA) Geospatial Response Office and Oak Ridge National Laboratory (ORNL).
7. Sources of information for properties not serviced by CWA are CWA correspondence in December 2025 and responses from property owner water use questionnaires.

LANGAN

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Project

MIPC CHELSEA FACILITY

920 CHERRY TREE ROAD
ASTON TOWNSHIP

DELAWARE COUNTY PENNSYLVANIA

Drawing Title

MIPC CHELSEA FACILITY

Project No. 220240201	Figure 1
Date 3/2/2026	
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ATTACHMENTS

Attachment 1

Pace Analytical Lab SOP for Method TO-15

LANGAN

Determination of Volatile Organic Compounds in Air Using Specially-Prepared Canisters and Analyzed by GC/MS

References: **Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air - Second Edition.** U.S. Environmental Protection Agency. EPA/625/R-96/010b. Office of Research and Development National Risk Management Research Laboratory. Center for Environmental Research Information. Cincinnati, Ohio. January 1999.

Method TO-15: Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters and Analyzed By Gas Chromatography Mass Spectrometry (GC/MS). U.S. Environmental Protection Agency. EPA/625/R-96/010b. Office of Research and Development National Risk Management Research Laboratory. Center for Environmental Research Information. Cincinnati, Ohio. January 1999.

1. Scope and Application

Matrices: Ambient Air, Soil Gas, Soil Vapor

Definitions: Refer to Section 16 and Alpha Analytical Quality Systems Manual

This SOP describes the procedure for the analysis of volatile organic compounds (VOCS) in ambient air. The whole air samples are collected in fused-silica lined (FSL) stainless steel canisters, or Tedlar® bags. The VOCs are subsequently separated by gas chromatography (GC) and measured by mass selective detector (MSD).

The organic compounds that are amenable to this method are listed in Table 9. Other compounds may also be amenable provided they meet the QA/QC requirements of the method.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of the GC/MS and in the interpretation of GC/MS data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability.

This SOP contains addendums for various state-specific requirements. The criteria in these addenda (Addendum C-F) must be adhered to for projects conducted under the state programs.

2. Summary of Method

Samples are collected in precleaned, evacuated FSL canisters or Tedlar® bags.

Samples are pre-concentrated using the Entech 7200 or 7200A Cryogenic Concentrator. A specified volume of sample is pulled using a vacuum pump through a mass flow controller. The sample is cryogenically concentrated to a volume of less than one mL on a Tenax® trap.

Following pre-concentration, the sample is refocused on the GC transfer line. This step further reduces the sample volume to less than one microliter for injection.

The sample is then injected into the GC, which is used to separate the compounds of interest. All compounds are detected using an MSD.

2.1 Method Modifications from Reference

Initial Calibration modifications: If a target analyte cannot meet the %RSD criteria for relative response factor calibration, then linear regression may be used. A minimum of five calibration points must be incorporated and a correlation coefficient of 0.995 or greater must be achieved. The calibration plot must be printed and approval by a supervisor must be obtained prior to calibration acceptance. If any compound is calibrated using linear regression then after the ICV and prior to any sample analysis, a low point standard must be analyzed to confirm there is no bias resulting from the linear regression calibration used. Recovery of the low point standard must be 60-140% using the linear regression curve.

Continuing calibration and laboratory controlled spike (LCS) modifications: The recoveries of all analytes must be within 70% to 130% of the true value. If more than 10% of the compounds fail these criteria, or if one compound has a recovery less than 50% or greater than 150% the LCS must be re-analyzed. If failure occurs a second time, the instrument must be re-calibrated. Recoveries greater than 150% may be acceptable, provided analytes are not detected in the samples.

Initial Calibration Verification modification: Two analytes are allowed to be greater than 30% RSD, but less than 40%.

Sample Duplicate modifications: Up to 10% of the target analyte detections may exceed acceptance criteria. If more variation occurs, the sample analysis must be repeated. If an analyte detected in one of the analysis at >5x the reporting limit, and not detected in the duplicate analysis, the analysis must be repeated. If an analyte is detected in one analysis at <5x the reporting limit and not detected in the duplicate analysis, the RPD is not calculable (NC) and the analysis does not have to be repeated. If an analyte is not detected in both the original and duplicate analysis, the RPD is NC.

Section 8.4.1.2 of the TO-15 method requires all canisters to be leak checked for a period of 24 hr via pressurization of the canister. The laboratory conducts the leak check by measuring the vacuum of the canister after a minimum of a 24 hr. period has elapsed, not by pressurizing the canister as per the method.

The % RSD for any analyte must be < 30%, as outlined in Section 10.2.2.7 of this SOP.

Humidified nitrogen is used in place of zero air due to the frequency of detection of VOCs in zero air, particularly at SIM detection limits.

There is no NIST-traceable second source standard currently available for the analytes listed in Table 1, Table 3B, and Table A-7.

3. Reporting Limits

Table 9 lists target analytes and Reported Detection Limit information.

4. Interferences

4.1 Contamination may occur in the sampling system if canisters are not properly cleaned before use. Additionally, all other sampling equipment (e.g., pump and flow controllers)

must be thoroughly cleaned to ensure that the filling apparatus will not contaminate samples.

4.2 System carryover can be a potential problem, particularly for the heavier molecular weight hydrocarbons. Carryover can occur after the analysis of standards or high-level samples. Measures that must be taken to remove this contamination can include the analysis of multiple blanks, lab air, and the purging of the autosampler with nitrogen.

4.3 High moisture content, methane levels and/or carbon dioxide levels may interfere with the chromatography and trapping of target analytes. Dilutions may be performed on these samples; however, the reporting limits will then be elevated.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

All employees performing laboratory procedures must have read and understood the Alpha Analytical Chemical Hygiene Plan. All laboratory procedures must be performed in accordance with the provisions and policies of the manual. All accidents, injuries, spills, or unsafe conditions must be reported immediately to the laboratory manager, and such occurrences must be thoroughly documented.

The analyst must wear a lab coat, gloves, and safety glasses while preparing solutions or handling samples.

Preparation of liquid standards must be performed under a properly functioning fume hood. Preparation and venting of gaseous standards must also be performed under a properly functioning fume hood.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

6.1.1 FSL canister samples can be collected as grab samples or as time-integrated samples. Time-integrated samples can be collected for a maximum of 12 hours using 2.7-liter canisters, or a maximum of 24 hours to 7 days using 6-liter canisters. One liter canisters are typically used for soil vapor sampling with a sampling flowrate of 100-200 ml/min.

6.1.1.1 Grab samples are collected by opening the canister valve and allowing the canister to fill to ambient pressure. This process takes approximately one minute.

6.1.1.2 Time-integrated samples require the use of a properly calibrated flow controller. The flow controller, if provided by Alpha, is calibrated prior to

sample collection and is documented in the Alpha ACS LIMs (Refer to Alpha SOP # 2190 for Canister and Flow Controller Preparation).

6.1.2 Tedlar® bag samples typically can be collected as grab or composite samples and may require a pumping system or evacuated box.

6.1.3 Upon receipt at the laboratory, all samples are assigned unique laboratory identification numbers, checked for possible discrepancies, etc. (See SOP # 1559.)

6.2 Sample Preservation

Canisters-None. Tedlar® bags-should be protected from light.

6.3 Sample Shipping

All samples must be accompanied by a chain of custody form, which documents the date, and time of sample collection.

6.4 Sample Handling

The pressure of all FSL canister samples is measured upon receipt at the laboratory and documented in the ACS LIMs (See Alpha SOP #2190). A pressure gauge is attached to the canister inlet, the canister valve is briefly opened and the pressure is recorded. The gauge apparatus used to measure ambient air samples must be separate from that used to measure soil vapor or other matrices known to have elevated levels of VOCs to avoid cross-contamination.

Samples with pressures greater than -15 inches Hg are considered acceptable for analysis.

Samples with less than -15 inches Hg should be pressurized to > -15 inches Hg in order for the concentrator system to accurately draw the correct volume, resulting in a dilution of the sample. For ambient air samples, the client must be notified prior to sample analysis since this dilution may cause reporting limits to be elevated above project action levels.

Any samples that undergo pressurization prior to analysis are documented in the instrument software. Refer to Section 10.3.3.6 for the calculation of dilution factors due to pressurization of samples.

Refer to SOP # 1559 for Sample Management information.

FSL canister and Tedlar® bag samples are stored in the Volatiles Laboratory until analysis has been completed. Tedlar® bag samples are stored in opaque containers.

The recommended holding time for the analysis of FSL canister samples for TO-15 is 30 days from date of collection. The recommended holding time for the analysis of Tedlar® bag samples for TO-15 is 48-72 hours from date of collection. Tedlar® bag samples requiring TO-15 analysis may be transferred into canisters upon receipt at the laboratory in order to extend the holding time of the sample to 30 days.

Samples designated by client to be held for subsequent analyses or are “on hold” are to be kept in a designated area in the laboratory. “Hold” samples are discarded upon client authorization or after holding time expiration date.

7. Equipment and Supplies

7.1 Microliter syringes: 10, 25,and 500 µL

7.2 Gas tight syringes: 1 mL, 5 mL, 25 mL, 50 mL, and 100 mL

7.3 FSL canisters: 1.0, 2.7, 6.0 and 15 Liter

7.4 Tedlar® bags: Various sizes. Alpha supplies 5-Liter sizes. All bags must have polypropylene fittings which are recommended for the analysis of Sulfides and Mercaptans (see App. A).

7.5 Stop watch

7.6 Sample Concentrator

7.6.1 The concentrator system consists of two separate pieces of equipment: (1) Entech Model 7016D VOC Autosampler, and (2) Entech Model 7200 or 7200A Cryogenic Concentrator using liquid nitrogen.

7.6.2 A vacuum pump (Vaccubrand Model ME2 or similar) delivers the sample from the autosampler to the cryogenic concentrator FSL-lined steel tubing.

7.7 Gas Chromatograph System

7.7.1 Gas chromatograph - Shimadzu 2010, 2030

7.7.2 Chromatographic column: Restek RTX-1; 60 meters, 0.25 mm or 0.32 mm ID, 1 micron film thickness

7.7.3 Transfer line from column to GC injection port: Hydroguard ™ 0.32 mm capillary tubing connected to column with Restek Vu-Union connector.

7.8 Mass Spectrometer System

7.8.1 Mass spectrometer - Shimadzu 2010, 2020

7.8.2 The mass spectrometer must be capable of scanning from 29 to 270 amu every 3 seconds or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum that meets all the criteria in Table 5 when 50 ng of 4- bromofluorobenzene is injected. For SIM (selective ion monitoring) analysis, the system must be capable of simultaneous SIM/full scan acquisition.

7.8.3 Data System - Shimadzu GC/MS Solutions software for data acquisition and Agilent Enviroquant version E.02.00 for data processing.

7.9 Dilution Systems

7.9.1 Entech 4600A Dynamic Dilution System- for performing sample dilutions in canisters and Entech 4700 Precision Diluter preparing calibration standards in canisters. .

7.10 Primary flow measurement device: BIOS Cell Defender 510 or equivalent

8. Reagents and Standards

8.1 DI Water or Carbon-filtered tap water

8.2 High purity purge and trap grade methanol (Fisher part # A453-1 or equivalent) for MS source cleaning

8.3 Ultra high purity (UHP) helium for the GC/MS system

8.4 Ultra high purity (UHP) nitrogen for standard preparation

8.5 NIST certified TO-15 gas standards, purchased from Linde (formerly Spectra Gases). Standards are stored at room temperature and expire per vendor's expiration date, unless re-certified. Recertified standards are received with an updated certificate of analysis which includes a new expiration date.

8.6 Neat chemicals: Listed in Table 1, Table A-1, and Table 3B, ≥ 98% purity.

8.7 Liquid nitrogen: For the concentrator system and/or GC cooling

8.8 Primary Standards

8.8.1 Primary standard mixtures of TO-15 analytes are purchased certified gaseous standards already prepared as well as gaseous standards prepared in the laboratory by injecting neat chemicals into Tedlar® bags (See Table 1).

8.8.2 Table 1 indicates volumes of neat chemicals that are injected into 20 L of zero air or UHP nitrogen to obtain primary standard concentrations for all analytes.

8.8.3 Purchased primary standards are assigned a CSS # (commercially supplied standard) upon receipt for tracking purposes. Preparation of primary standards must be entered into the primary standard preparation logbook (Form No.: 117-11).

8.8.4 Standards are valid per the manufacturer's expiration date as noted.

8.9 Secondary Standards

8.9.1 Prepare secondary standards in canisters using the Entech 4700 Precision Diluter at a minimum of two concentration levels. Table 3A and 3B outlines the preparation steps for each secondary standard.

8.9.2 Prior to preparation of the standards, verify that an appropriate vacuum exists in the canister (>0.5 psia). Figure 3 demonstrates the standard preparation system. Primary standards prepared in Tedlar bags are injected into a canister (typically

15 L) using an injection tee with a septum or transferred from purchased and / or prepared cylinders via the precision diluter.

8.9.3 Attach the transfer lines from the primary standards to the dynamic diluter.

8.9.4 Prior to the injection of the gaseous standards, allow the dynamic diluter to equilibrate for a approximately 25 minutes by allowing each standard channel to flush for a minimum of 5 min. Be sure the vent line is attached to the outlet.

8.9.5 After equilibrating the system, attach the canister to the outlet of the diluter. Flush line with nitrogen for 20 sec prior to attaching canister. Load in the appropriate configuration and standard preparation method (TO15 ICAL, DIAZ, or TO15 LCS) into the precision dilution software for the corresponding target concentration (TO15 ICAL 100 ppbV, TO15 ICAL 10 ppbV).

Equation 1: Flow rate calculation:

$$T_f = V_{std} / F_{std}$$

Where:

T_f = standard transfer time, minutes
V_{std} = standard volume, mL
F_{std} = standard flowrate, mL/min

8.9.6 Inject the appropriate amount of Tedlar bag primary standard and/or the low vapor pressure compounds listed in Table 3B into the injection port tee. This injection must be done while the canister is below atmospheric pressure.

8.9.7 When all the primary standards have been added to the canister, the canister will be pressurized to the programmed final pressure using the precision diluter.

NOTE: Standard canisters prepared for analysis using the autosampler must have a maximum pressure of 30 psia to ensure proper and consistent sampling by the instrument.

8.9.8 Label the canister accordingly and record the standard preparation in the secondary standard (SS) preparation logbook (Form No.: 12925).

8.9.9 The ICV/LCS standard is prepared in the same manner, using primary standards of differing lot #s, at a concentration of 10 ppbV

Secondary standards are valid for 6 months.

8.10 Internal Standard and BFB Tuning Standard/Surrogate Standard

An internal standard (Bromochloromethane, 1,4-Difluorobenzene, and Chlorobenzene-D5) and tuning/surrogate standard containing Toluene-D8, 1,2-Dichloroethane-D4, and Bromofluorobenzene (BFB) are prepared as two separate gas standards at 25 ppbV (2

year expiration date). The internal standards and BFB / surrogates are loaded onto the sample trap prior to the calibration standard(s), sample, or QC sample(s) via a mass flow controller. The concentration of the internal standard and BFB / surrogates added is based upon the nominal concentration of sample that is analyzed. If the nominal volume of sample is 250 mL, then 100 mL of the 25 ppbV internal standard mix will yield a true value of 10 ppbV for the internal standards and BFB. Using equation 7, the ug/m^3 equivalent of BFB injected 179 ug/m^3 or 179 ng/L (MW of BFB = 175). Thus, the total ng injected is:

Total ng = 179 ng/L x 0.100 L = 17.9 ng

8.11 Instrument Calibration Standards

Calibration standards are prepared by injecting different volumes of the secondary standards into the concentrator/GC/MS system. The low standard will be used to establish the reporting limit for sample analyses. These are described in more detail in Section 10.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. Quality control limits may also be found in the Laboratory Information Management System(LIMs)

At a minimum, for each day of analysis, a Continuing Calibration standard, Laboratory Method Blank, Laboratory Control Spike and Laboratory Duplicate must be analyzed. Laboratory Control Spike Duplicate (LCSD) will be analyzed only upon client request.

9.1 Laboratory Method Blank(s)

A FSL canister pressurized to 30 psia with humidified nitrogen is utilized as the Laboratory Method Blank. This method blank must be free of target analyte contamination at or above the reporting limit. If it is not, the system must be evaluated for possible sources of contamination. Once the source is determined and eliminated, the Blank must be reanalyzed.

A Laboratory Method Blank must be run after samples suspected of being highly contaminated to determine if sample carryover has occurred. If samples have been analyzed using an autosampler, data must be evaluated for potential carryover and re-analyses conducted, as appropriate.

9.2 Laboratory Control Sample (LCS) / Laboratory Control Spike Duplicate (LCSD)

NOTE: A Laboratory Control Spike Duplicate is only performed when specified by the project requirements and/or upon Client request.

Laboratory Control Spike - A Laboratory Control Spike (LCS) is prepared by spiking an evacuated FSL canister with a different primary standard solution than that used for the calibration or a purchased gaseous standard with the components of interest may be used. If the recovery is not within acceptance criteria, the LCS may be analyzed a second time. If the LCS failure continues, the instrument must be recalibrated. Refer to Section 12 for appropriate corrective actions to be taken. QC limits are subject to change for any particular analyte, if deemed necessary after review of QC control limits.

9.3 Initial Calibration Verification (ICV)

A mid-range calibration standard must be analyzed after the initial calibration and prior to sample analysis, and must be a different source than that used for the initial calibration. See section 10.4.1 for additional criteria. Otherwise, sample analysis may proceed.

9.4 Continuing Calibration Verification (CCV)

A mid-range calibration standard must be analyzed prior to sample analysis. This standard is of a different source than that used for the LCS/LCSD pair, typically the same source as the initial calibration standards. See section 10.4. or additional criteria. If repeated failure of the CCV occurs, the instrument must be recalibrated. Otherwise, sample analysis may proceed. The LCS may also be utilized as the continuing calibration unless otherwise defined in an addendum.

9.5 Matrix Spike

Not applicable.

9.6 Laboratory Duplicate

Laboratory Duplicate is a replicate analysis of a sample. The RPD of duplicate analyses must not exceed 25. Up to 10% of the target analyte detections may exceed acceptance criteria. The criteria does not need to be applied to concentrations less than 5X the reporting limit. If more variation occurs, the sample analysis must be repeated. If an analyte is detected in one analysis at >5x the reporting limit and not detected in the duplicate analysis, the analysis must be repeated. If an analyte is detected in one analysis at <5x the reporting limit and not detected in the duplicate analysis, the RPD is not calculable (NC) and the analysis does not have to be repeated. If an analyte is not detected in both the original and duplicate analyses, the RPD is NC. Equation 9 is used to calculate the RPD.
The sample chosen for duplicate analysis should not be a trip blank, field blank, or equipment blank. The sample chosen for duplicate analysis must be rotated among clients and/or sites. If possible, field duplicates should not be chosen for duplicate analysis, nor should outside air samples if indoor air samples are also included in the analytical batch. Refer to Appendices D - F for agency –specific criteria on laboratory duplicate criteria.

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Equation 9: RPD Calculation

$$\mathbf{RPD = ABS(C_s - C_d) / [(C_s + C_d)/2]*100}$$

where:

RPD = relative percent difference
C_s = concentration in original sample analysis
C_d = concentration in duplicate sample analysis

9.7 Method-specific Quality Control Samples

9.7.1 BFB Tune - A successful BFB spectrum must meet the criteria in Table 5 prior to sample analysis. If a successful BFB spectrum is not obtained, the MS must be retuned and the BFB spectrum re-evaluated prior to analyzing samples.

9.7.2 Internal Standards - The internal standard area counts of each sample, blank, and Laboratory Control Sample are evaluated against the corresponding

continuing calibration standard. The internal standard area counts must be within 60-140% of the continuing calibration standard area counts. If the retention times of the internal standards must be within +/- 0.33 min. If the internal standards fall outside this range, the sample, blank, or Laboratory Control Sample must be reanalyzed. In addition, area counts for internal standards for continuing calibration must be within 60-140% recovery of initial calibration. Refer to Sect. 12 for contingencies on samples exhibiting internal standard recovery failures.

9.7.3 TIC Internal Standards - Internal standards used for the quantitation of TICs must be evaluated by comparing the total ion area counts of the internal standards in the samples to the total ion area counts of the internal standards in the blanks. The internal standard area counts must be within 50-200% of the blank area counts. If the internal standards fall outside this range, a different internal standard or an estimated internal standard total ion area must be used to quantitate the TIC. This estimate can be done by using the total ion area from a blank or a clean sample within the analytical batch.

9.8 Method Sequence

- BFB Tune Check
- Calibration Standards (initial) or Continuing Calibration
- Laboratory Control Sample (may be used as the ICV or CCV)
- Laboratory Control Sample Duplicate (if needed)
- Laboratory Method Blank
- Samples
- Laboratory Duplicate

Injections may be made until 24 hours after the injection used to check the BFB tune.

All analytical sequences must be recorded in the instrument software and documented in the instrument logbook (Form 117-09).

10. Procedure

10.1 Equipment Set-up

10.1.1 Canister Cleaning and Certification

Refer to Alpha SOP #2190 for canister and flow controller preparation.

10.1.2 Sample Preparation and Concentration

Ensure the integrity of the canister sample as described in Section 6.4. General description of procedure: A 3-stage concentration technique called Cold-Trap Dehydration is used to analyze VOC's in air. The air sample is first concentrated to about a 0.5cc volume by drawing an aliquot of sample simultaneously through a cold trap (no packing material) and then through a Tenax trap. The cold trap is then heated to 10 ^{o}C and is held there while slowly passing helium through it to transfer these compounds to the Tenax trap, leaving most of the moisture in the cold trap. Sweeping the VOC's from the first to the second trap with only 20cc of helium results in a transfer of less than 0.5 µL of water (40 mL @ 100% RH @ 10 ^{o}C) which can be easily handled by benchtop mass spectrometers. The 20 cc transfer volume also serves to flush the CO_2 through the Tenax trap. After transfer to the second trap, the VOC's are back-flushed while heating to be further focused on an open-tubular focusing trap (cryofocuser) for rapid injection onto the analytical column. Internal standard is added directly to the first stage cryogenic trap prior to the sample by a mass flow controller (MFC). MFC controlled introduction is advantageous over loop injection as it remains consistent with the mechanism used to measure the sample volume.

Connect the canisters or Tedlar® bag(s) to the Entech 7016D Autosampler. For FSL canisters: Align the tubing from one of the 16 positions to the canister inlet position. Push the inlet line into the orifice of the canister and hold in place while tightening the fitting finger tight. Turn the stainless steel nut ¼ turn more with a wrench. The canister valves must be closed at this point. For Tedlar® bags: Connect the valve of the Tedlar® bag with the autosampler line using an adapter fitting.

For canister samples, leak check all inlet connections using the leak check procedure included with the Entech software. The software will indicate if there is a change in vacuum over a period of 30 sec. The vacuum must not increase more than 2 psia. Analysis cannot begin until the leak check has passed for each canister being tested and/or the source of the leak has been determined..

Open the canister or bag valves.

Set up the sequence of the Entech system to withdraw 250 mL from each sample. If high concentrations are expected, lower volumes can be used (minimum of 25 mL).. Samples suspected to contain elevated concentrations (i.e. soil vapor, sub-slab, landfill gas) should be pre-screened prior to analysis to obtain more precise dilution information. If screening results indicate elevated concentrations of non-target analytes, the sample should be diluted such that the peak height of the non-target analyte is approximately 10X greater than the peak height of the first internal standard. Recommended concentrator operating parameters are provided in Table 6.

10.2 Initial Calibration

10.2.1 GC Conditions (Shimadzu 2010, 2030)

Oven program: 25^{o} C, hold for 5.0 minutes, then:

Ramp 1: 100^{o} C at 8.0^{o} C / min.; hold for 0.0 min

Ramp 2: 220° C at 25° C / min.; hold for 4.0 min

Gas Flows

Helium carrier gas flow program: 2.0 mL/min for entire run (23.18 min)

Sample Injection

Injection mode:	split
Injection port temperature:	250^0 C
Inlet pressure:	27.3 psi
Total flow:	39.3 mL/min
Split ratio:	17.3
Split flow:	34.6 mL/min
Gas saver flow:	OFF

10.2.2 MS Conditions

Temperature of MSD transfer line: 250^0 C

Temperature of MS Quad: 150^0 C

Temperature of MS Source: 230^0 C

Solvent Delay: 3.0 minutes

Scanning Parameters: 29-270 amu until 10 min, scan rate = 5.52 scans/sec; then 35-270 amu, scan rate = 3.1 scans/sec. Threshold = 150. Sampling rate = 2. EM offset-variable to achieve response of 200K area counts (+/- 25K) for the internal standard bromochloromethane.

10.2.3 Daily GC/MS Performance Check

10.2.3.1 The first analysis of the day is typically a tune evaluation. The GC/MS system is checked to confirm that acceptable performance criteria for bromofluorobenzene (BFB), which is in surrogate mixture, are achieved. These criteria must be met prior to analyzing further standards, blanks and samples.

10.2.3.2 A maximum injection of 50 ng must successfully meet the BFB spectrum criteria in Table 5.

10.2.3.3 If the spectrum of BFB does not meet the above stated criteria, the analysis must be repeated. If the spectrum of BFB still does not meet these criteria, the GC/MS instrument must be re-tuned.

10.2.3.4 The Daily GC/MS Performance Check must be analyzed every 24 hours or less.

10.2.4 Initial Calibration

10.2.4.1 Analyze a minimum of five different levels by analyzing various volumes of the secondary standards prepared in Table 3 (Table A-3 for sulfide/mercaptan analysis). The lowest standard will be at or below the

reporting limit. If the response is not linear at the lowest level for the higher molecular weight compounds, this point must not be included in the calibration curve for these compounds. As a result, the analysis of more than five levels may be required in order to ensure a minimum of five calibration points for each analyte.

Table 4 lists the calibration standard levels and the volumes of the secondary standards needed to achieve these levels.

10.2.4.2 The true value of each of these calibration points is determined by applying a dilution factor that is based on the volume of sample extracted from the canister for each calibration point. Assuming that a volume of 250 mL will be the maximum volume extracted from the samples; this will be the "1X" volume. A dilution factor can be calculated using Equation 2.

Equation 2: Calculation of Instrument Dilution Factor

$$\mathbf{DF = V_{1X} / V_{actual}}$$

where:

DF = dilution factor
V_{1X} = maximum volume sampled, mL
V_{actual} = actual volume sampled for samples and standards

10.2.4.3 Analyze each calibration standard according to the procedures specified in Section 10. The true value of each calibration point is determined by dividing the concentration of the canister by the dilution factor determined using Equation 2.

10.2.4.4 Tabulate the area response of the characteristic ions against the amount for each analyte and internal standard and calculate relative response factors (RRF) for each compound using Equation 3. Perform this calculation for each calibration standard.

Equation 3: Relative Response Factor for Individual Target Analytes

$$\mathbf{RRF = [(A_{EC}) * (C_i)] / [(A_{EI}) * (C_c)]}$$

where:

RRF = relative response factor
A_{EC} = area count of the extracted ion for the analyte of interest
C_i= amount of internal standard (ppbV)
A_{EI} = area count of the extracted ion for the associated internal standard
C_c = amount of analyte of interest (ppbV)

Table 7 lists all TO-15 analytes, internal standards and the associated quantitation ion.

Table 8 lists the internal standards and the associated TO-15 analytes.

10.2.4.5 Calculate the average response factor for each of the target analytes by the following equation (AVG_x = SUM(RFs) / total # of RFs).

10.2.4.6 Calculate the percent relative standard deviation (%RSD) of the response factors over the secondary range of the curve for each of the target analytes using Equation 4.

Equation 4: Percent Relative Standard Deviation

$$\%RSD = [(SD_n - 1) / (AVG_x)] * 100]$$

where:

%RSD = percent relative standard deviation
SD_n -1 = standard deviation (n-1 degrees of freedom)
AVG_x = average response factor from the initial calibration curve

This task can also be accomplished using the quantitation software provided by the instrument manufacturer.

10.2.4.7 If the %RSD is <30 for each analyte, linearity can be assumed for the associated target analyte and sample analysis may proceed. If the curve fit is using average response factor, RSD (analogous to RSE) is the measure of relative error, and no additional calculation is required.

If the %RSD is >30 for any analyte, the integrations must be evaluated and the calculations verified. If a %RSD <30 cannot be achieved, it is acceptable for two (2) of the analytes to be above 30%, but below 40% RSD (applies to analytes flagged with a “C” on the Enviroquant initial calibration summary table).

Alpha may use the following modified acceptance criteria only for projects that have documentation and approval within the QAPP by the quality assurance project planners, and also for analytes not listed in EPA Method TO-15:

10.2.4.8 If the %RSD is >30 for any analyte, the integrations must be evaluated and the calculations verified. If a %RSD <30 cannot be achieved, it is acceptable for 10% of the total analytes to be above 30%, but below 50% RSD. Before acceptance of such a Calibration Curve, it must be confirmed with the approval of the Section Supervisor and/or the Project Manager that these analytes are typically and historically "trouble" analytes or "poor performers" (typically compounds listed in Table 3B), and that all Client and Project Data Quality Objectives (DQOs) will still be met when analyzing samples using this calibration. Refer to Appendices D - F for agency –specific criteria regarding initial calibration acceptance criteria.

Calibration points may be removed from the calibration curve to meet the 30% RSD criteria, so long as five consecutive points remain in the calibration curve, and the following procedure is followed:

- Remove high level calibration points
- Remove low-level calibration points; reporting limits will need to be elevated, however.

10.2.4.9 If calibration points in the mid-level range need to be removed due to a sequence error or instrument malfunction, the entire calibration level must be removed from the calibration curve. If the %RSD >30, a calibration curve is generated using the EnviroQuant quantitation software.

Correlation Coefficient calculation is performed by the Enviroquant software as follows;

$$r = \frac{n(\Sigma xy) - (\Sigma x)(\Sigma y)}{\sqrt{[\, n\Sigma x^2 - (\Sigma x)^2 \,][\, n\Sigma y^2 - (\Sigma y)^2 \,]}}$$

Where:

r = Correlation Coefficient

n = number of standards measured

x = true concentration of the standard

y = observed concentration of the standard

The correlation coefficient (linear) for the calibration curve must be greater than 0.995. If these criteria cannot be met, prepare a new set of calibration standards and recalibrate the instrument. NOTE: Quadratic calibration in any form is not acceptable.

Authorization from the department supervisor is required prior to using linear regression calibration. Linear regression is only allowed if certain criteria listed below are met:

- The minimum number of points for a linear regression curve is five points.
- The curve must be plotted and printed and turned in with the raw data.
- A calibration standard must be analyzed at the low point of the curve. Recovery of the low point standard must be 60-140% using the linear regression curve.

  The recovery of the compound for the continuing calibration / LCS must be within 70-130%.

10.2.4.10 The reference spectra for all target analytes are reviewed for both assignments and purity for all instruments. In addition, this process of reviewing all spectra continues whenever a new calibration is completed.

Reference spectra should be updated with each initial calibration performed with the midpoint standard of the calibration.

10.2.4.11 Internal Standard Criteria for Initial Calibration Levels and ICV.

The mean response for each internal standard compound is calculated over the initial calibration range. The area response at each calibration level must be within 60-140% of the midpoint area response over the initial calibration range for each internal standard. If recovery is outside the range, re-analyze calibration level. This criteria must be met prior to sample analysis.

All of these criteria must be met prior to sample analysis.

10.3 Equipment Operation and Sample Processing

10.3.1 GC/MS ANALYSIS

10.3.1.1 The Entech 7200 or 7200A Concentrator is programmed to the specific analytical conditions listed in Table 6 (Entech method Alpha_TO15.CTD) and the GC/MS parameters are set to those listed in Sections 10.3.1 and 10.3.2. (Enviroquant method TO15-SFS.M (SIM and full scan) or TO15_FS_35C.M (full scan only, for sulfide & mercaptan analysis in App. A)).

10.3.1.2 The BFB spectrum is evaluated by analyzing a Laboratory Method Blank and adding 100 mL of the BFB/surrogate mix.

10.3.1.3 A continuing calibration and/or a laboratory control spike is analyzed. See sect. 9.2 for acceptable criteria, and refer to Appendices D - F for agency – specific criteria on continuing calibration and laboratory control spike criteria.

10.3.1.4 A Laboratory Method Blank is analyzed. The Laboratory Method Blank consists of the analysis of 250 mL from a canister of humidified nitrogen. The method blank must be free of target analyte contamination at or above the reporting limit.

10.3.1.5 A 250-mL aliquot of sample is preconcentrated on the Entech 7200 or 7200A concentrator and injected onto the GC column. For soil vapor samples, or other samples that may contain elevated levels, the aliquot amount must be determined using the results from a pre-screening analysis. Sample concentrations are determined using the following equation:

$$ppbV = [(A_{EC}) * (C_i)] / [(A_{EI}) * (RRF)]$$

10.3.1.6 Instrument Dilutions and Sub-Atmospheric Sample dilutions

10.3.1.6.1 For dilutions, smaller sample volumes (<250 mL) are analyzed. The smallest volume that can be analyzed with accuracy using the Entech concentrator is 10 mL. The dilution factor is accounted for by entering the volume analyzed in the sample calculation discussed in Section 10.2.2.2 (Equation 2).

10.3.1.6.2 Samples that arrive at the laboratory with pressures below -15 inches Hg should be pressurized with nitrogen to greater than -15 inches Hg, as discussed in Section 6.4. This pressurization results in a dilution factor. The dilution factor is calculated using Equation 6, and the canister dilution spreadsheet (Form No.: 117-05). Attach a green tag to the canister with the pressurization information (initial pressure and final pressure) recorded on the tag.

Equation 6: Dilution Factor for Pressurization of Subatmospheric Samples: Three Steps

Step 1: Calculate the volume in the canister prior to pressurization (Assume a 2.7-liter canister is used).

$$\mathbf{V_{ci} = 2.7 * P_I / 14.696}$$

Step 2: Calculate the volume in the canister after pressurization.

$$\mathbf{V_{cf} = 2.7 * P_F / 14.696}$$

Step 3: Calculate the dilution factor.

$$\mathbf{DF = V_{cf} / V_{ci}}$$

where:

V_{ci}= volume of air in canister prior to pressurization, L

P_I = pressure reading of canister prior to pressurization (psia)

V_{cf} = volume of air in canister after pressurization, L

P_F = pressure reading of canister after pressurization (psia)

DF = dilution factor

14.696 = atmospheric pressure (psia)

10.3.1.6.3 If samples require larger dilutions than pressurization and instrument dilutions, a syringe dilution into an additional canister or Tedlar bag (typically used only for App. A analytes) with a known volume of nitrogen is required.

10.3.1.6.4 Fit a VCO® adapter with a septa to the pressurized sample canister. With a gastight syringe remove appropriate sample size for dilution. Allow sample to flow through syringe for 1 – 2 seconds to flush syringe prior to volumizing. Inject the sample aliquot into a Tedlar bag. If using an evacuated canister, connect the canister to an injection port tee (see Figure 3) attached to the dynamic diluter. Inject the aliquot of sample while a steady stream of Nitrogen is flowing into the dilution canister. Pressurize this canister to 30 psia. Attach a green tag to the canister with dilution information recorded on the tag. Use the dilution calculation worksheet (Form No.: 117-05) to calculate resulting dilutions.

10.3.2 Qualitative Identifications

10.3.2.1 An analyst competent in the interpretation of mass spectra must identify the target analytes by comparison of the sample mass spectrum to the mass spectrum of the standard. Two criteria must be satisfied to verify the identification: (1) elution of the component in the sample at the same GC relative retention time (RRT) as the component in the standard, and (2) agreement of the sample component and standard component mass spectra.

10.3.2.2 For establishing correspondence of the GC RRT, the RRT of the component in the sample must compare within ± 0.06 RRT units of the RRT of the component in the standard. If co-elution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT must be assigned using extracted ion current profiles for the ion unique to the component of interest.

10.3.2.3 For comparison of the standard and sample component mass spectra, mass spectra of standards obtained on the GC/MS under the same instrument conditions are required. Reference spectra should be updated for each initial calibration performed, using the mid-level standard. Once obtained, these standard spectra may be used for identification and reference purposes.

10.3.2.4 The requirements for qualitative verification by comparison of mass spectra are as follows:

- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.
- The relative intensities of ions specified must agree within ± 20% between the standard and sample spectra.
- Ions greater than 10% in the sample spectrum must be considered and accounted for by the analyst making the comparison.

Table 7 lists the primary and secondary ions for all analytes.

10.3.2.5 Manual integrations: for peaks that are observed to be not integrated correctly by the quantitation software, manual integrations must be performed. Please refer to the manual integration SOP for further instruction on how to properly perform and document manual integrations (Alpha SOP # 1731).

10.3.2.6 **Tentatively identified compounds (TICs)-**A library search may be performed for non-target sample components for the purpose of tentative identification, as requested by the client. Mass spectra are compared to the National Institute of Standards and Technology Mass Spectral Library (2002 version), and a qualitative match is determined by the analyst. Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when

compared to each other. Refer to Appendices D - F for agency –specific criteria on TIC reporting.

10.3.2.7 Guidelines for making tentative identification:

- Relative intensities of major ions in the reference spectrum (ions greater than 20% of the most abundant ion) must be present in the sample spectrum.
- The relative intensities of the major ions must agree within ± 30%.
- Molecular ions present in the reference spectrum must be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum must be reviewed for possible background contamination or presence of coeluting compounds.
- If, in the technical judgment of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound will be reported as "Unknown". The mass spectral interpretation specialist should give additional classification of the unknown compound, if possible (i.e., unknown aromatic, unknown hydrocarbon, unknown acid, unknown chlorinated compound)..

10.4 Continuing Calibration

10.4.1 Calibration Verification

10.4.1.1 The initial calibration must be verified through the analysis of an Initial Calibration Verification (ICV) sample. (The ICV may also be used to satisfy LCS requirements.) This analysis must be performed every time an initial calibration is performed.

10.4.1.2 The ICV must be prepared using a purchased gaseous standard (from a different lot # or separate vendor) with the components of interest in an evacuated FSL canister. Follow the standard preparation procedure for the calibration standards outlined in Section 8.0. The standard must be prepared at or below the midpoint of the calibration curve.

See section 10.4.2.6 for acceptable criteria and Section 12 for corrective actions.

10.4.2 Continuing Calibration

10.4.2.1 A continuing calibration check must be performed daily prior to sample analysis. The continuing calibration standard must be one of the initial calibration levels.

10.4.2.2 Analyze a calibration standard that is at the midpoint of the calibration curve.

10.4.2.3 The LCS standard may be utilized as the continuing calibration check, provided that all target analytes of interest are present in the LCS standard.. Refer to Appendices D - F for agency –specific criteria on LCS criteria.

10.4.2.4 Evaluate continuing calibration for internal standard recoveries. Recoveries must be between 60-140%. If not, the CCV will be re-analyzed.

10.4.2.5 Calculate the percent difference (%D) of the continuing calibration response factor from the initial calibration average response factor using Equation 5.

Equation 5: Percent Difference

$$\%\ D = [(C_{found})-(C_{true}) / (C_{true})] * 100$$

where:

%D = percent difference

C_{found} = amount of the analyte detected in the standard (ppbV)
C_{true} = true amount of the analyte in the standard (ppbV)

This task can also be accomplished using the quantitation software provided by the instrument manufacturer.

10.4.2.6 Acceptance Criteria

The acceptance criteria is less than 30% RSD for any analyte, with an allowance of two analytes to be greater than 30%, but less than 40%.

Alpha may use the following modified acceptance criteria only for projects that have documentation and approval within the QAPP by the quality assurance project planners, and also for analytes not listed in EPA Method TO-15:

If the %RSD is <30 for each analyte, linearity can be assumed for the associated target analyte and sample analysis may proceed.

10.4.2.7 If the %RSD is >30 for any analyte, the integrations must be evaluated and the calculations verified. If a %RSD <30 cannot be achieved, it is acceptable for 10% of the total analytes to be above 30%, but below 50% RSD. Before acceptance of such a Calibration Curve, it must be confirmed with the approval of the Section Supervisor and/or the Project Manager that these analytes are typically and historically "trouble" analytes or "poor performers" (typically compounds listed in Table 3B), and that all Client and Project Data Quality Objectives (DQOs) will still be met when analyzing samples using this calibration. . Refer to Appendices D - F for agency –specific criteria on initial calibration acceptance criteria.

10.4.2.8 Refer to Sect. 12 for additional procedures regarding continuing calibration acceptance criteria and corrective actions if criteria are not met.

10.5 Preventive Maintenance

Ion source cleaning – typically prior to initial calibration.

Electron Multiplier (EM)-changed when the voltage setting required to achieve adequate response approaches 1900. (Agilent MS only).

Rough pump oil changed annually.

Transfer lines, concentrator traps, and the GC guard column should be changed semi-annually, or when system repeatedly fails initial calibration.

11. Data Evaluation, Calculations and Reporting

11.1 Calculations

11.1.1 Individual Target Analytes: The average response factor from the initial calibration is used to calculate the amount of analyte detected in the sample analyses. Standards are prepared on a ppbV basis, so if no dilution is performed, values can be reported from the quantitation report without any calculations. Dilution factors are calculated using Equation 2. Equation 7 shows the conversion of ppbV to µg/m^3 .

Equation 7: Conversion of ppbV to µg/m^3

µg/m^3 = (ppbV) * MW / 24.45

where:

24.45 = molar gas constant (g/g-mole)
MW = molecular weight of the compound of interest (Table 1 and 2 lists the molecular weights of the target analytes)

11.1.2 TICS: An estimated amount for the TIC is calculated using the total area of the TIC, the total area of the internal standard assigned by the quantitation software, and a response factor of 1.000 (Equation 8). If the internal standard assigned by the quantitation software exhibits significant interference from other analytes, the next closest eluting internal standard will be utilized. Refer to Appendices D – F for agency-specific criteria on reporting TICS.

Equation 8: Calculation of TIC Results in ppbV

ppbV = [(A_T) * (C_{IS})] / [(A_{IS-T}) * (1.000)]

where:

A_T = total ion area of the TIC to be measured

C_{IS} = amount of the internal standard

A_{IS-T} = total ion area of the closest eluting internal standard

The integration of target analytes and internal standards must be performed from valley to valley.

11.1.3 Percent Recovery

$$\% \text{ Recovery} = \frac{C_x}{C_t} \text{ X } 100$$

where:
C_x = measured concentration of compound
C_t = true concentration of compound

11.2 Data Package

11.2.1 Canister Cleaning Information

A copy of the data for the batch certification analysis associated with the FSL canisters must be on file. The raw data must include a sample chromatogram, quantitation report, and spectra of all positive results.

11.2.2 BFB Tune Checks

Tune checks must be included for all days of analysis, including initial calibration. Raw data must include the chromatogram, mass spectra, and summary of relative abundances of the BFB ions.

11.2.3 Calibration Data

- Initial calibration summary (including average response factors, %RSDs, and copies of calibration curves, if appropriate) for target analytes and all calibration chromatograms must be on file.
- Continuing calibration summaries (including %Ds) for individual analytes.
- Chromatograms and quantitation reports associated with all standards used, in the initial and continuing calibrations.

11.2.4 QA/QC

- Internal standard responses and % recoveries vs. the continuing calibration.
- Quantitation report and chromatogram for laboratory control spike (and laboratory control spike duplicate, if requested).
- Quantitation reports, chromatograms, and spectra of positive results for all blanks.
- Copy of the instrument runlog.

11.2.5 Sample Data

- Quantitation reports, chromatograms, spectra of positive results, negative proofs, and pre- and post-manual integrations for all LCSs, samples, and duplicates.
- A copy of the canister dilution worksheet, Form No.: 117-05 (if any canister pressurizations or canister dilutions are performed).

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation.

Holding time exceedence and/or container damage is noted on the Sample Delivery Group form.

Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

Review of standards, blanks and standard response for acceptable performance occurs for each batch of samples. Record any trends or unusual performance on a nonconformance action form. The method blank must be free of target analyte contamination at or above the reporting limit. If it is not, the system must be evaluated for possible sources of contamination. Once the source is determined and eliminated, the method blank must be reanalyzed.

If the ICV, CCV, LCS or LCSD recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked samples is suspect and is only reported for regulatory compliance purposes with the appropriate Narratives. Immediate corrective action includes reanalyzing all affected samples (provided sufficient volume of sample remains) by using any retained sample before the expiration of the holding time. If sufficient volume is not available, Alpha will narrate accordingly. Analytes that fail ICV, CCV and LCS criteria due to elevated recoveries may be reported, provided there are no detections in the associated samples.

Samples exhibiting internal standard recovery failures must be re-analyzed at the same dilution level if instrument malfunction is suspected to be the cause, or at a lesser dilution if sample matrix or concentration levels of target and/or non-target analytes are suspected of being the cause. If recovery failures are observed upon re-analysis, narrate bias accordingly (negative if high recovery, positive if low recovery).

When applicable criteria is not met (ICV, CCV, LCS, IS), Alpha will narrate bias which will be included in the opening narrative of the report.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP # 1732. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP # 1739 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP # 1732 MDL/LOD/LOQ Generation

SOP # 1739 IDC/DOC Generation

SOP # 1797 Hazardous Waste & Sample Disposal

SOP # 1731 Manual Integration

Form 117-05: Canister Dilution Worksheet Template

Form 117-09: Instrument Run Log

Form 117-11: Primary Standard Preparation Log

Form 12925: Secondary Standard Preparation Log

16. Attachments

Table 1	TO-15 Tedlar® Bag Stock Standard Preparation for LCS
Table 2A	TO-14 Primary Mix #1 & TO-15 Mix #2 Stock Standard Cylinder
Table 2B	TO-15 Custom Mix #3 Stock Standard Cylinder
Table 2C	TO-15 Custom Mix #4 Stock Standard Cylinder
Table 2D	TO-15 Custom Mix #5 Stock Standard Cylinder
Table 3A	Summary of Working Standard Preparation
Table 3B	Preparation of Calibration Standards for Low Vapor Pressure Compounds
Table 4	Calibration Standard Levels
Table 5	BFB Key Ions and Abundance Criteria
Table 6	Entech 7200 or 7200A /7016D Operating Parameters
Table 7	Quantitation and Secondary Ions for TO-15 Analytes and Internal Standards
Table 8	Internal Standards and the Associated Target Analytes
Table 9A	TO-15 Target Analytes and Reporting Limits-Standard List
Table 9B	TO-15 Target Analytes and Reporting Limits-Additional Analytes

Appendix A	Cold Trap Dehydration technique (CTD) for Analysis of Sulifides and Mercaptans
Appendix B	Data Acquisition Parameters and Analysis Modifications for Conducting SIM Analysis
Appendix C	Modifications to Data Review and Case Narrative to Comply with MADEP MCP-TO-15 Method
Appendix E	Modifications to Data Review and Case Narrative to Comply with 2014 NJDEP Technical Guidance for EPA Method TO-15
Appendix F	Modifications to Data Review and Case Narrative to Comply with Ohio EPA Voluntary Action Program (VAP) Requirements for EPA Method TO-15

DEFINITIONS

Absolute canister pressure - Pg + Pa, where Pg = gauge pressure in the canister (psig) and Pa = barometric pressure.

Absolute pressure - Pressure measured with reference to absolute zero pressure (as opposed to atmospheric pressure), usually expressed as kPA, mm Hg, or psia (pounds per square inch absolute).

Cryogen - The refrigerant used to obtain very low temperatures in the cryogenic trap of the analytical system. A typical cryogen is liquid nitrogen (bp = -196^0C).

Gauge pressure - Pressure measured above atmospheric pressure (as opposed to absolute pressure). Zero gauge is equal to ambient atmospheric (barometric) pressure. Units = psig (pounds per square inch gauge).

ppmV – parts per million on a volume basis.

ppbV – parts per billion on a volume basis

psia – pounds per square inch absolute

Relative retention time (RRT)– retention time (RT) ratio of the target analyte and the internal standard used to quantitate (RT target / RT internal standard).

Table 1

TO-15 Tedlar® Bag Stock Standard Preparation- LCS/ICV Standard

ICV / LCS Standard				
COMPOUND (liquids)	**MOL WGT**	**Density ug/uL**	**uL injected***	**FINAL ppmV**
Acetone	58.1	791	12.0	200
Isopropyl alcohol	60.1	785	4.8	76.7

All neat chemicals are injected into a Tedlar® bag containing 20 Liters of zero air or UHP nitrogen.

See Table A-1 & Table A-4 for sulfide/mercaptan stock standard preparation

Table 2A

TO-15 Purchased Primary Standard Mix

TO-14 Primary Standard Mix #1					
COMPOUND	**MOL WGT**	**Conc. ppmV**	**COMPOUND**	**MOL WGT**	**Conc. ppmV**
dichlorodifluoromethane	120.92	1.0	cis-1,3-dichloropropene	110.97	1.0
chloromethane	50.49	1.0	trans-1,3-dichloropropene	110.97	1.0
Freon-114	170.92	1.0	1,1,2-trichloroethane	133.41	1.0
vinyl chloride	62.5	1.0	toluene	92.14	1.0
bromomethane	94.94	1.0	1,2-dibromoethane	187.87	1.0
chloroethane	64.52	1.0	tetrachloroethene	165.83	1.0
trichlorofluoromethane	137.37	1.0	chlorobenzene	112.56	1.0
1,1-dichloroethene	96.94	1.0	ethylbenzene	106.17	1.0
methylene chloride	84.93	1.0	m-xylene	106.17	1.0
Freon-113	187.38	1.0	p-xylene	106.17	1.0
trans-1,2-dichloroethene	98.96	1.0	styrene	104.15	1.0
1,1-dichloroethane	98.96	1.0	1,1,2,2-tetrachloroethane	167.85	1.0
cis-1,2-dichloroethene	96.94	1.0	o-xylene	106.17	1.0
chloroform	119.38	1.0	1,3,5-trimethylbenzene	120.2	1.0
1,2-dichloroethane	98.96	1.0	1,2,4-trimethylbenzene	120.2	1.0
1,1,1-trichloroethane	133.41	1.0	1,3-dichlorobenzene	147.0	1.0
benzene	78.11	1.0	1,4-dichlorobenzene	147.0	1.0
carbon tetrachloride	153.82	1.0	1,2-dichlorobenzene	147.0	1.0
1,2-dichloropropane	113	1.0	1,2,4-trichlorobenzene	181.45	1.0
trichloroethene	131.38	1.0	hexachlorobutadiene	260.76	1.0

TO-15 Primary Standard Mix #2		
COMPOUND	**MOL WGT**	**Conc. ppmV**
Propylene	42.08	1.0
1,3-butadiene	54.09	1.0
Vinyl bromide	106.96	1.0
Acetone	58.08	1.0
Isopropyl alcohol	60.1	1.0
Carbon disulfide	76.14	1.0
3-chloropropene	76.53	1.0
Trans-1,2-dichloroethene	96.94	1.0
Methyl-tert butyl ether	88.15	1.0
Vinyl acetate	86.09	1.0
2-butanone (MEK)	72.11	1.0
Hexane	86.18	1.0
Ethyl acetate	88.11	1.0
Tetrahydrofuran	72.11	1.0
Cyclohexane	84.16	1.0
Bromodichloromethane	163.83	1.0
1,4-dioxane	88.11	1.0
2,2,4-trimethylpentane	114.23	1.0
Heptane	100.21	1.0
4-methyl-2-pentanone (MIBK)	100.16	1.0
2-hexanone	100.16	1.0
Dibromochloromethane	208.29	1.0
Bromoform	252.75	1.0
Benzyl chloride	126.59	1.0
4-ethyl toluene	120.2	1.0

Table 2B

TO-15 Purchased Custom Mix #3

TO-15 Custom Standard Mix					
COMPOUND	**MOL WGT**	**Conc. ppmV**	**COMPOUND**	**MOL WGT**	**Conc. ppmV**
Propane	44.10	1.0	n-Octane	114.23	1.0
Chlorodifluoromethane	86.47	1.0	1,1,1,2-Tetrachloroethane	167.85	1.0
Methanol	32.04	5.0	1,2,3-Trichloropropane	147.43	1.0
n-Butane	58.12	1.0	Nonane	128.26	1.0
Dichlorofluoromethane	102.92	1.0	Isopropylbenzene	120.19	1.0
Ethanol	46.07	5.0	Bromobenzene	157.01	1.0
Acetonitrile	41.05	1.0	2-Chlorotoluene	126.58	1.0
Acrolein	56.10	1.0	n-Propylbenzene	120.19	1.0
n-Pentane	72.20	1.0	4-Chlorotoluene	126.58	1.0
Acrylonitrile	53.10	1.0	tert-Butylbenzene	134.20	1.0
Ethyl Ether	74.12	1.0	n-Decane	142.28	1.0
tert-Butyl Alcohol	74.12	1.0	sec-Butylbenzene	134.20	1.0
2,2-Dichloropropane	112.99	1.0	p-Isopropyltoluene	134.22	1.0
Di-Isopropyl Ether	102.17	1.0	n-Butylbenzene	134.20	1.0
Tert-Butyl Ethyl Ether	102.20	1.0	1,2-Dibromo-3-chloropropane	236.33	1.0
1,1-Dichloropropene	110.97	1.0	n-Undecane	156.31	1.0
Tert Amyl Methyl Ether	102.17	1.0	Naphthalene	128.17	1.0
Dibromomethane	173.83	1.0	n-Dodecane	170.33	1.0
1,3-Dichloropropane	112.99	1.0	1,2,3-Trichlorobenzene	181.45	1.0
n-Butyl Acetate	116.16	1.0			

All mixes currently purchased fromPraxair (formerly Linde and Spectra Gases)

Table 2C

TO-15 / PIANO Custom Mix #4

COMPOUND (liquids)	Boiling Pt, deg C	Molecular Weight	Density ug/uL	uL injected*	FINAL ppmV
1,1-difluoroethane (gas)	-24.7	66.05	NA	10 mL	5.0
1-ethyl-1-methylcyclopentane	121.55	112.21	785.4	11.9	1.0
Indan	177	118.18	965.0	10.2	1.0
Indene	182	116.16	996.0	9.7	1.0
1,2,3-trimethylbenzene	176	120.19	890.0	11.2	1.0
Acetaldehyde	20.2	44.05	785	23.3	5.0
Acetone	56.1	58.08	784.5	24.6	4.0
isopropyl alcohol	82.6	60.1	786	9.5	1.5
methyl methacrylate	101	100.1	940	8.8	1.0

Table 2D

TO-15 / PIANO Custom Mix #5

COMPOUND (liquids)	Boiling Pt, deg C	Molecular Weight	Density ug/uL	uL injected*	FINAL ppmV
Thiophene	83	84.14	1060	6.6	1.0
2-Ethylthiophene	133	112.19	990	9.4	1.0
2-methyllthiophene	114	98.17	1016	8.0	1.0
3-Methylthiophene	113	98.17	1017	8.0	1.0

* both mixes #4 and #5 prepared in 29.5 L high pressure cylinders, pressurized to 995 psia with UHP nitrogen. Total volume of standard is 1997 L. Two year expiration date.

Table 3A

Summary of Secondary Standards Preparation

Primary Standard	Primary Standard Conc. ppmV	Volume of Primary Standard Injected into canister	Primary Standard Transfer Method	Final Volume canister (L)	Final Concentration ppbV **
Secondary standards prepared using precision dilution system (Entech 4700)					
TO-15 Mixes #1 - #5	1.0	3000 mL	Pressure differential	30	100
TO-15 Mixes #1 - #5	1.0	300 mL	Pressure differential	51	10 ***
Secondary standards prepared via serial dilution					
100 ppbV ICAL mix	1.0	300 mL	Syringe Injection	30	1.0
100 ppbV ICAL mix	0.1 *	30 mL	Syringe Injection	30	0.1

All standards prepared using humidified nitrogen.

* This calibration standard is used for TO-15 SIM analysis only (see Appendix B).

** The following analytes have concentrations that are greater than the listed concentration

Methanol, acetylaldehyde, and ethanol – 5 times greater

m&p-xylene- 2 times greater

Isopropyl alcohol-2.5 times greater

*** 10 ppbV standards that are prepared at a pressure of 50 psia are split out into additional empty 15L canisters to reduce the pressure in the standard and allow for additional canisters to be prepared for continuing calibration usage.

Table 3B

Preparation of Calibration Standards for Low Vapor Pressure Compounds

COMPOUND (solids)	Vapor Pressure* (P), atm	Molecular Weight	Volume (V) extracted, mL	Gas Constant (R) (L atm/gm mol K)	T, °K	n**	Final Volume, L	mg	ug/m³	ppbV
1-methylnaphthalene	7.11E-05	142.20	7.1	0.082057	298.1	2.44E-08	51	0.00347	115.7	10
1-methylnaphthalene	7.11E-05	142.00	42	0.082057	298.1	1.22E-07	30	0.0173255	577.5	100
2-methylnaphthalene	8.96E-05	142.00	5.8	0.082057	298.1	2.491E-08	51	0.0035373	117.9	10.2
2-methylnaphthalene	8.96E-05	142.00	34	0.082057	298.1	1.246E-07	30	0.0176867	589.6	101.6
benzothiophene	7.70E-05	134.20	6.5	0.082057	291.5	2.446E-08	51	0.0032824	109.4	10.0
benzothiophene	7.70E-05	134.20	38	0.082057	291.5	1.223E-07	30	0.016412	547.1	100

Approximately 5.0 g of solid material was allowed to stand in a 250 mL jar w/ septa cap for 30 min prior to removal of vapor phase aliquot. The aliquot was then spiked directly into secondary standard.

All vapor pressure values from Lange's Handbook of Chemistry & Physics

Table 4

Calibration Standard Levels

Calibration Level	Amount (ppbV)	Volume / Secondary Standard
1	0.20	50 mL of 1.0 ppbV sec. standard
2	0.50	125 mL of 1.0 ppbV sec. standard
3	1.0	250 mL of 1.0 ppbV sec. standard
4	5.0	125 mL of 10 ppbV sec. standard
5	10	250 mL of 10 ppbV sec. standard
6	20	50 mL of 100 ppbV sec. standard
7	50	125 mL of 100 ppbV sec. standard
8	100	250 mL of 100 ppbV sec. standard

Table 5

BFB Key Ions and Abundance Criteria

Mass	Ion Abundance Criteria
50	8.0-40.0 percent of the base peak
75	30.0-66.0 percent of the base peak
95	Base peak, 100 percent relative abundance
96	5.0-9.0 percent of the base peak
173	Less than 2.0% of mass 174
174	50.0 to 120.0% of mass 95
175	4.0-9.0 percent of mass 174
176	Greater than 93.0 percent but less than 101.0 percent of mass 174
177	5.0-9.0 percent of mass 176

Table 6

ENTECH 7016D/ 7200 or 7200A Operating Parameters

Module 1 (Cold Trap)	
Parameter	**Setting**
Trapping Temperature	-40° C
Internal standard / surrogate volume	100 mL
Internal standard / surrogate flow rate	100 mL / min
Nominal Sample volume (may vary depending on sample concentrations)	250 mL
Sample flow rate, mL / min	100 mL / min
Preheat Temperature	10° C
Desorb Temperature	10° C
Bake Temperature	220° C
Bake Time	10 min
Module 1 to Module 2 transfer volume / rate	20 cc @ 5.0 cc/min
Module 2 (Tenax trap)	
Parameter	**Setting**
Trapping Temperature	-65° C to -75° C
Desorb Temperature	220° C
Bake Temperature	220° C
Module 2 to Module 3 desorb time	3.5 min
Module 3 (Cryofocusser)	
Parameter	**Setting**
Cryofocusing Temperature	-130° C to -190° C
Desorb Temperature	Approx. 90° C
Module 3 to GC desorb time	3.0-3.5 min
Bake temperature / event	Approx. 90° C / event 3
Delay time	13-17 min

Table 7
Quantitation and Secondary Ions for TO-15 Analytes and Internal Standards

Compound	Quant. Ion	Sec. Ion(s)
bromochloromethane	49	130
chlorodifluoromethane	51	67
propylene	41	39, 42
propane	29	43,39
dichlorodifluoromethane	85	87
chloromethane	50	52
Freon-114	85	87, 135
methanol	31	32,29
vinyl chloride	62	64,
1,3-butadiene	54	39
butane	43	41,58
bromomethane	94	96
chloroethane	64	66
dichlorofluoromethane	67	69, 47
ethanol	31	45
acetonitrile	41	40
vinyl bromide	106	108
acrolein	56	55,29
acetone	43	58
trichlorofluoromethane	101	103
isopropyl alcohol	45	59
acrylonitrile	53	52,51
pentane	43	57,72
ethyl ether	31	59,45
1,1-dichloroethene	61	96, 63
Tertiary butyl Alcohol	59	41, 43
methylene chloride	49	84
3-chloropropene	41	39, 76
carbon disulfide	76	44
Freon 113	101	85, 151
trans-1,2-dichloroethene	61	96, 98
1,1-dichloroethane	63	65
MTBE	73	57, 43
vinyl acetate	43	86
2-butanone	43	72
cis-1,2-dichloroethene	61	96, 98
chloroform	83	85, 47
1,2-dichloroethane	62	49, 63, 64
acetaldehyde	29	43, 44

Compound	Quant. Ion	Sec. Ion(s)
1,4-difluorobenzene	114	63
n-hexane	57	43, 86
diisopropyl ether	87	45, 59
ethyl acetate	61	43, 70
2,2-dichloropropane	77	41, 97
tetrahydrofuran	42	71, 72
tert-butyl ethyl ether	59	87, 57
1,2-dichloroethane-D4	65	67, 102
1,1,1-trichloroethane	97	61, 119
1,1-dichloropropene	75	39,110
benzene	78	52
carbon tetrachloride	117	119, 82
cyclohexane	56	84, 41
tert-amyl methyl ether	73	43, 87
dibromomethane	93	95, 174
1,2-dichloropropane	63	39, 62
bromodichloromethane	83	85, 129
trichloroethene	130	132, 97
1,4-dioxane	88	58
2,2,4-trimethylpentane	57	41, 99
n-heptane	43	57, 100
cis-1,3-dichloropropene	75	39, 77
4-methyl-2-pentanone	43	58, 100
methyl methacrylate	41	69, 100
trans-1,3-dichloropropene	75	39, 77
1,1,2-trichloroethane	97	61, 83
Thiophene	84	45, 58
chlorobenzene-D5	54	82, 117
toluene	91	92
toluene-D8	98	100
1,3-dichloropropane	76	41,49
2-hexanone	43	58, 100
dibromochloromethane	129	127, 131
1,2-dibromoethane	107	109
butyl acetate	73	43, 56
octane	85	43, 57, 114
tetrachloroethene	166	94, 131
1,1,1,2-tetrachloroethane	131	95, 133
chlorobenzene	112	77, 114
ethylbenzene	91	106
m+p-xylene	91	106

Compound	Quant. Ion	Sec. Ion(s)
bromoform	173	171, 175
styrene	104	103, 78
1,1,2,2-tetrachloroethane	83	85
o-xylene	91	106
1,2,3-trichloropropane	75	39, 110
nonane	43	57, 128
bromofluorobenzene	95	75, 174
isopropylbenzene	105	120
bromobenzene	77	156
2-chlorotoluene	126	91
n-propylbenzene	120	91
4-chlorotoluene	91	126
4-ethyl toluene	105	91, 120
1,3,5-trimethylbenzene	105	91, 120
tert-butlybenzene	119	134
1,2,4-trimethylbenzene	105	91, 120
decane	57	43, 142
benzyl chloride	91	126
1,3-dichlorobenzene	146	75, 111
1,4-dichlorobenzene	146	75, 111
sec-butylbenzene	105	134
p-isopropyltoluene	119	134
1,2-dichlorobenzene	146	75, 111
n-butylbenzene	91	134
1,2-dibromo-3-chloropropane	75	39, 157
undecane	57	43, 71, 156
dodecane	57	43
1,2,4-trichlorobenzene	180	109, 145
naphthalene	128	102
1,2,3-trichlorobenzene	180	109, 145
hexachlorobutadiene	225	118, 260
2-methylthiophene	97	45, 98
3-methylthiophene	97	45, 98
2-ethylthiophene	97	45, 112
1,2,3-trimethylbenzene	105	120
indan	117	91, 118
indene	115	89, 116
1,2,4,5-tetramethylbenzene	119	91, 134
benzothiophene	134	63, 89
2-methylnaphthalene	142	115, 141
1-methylnaphthalene	142	115, 141

Table 8

Internal Standards and the Associated Target Analytes

bromochloromethane		1,4-difluorobenzene	chlorobenzene-D5	
chlorodifluoromethane	trans-1,2-dichloroethene	hexane	toluene	decane
propylene	1,1-dichloroethane	diisopropyl ether	toluene-D8	benzyl chloride
propane	MTBE	tert-butyl ethyl ether	1,3-dichloropropane	1,3-dichlorobenzene
dichlorodifluoromethane	vinyl acetate	1,2-dichloroethane-D4	2-hexanone	1,4-dichlorobenzene
chloromethane	2-butanone	1,1,1-trichloroethane	dibromochloromethane	sec-butylbenzene
Freon-114	cis-1,2-dichloroethene	1,1-dichloropropene	1,2-dibromoethane	p-isopropyltoluene
methanol	chloroform	benzene	butyl acetate	1,2-dichlorobenzene
vinyl chloride	1,2-dichloroethane	carbon tetrachloride	Octane	n-butylbenzene
1,3-butadiene	trans-1,2-dichloroethene	cyclohexane	tetrachloroethene	1,2-dibromo-3-chloropropane
butane	1,1-dichloroethane	tert-amyl methyl ether	1,1,1,2-tetrachloroethane	undecane
bromomethane	acetaldehyde	dibromomethane	Chlorobenzene	dodecane
chloroethane	ethyl acetate	1,2-dichloropropane	Ethylbenzene	1,2,4-trichlorobenzene
dichlorofluoromethane	2,2-dichloropropane	bromodichloromethane	m+p-xylene	naphthalene
ethanol	tetrahydrofuran	trichloroethene	Bromoform	1,2,3-trichlorobenzene
acetonitrile		1,4-dioxane	Styrene	hexachlorobutadiene
vinyl bromide		2,2,4-trimethylpentane	1,1,2,2-tetrachloroethane	2-methylthiophene
acrolein		heptane	o-xylene	3-methylthiophene
acetone		cis-1,3-dichloropropene	1,2,3-trichloropropane	2-ethylthiophene
trichlorofluoromethane		4-methyl-2-pentanone	Nonane	1,2,3-trimethylbenzene
isopropyl alcohol		methyl methacrylate	bromofluorobenzene	indan
acrylonitrile		trans-1,3-dichloropropene	isopropylbenzene	indene
pentane		1,1,2-trichloroethane	bromobenzene	1,2,4,5-tetramethylbenzene
ethyl ether		thiophene	2-chlorotoluene	benzothiophene
1,1-dichloroethene			n-propylbenzene	2-methylnaphthalene
Tertiary butyl Alcohol			4-chlorotoluene	1-methylnaphthalene
methylene chloride			4-ethyl toluene	
3-chloropropene			1,3,5-trimethylbenzene	
carbon disulfide			tert-butlybenzene	
Freon 113			1,2,4-trimethylbenzene	

Table 9A

TO-15 Target Analytes and Reporting Limits
Standard List

COMPOUND	CAS #	Standard Reporting Limit, ppbV	Standard Reporting Limit, ug/m^3
1,1,1-trichloroethane	71-55-6	0.2	1.09
1,1,2,2-tetrachloroethane	79-34-5	0.2	1.37
1,1,2-trichloroethane	79-00-5	0.2	1.09
1,1-dichloroethane	75-34-3	0.2	0.81
1,1-dichloroethene	75-35-5	0.2	0.79
1,2,4-trichlorobenzene	120-82-1	0.2	1.48
1,2,4-trimethylbenzene	95-63-6	0.2	0.98
1,2-dibromoethane	106-93-4	0.2	1.54
1,2-dichlorobenzene	95-50-1	0.2	1.2
1,2-dichloroethane	107-06-2	0.2	0.81
1,2-dichloropropane	78-87-5	0.2	0.92
1,3,5-trimethylbenzene	108-67-8	0.2	0.98
1,3-butadiene	106-99-0	0.2	0.44
1,3-dichlorobenzene	541-73-1	0.2	1.2
1,4-dichlorobenzene	106-46-7	0.2	1.2
1,4-dioxane	123-91-1	0.2	0.72
2,2,4-trimethylpentane	540-84-1	0.2	0.93
2-butanone	78-93-3	0.5	1.48
2-hexanone	591-78-6	0.2	0.82
3-chloropropene	107-05-1	0.2	0.63
4-Ethyltoluene	622-96-8	0.2	0.98
Acetone	67-64-1	1.0	2.38
benzene	71-43-2	0.2	0.64
Benzyl Chloride	100-44-7	0.2	1.03
bromodichloromethane	75-27-4	0.2	1.34
bromoform	75-25-2	0.2	2.07
bromomethane	74-83-9	0.2	0.78
carbon disulfide	75-15-0	0.2	0.62
carbon tetrachloride	56-23-5	0.2	1.26
chlorobenzene	108-90-7	0.2	0.92
chloroethane	75-00-3	0.2	0.53
chloroform	67-66-3	0.2	0.98

COMPOUND	CAS #	Standard Reporting Limit, ppbV	Standard Reporting Limit, ug/m^3
chloromethane	74-87-3	0.2	0.41
cis-1,2-dichloroethene	156-59-2	0.2	0.79
cis-1,3-dichloropropene	10061-01-5	0.2	0.91
cyclohexane	110-82-7	0.2	0.69
dibromochloromethane	124-48-1	0.2	1.7
dichlorodifluoromethane	75-71-8	0.2	0.99
ethanol	64-17-5	2.5	4.71
ethyl acetate	141-78-6	0.5	1.8
ethylbenzene	100-41-4	0.2	0.87
Freon-113	76-13-1	0.2	1.53
Freon-114	76-14-2	0.2	1.4
hexachlorobutadiene	87-68-3	0.2	2.13
hexane	110-54-3	0.2	0.7
isopropyl alcohol	67-63-0	0.5	1.23
methylene chloride	75-09-2	0.5	1.74
MIBK	108-10-1	0.5	2.1
MTBE	1634-04-4	0.2	0.72
m+p-xylene	108-38-3 106-42-3	0.4	1.74
n-heptane	142-82-5	0.2	0.82
o-xylene	95-47-6	0.2	0.87
propylene	115-7-1	0.5	0.85
styrene	100-42-5	0.2	0.85
tetrachloroethene	127-18-4	0.2	1.36
tetrahydrofuran	109-99-9	0.5	1.48
toluene	108-88-3	0.2	0.75
trans-1,2-dichloroethene	156-60-5	0.2	0.79
trans-1,3-dichloropropene	10061-02-6	0.2	0.91
trichloroethene	79-01-6	0.2	1.07
trichlorofluoromethane	75-69-4	0.2	1.12
vinyl acetate	108-05-4	0.5	1.75
vinyl bromide	593-60-2	0.2	0.87
vinyl chloride	75-01-4	0.2	0.51

Table 9B

TO-15 Target Analytes and Reporting Limits
Additional Analytes

COMPOUND	CAS #	Standard Reporting Limit, ppbV	Standard Reporting Limit, ug/m^3
AP-42 Analytes			
acrolein	107-02-8	0.50	1.15
acrylonitrile	107-13-1	0.50	1.08
butane	106-97-8	0.20	0.48
Chlorodifluoromethane	75-45-6	0.20	0.71
Dichlorofluoromethane	75-71-8	0.20	0.84
n-Pentane	109-66-0	0.20	0.59
Propane	74-98-6	0.50	0.90
MADEP MCP 8260 Analytes			
1,1,1,2-tetrachloroethene	630-20-6	0.20	1.37
1,1-dichloropropene	563-58-6	0.20	0.91
1,2,3-trichlorobenzene	87-61-6	0.20	1.48
1,2,3-Trichloropropane	96-18-4	0.20	1.20
1,3-dichloropropane	142-28-9	0.20	0.92
2,2-dichloropropane	594-20-7	0.20	0.92
2-chlorotoluene	95-49-8	0.20	1.03
4-chlorotoluene	106-43-4	0.20	1.03
bromobenzene	108-86-1	0.20	1.28
1,2-dibromo-3-chloropropane	96-12-8	0.20	1.93
dibromomethane	74-95-3	0.20	1.42
diisopropyl ether	108-20-3	0.20	0.84
isopropylbenzene	98-82-8	0.20	0.98
isopropyltoluene	99-87-6	0.20	1.10
naphthalene	91-20-3	0.20	1.05
n-butylbenzene	104-51-8	0.20	1.10
n-propylbenzene	103-65-1	0.20	0.98
sec-butylbenzene	135-98-8	0.20	1.10
tert-amyl methyl ether	994-05-8	0.20	0.84
tert-Butyl ethyl ether	637-92-3	0.20	0.84
tert-butylbenzene	98-06-6	0.20	1.10

COMPOUND	CAS #	Standard Reporting Limit, ppbV	Standard Reporting Limit, ug/m^3
NYDEC Petroleum Indicator Compounds			
nonane	111-84-2	0.20	1.05
octane	111-65-9	0.20	0.93
undecane	1120-21-4	0.20	1.28
decane	124-18-5	0.20	1.16
dodecane	112-40-3	0.20	1.39
indene	95-13-6	0.20	0.95
Indan	496-11-7	0.20	0.97
thiophene	110-02-1	0.20	0.69
2-methylthiophene	554-13-3	0.20	0.80
3-methylthiophene	616-44-4	0.20	0.80
2-ethyl thiophene	872-55-9	0.20	0.92
benzothiophene	934-80-5	0.50	2.74
1,2,3-trimethylbenzene	526-73-8	0.20	0.98
1,2,4,5-tetramethylbenzene	95-93-2	0.20	1.10
2-methylnaphthalene	91-57-6	1.0	5.8
1-methylnaphthalene	90-12-0	1.0	5.8
Project Specific Analytes			
acetaldehyde	75-07-0	2.5	4.51
Acetonitrile	75-05-8	0.20	0.34
butyl acetate	123-86-4	0.50	2.38
ethyl ether	60-29-7	0.20	0.61
methanol	67-56-1	5.0	6.55
tert-butyl alcohol	75-65-0	0.50	1.51
Methyl methacrylate	80-62-6	0.50	2.05
All reporting limits are subject to change.			

Appendix A

Cold Trap Dehydration technique (CTD) for Analysis of Sulfides and Mercaptans by EPA TO-15

Target analytes:

Compound	CAS#	Reporting Limit, ppbV
Hydrogen sulfide	7783-06-4	2.0
Carbonyl sulfide	463-58-1	2.0
Methyl mercaptan	74-93-1	2.0
Ethyl mercaptan	75-08-1	0.5
Dimethyl sulfide	75-18-3	0.5
carbon disulfide	75-15-0	0.5
Isopropyl Mercaptan	75-33-2	0.5
tert-Butyl Mercaptan	75-66-1	0.5
n-Propyl Mercaptan	107-03-9	0.5
Ethyl Methyl Sulfide	624-89-5	0.5

Compound	CAS#	Reporting Limit, ppbV
Thiophene	110-02-1	0.5
Isobutyl Mercaptan	513-44-0	0.5
diethyl sulfide	352-93-2	0.5
Butyl Mercaptan	109-75-5	2.0
dimethyl disulfide	624-92-0	0.5
3-Methylthiophene	616-44-4	0.5
Tetrahydrothiophene	110-01-0	0.5
2-Ethylthiophene	872-55-9	0.5
2,5-Dimethylthiophene	638-02-8	0.5
Diethyl Disulfide	110-81-6	0.5
All reporting limits are subject to change.		

The cold trap dehydration method requires a blank trap (i.e. no trapping material) be installed in module 1 of the Entech 7200 or 7200A concentrator. This trap is cooled and a 250 mL aliquot of sample is allowed to pass through this trap and then directly onto the Tenax trap in module 2, which is also cooled (see Table A-5 for setpoints). The sample is then transferred to module 3 (cryofocusser) via ballistic heating. All requirements stated in this SOP must be applied to any TO15-Sulfide/Mercaptan analysis conducted in the laboratory.

SOP modifications:

Standard preparation and calibration procedures for these analytes are listed in Table A-1 through A-5. Quantitation parameters are listed in Table A-8. Table A-7 lists modified GC conditions.

Section 9.2.5 and 9.5.3.1: Use the Entech method alpha_H2S&SULF.CTD in place of the alpha_TO15.MPT method.

A second source laboratory check standard (LCS) is not readily available for these analytes. An LCS standard is prepared at a different concentration than the initial calibration standards using the same stock standard.

Table A-1

Sulfide/Mercaptan Primary Standard Mix #1

COMPOUND	CAS#	Molecular Weight	Concentration, ppmV
hydrogen sulfide	7783-06-4	34.08	5.0
Carbonyl sulfide	463-58-1	60.08	5.0
Methyl mercaptan	74-93-1	48.11	5.0
ethyl mercaptan	75-08-1	62.14	1.0
dimethyl sulfide	75-18-3	62.14	1.0
carbon disulfide	75-15-0	76.1	1.0
Isopropyl Mercaptan	75-33-2	76.2	1.0
tert-Butyl Mercaptan	75-66-1	90.19	1.0
n-Propyl Mercaptan	107-03-9	76.16	1.0
Ethyl Methyl Sulfide	624-89-5	76.16	1.0
Thiophene	110-02-1	84.1	1.0
Isobutyl Mercaptan	513-44-0	90.19	1.0
diethyl sulfide	352-93-2	90.2	1.0
Butyl Mercaptan	109-79-5	90.19	4.0
3-Methylthiophene	616-44-4	98.17	1.0
Tetrahydrothiophene	110-01-0	88.17	1.0
2-Ethylthiophene	872-55-9	112.19	1.0
2,5-Dimethylthiophene	638-02-8	112.19	1.0

Table A-2

Sulfide/Mercaptan Primary Standard Mix #2

COMPOUND	CAS#	Molecular Weight	Concentration, ppmV
dimethyl disulfide	624-92-0	94.2	1.0

Table A-3

Sulfide/Mercaptan Primary Standard Mix #3

COMPOUND	CAS#	Molecular Weight	Concentration, ppmV
Diethyl Disulfide	110-81-6	122.25	1.0

Table A-4

Summary of Secondary Standards Preparation for Sulfides and Mercaptan Analysis

Primary Standard	Primary Standard Conc. ppmV	Volume of Primary Standard Injected into Tedlar® Bag	Primary Standard Transfer Data	Final Volume Tedlar® Bag (L)	Final Concentration ppbV
Secondary standards prepared using gas-tight syringes					
Tedlar® bag primary standard-Low	1- 5ppmV	20 mL	Syringe Injection	4.0	5.0 / 20.0 / 20
Tedlar® bag primary standard-High	1- 5ppmV	400 mL	Syringe Injection	4.0	100 / 400 / 500
Tedlar® bag primary standard-LCS	1- 5ppmV	40 mL	Syringe Injection	4.0	10 / 40 / 50

Table A-5

Calibration Standard Levels

Calibration Level	Amount (ppbV)	Volume / Secondary Standard
1	0.50	25 mL of 5.0 ppbV sec. standard
2	1.0	50 mL of 5.0 ppbV sec. standard
3	5.0	250 mL of 5.0 ppbV sec. standard
4	10	25 mL of 100 ppbV sec. standard
5	20	50 mL of 100 ppbV sec. standard
6	50	125 mL of 100 ppbV sec. standard
7	80	200 mL of 100 ppbV sec. standard
8	100	250 mL of 100 ppbV sec. standard

Table A-6

ENTECH & 7016D/7200 or 7200A Operating Parameters for CTD Method

Module 1 (Blank Trap)	
Parameter	**Setting**
Trapping Temperature	-20° C
Internal standard volume	100 mL
Internal standard flow rate	60 mL / min
Sample volume (may vary depending on sample concentrations)	250 mL
Sample flow rate	100 mL / min
Preheat Temperature	10° C
Desorb Temperature	10° C
Bake Temperature	220° C
Bake Time	10 min.
Module 2 (Tenax trap)	
Parameter	**Setting**
Trapping Temperature	-70° C
Desorb Temperature	180° C
Bake Temperature	220° C
Module 2 to Module 3 desorb time	3.5 min
Module 3 (Cryofocusser)	
Parameter	**Setting**
Cryofocusing Temperature	-130° C
Desorb Temperature	Approx. 70° C
Module 3 to GC desorb time	2 min
Bake temperature / event	Approx. 90° C / event 3
Delay time	10 min

Table A-7

Internal Standard (IS) Assignments and Quantitation Ions for Sulfides & Mercaptans

Compound	Quant Ion	Sec. Ion(s)
Bromochloromethane (IS)	49	130
Hydrogen sulfide	34	33, 36
Carbonyl sulfide	60	62, 32
Methyl mercaptan	47	48, 45
ethyl mercaptan	62	47, 29
dimethyl sulfide	62	45, 47
carbon disulfide	76	44, 78
Isopropyl Mercaptan	43	41, 76
tert-Butyl Mercaptan	41	57, 90
n-Propyl Mercaptan	76	47, 43
Ethyl Methyl Sulfide	61	76, 48

Compound	Quant Ion	Sec. Ion(s)
1,4-difluorobenzene (IS)	114	63
Thiophene	84	58, 45
Isobutyl Mercaptan	41	56, 90
diethyl sulfide	75	90, 47
Butyl Mercaptan	56	41, 90
dimethyl disulfide	94	79, 45

Compound	Quant Ion	Sec. Ion(s)
Chlorobenzene-D5 (IS)	54	82, 117
3-Methylthiophene	97	98, 45
Tetrahydrothiophene	60	88, 45
2-Ethylthiophene	97	112, 45
2,5-Dimethylthiophene	111	112,97
Diethyl Disulfide	122	66, 94

Appendix B

Data Acquistion Parameters and Analysis Modifications for Conducting SIM Analysis

SIM analysis is conducted when full scan sensitivity does not meet the data quality objectives (DQO) of the project and/or regulatory criteria. The acquisition method used to acquire full scan data simultaneously acquires SIM data using the SIM ions and windows specified in Table B-1. The following modifications to the full scan SOP must be done to generate data using the SIM signal:

- SIM level calibration standards must be analyzed w/ the full scan curve (0.02,0.05, and 0.1 ppbV)
- A calibration curve is generated using the SIM signal utilizing the lower level calibration standards and must meet the same criteria as the full scan calibration criteria.
- The continuing calibration /LCS should be analyzed at a lower concentration (5.0 ppbV). If a separate continuing calibration run is needed, the continuing calibration level of 10 ppbV may be utilized. Laboratory Method Blanks must be evaluated for the SIM reporting limit as listed in Table B-2.

The SIM signal only acquires data for a limited target analyte list. These target analytes and reporting limits are listed in Table B-2. Additional ions have been added to allow for more analytes to be added, if requested by client. All requirements stated in this SOP must be applied to any TO15-SIM analysis conducted in the laboratory.

Table B-1

Calibration Standard Levels for SIM Analysis

Calibration Level	Amount (ppbV)	Volume / Secondary Standard
1	0.02	50 mL of 0.10 ppbV sec. standard
2	0.05	125 mL of 0.1 ppbV sec. standard
3	0.10	250 mL of 0.1 ppbV sec. standard
4	0.20	50 mL of 1.0 ppbV sec. standard
5	0.50	125 mL of 1.0 ppbV sec. standard
6	1.0	250 mL of 1.0 ppbV sec. standard
7	5.0	125 mL of 10 ppbV sec. standard
8	10	250 mL of 10 ppbV sec. standard
9	20	50 mL of 100 ppbV sec. standard
10	50	125 mL of 100 ppbV sec. standard

Table B-2

Seletive Ion Monitoring (SIM) Groupings

Group #	1	2	3	5	6	7	8	9	10	11	12
Group Start Time, min	0	5.9	8.75	10.1	10.9	11.6	13.8	14.6	16.6	18.8	20.5
Dwell time, sec	25	10	25	25	25	15	25	15	3	5	25
Cycles/sec (calc)	2	2.5	3.3	2.1	2.3	1.8	5.7	2.2	7	7	2.3
Analyte Range, Compund #	C2-C7	C8-C20	C21-C26	C27-C29, BCM (IS)	C30-C34	C35-C44, 1,4-DFB (IS)	C45-C46	C47-C55	C56-C67, CHB-D5 (IS)	C68-C76	C77-C80
Ions	29	29 63	43	41	42	39 85	39	39 92	39 106	39	43
	31	31 64	57	43	49	41 87	43	41 94	43 110	43	57
	32	39 66	61	45	51	43 88	58	43 97	45 112	57	63
	39	40 67	63	47	57	45 93	75	45 98	54 114	71	89
	41	41 69	65	49	59	52 95	77	49 100	57 117	75	102
	42	43 72	72	57	62	56 97	100	56 107	75 120	89	109
	43	44 76	73	59	63	57 99		57 109	77 126	91	115
	44	45 84	86	61	64	58 100		58 114	78 128	105	118
	50	47 85	96	70	65	62 110		61 127	82 131	111	128
	51	49 94	98	77	67	63 114		73 129	83 133	115	134
	52	51 96	117	83	71	69 117		75 131	85 156	116	141
	54	52 101	198	85	72	73 119		76 166	91 171	117	142
	58	53 103		86	87	75 129		77	95 173	118	145
	62	55 106		87	97	78 130		83	97 174	119	180
	64	56 108		96	102	82 132		85	103 175	120	225
	67	57 151		97	119	83 174		91	104	126	260
	85	58		98		84			105	134	
	87	59		130						142	
	135	61								146	
										156	
										157	

Table B-3

TO15-SIM Target Analytes and Reporting Limits

COMPOUND	CAS #	SIM Reporting Limit, ppbV	SIM Reporting Limit, ug/m^3
1,1,1-trichloroethane	71-55-6	0.02	0.109
1,1,2,2-tetrachloroethane	79-34-5	0.02	0.137
1,1,2-trichloroethane	79-00-5	0.02	0.109
1,1-dichloroethane	75-34-3	0.02	0.081
1,1-dichloroethene	75-35-5	0.02	0.079
1,2,4-trimethylbenzene	95-63-6	0.02	0.098
1,2-dibromoethane	106-93-4	0.02	0.154
1,2-dichlorobenzene	95-50-1	0.02	0.12
1,2-dichloroethane	107-06-2	0.02	0.081
1,2-dichloropropane	78-87-5	0.02	0.092
1,2-dibromo-3-chloropropane	96-12-8	0.02	0.193
1,3,5-trimethylbenzene	108-67-8	0.02	0.098
1,3-butadiene	106-99-0	0.02	0.044
1,3-dichlorobenzene	541-73-1	0.02	0.12
1,4-dichlorobenzene	106-46-7	0.02	0.12
1,4-dioxane	123-91-1	0.10	0.36
2-hexanone	591-78-6	0.20	0.82
2,2,4-trimethylpentane	540-84-1	0.20	0.93
3-chloropropene	107-05-1	0.20	0.63
4-Ethyltoluene	622-96-8	0.02	0.098
benzene	71-43-2	0.10	0.223
benzyl chloride	100-44-7	0.20	1.03
bromodichloromethane	75-27-4	0.02	0.134
bromoform	75-25-2	0.02	0.207
bromomethane	74-83-9	0.02	0.078
carbon disulfide	75-15-0	0.20	0.62
hexachlorobutadiene	87-68-3	0.05	533
hexane	110-54-3	0.20	0.7
heptane	142-82-5	0.20	0.82
isopropyl alcohol	67-63-0	0.50	1.23
methylene chloride	75-09-2	0.50	1.74
MTBE	1634-04-4	0.02	0.072
m+p-xylene	108-38-3 106-42-3	0.04	0.174
o-xylene	95-47-6	0.02	0.087
propylene	115-7-1	0.50	0.85
styrene	100-42-5	0.02	0.085
tetrachloroethene	127-18-4	0.02	0.136
tetrahydrofuran	109-99-9	0.5	1.48
toluene	108-88-3	0.05	0.188
trans-1,2-dichloroethene	156-60-5	0.02	0.079
trans-1,3-dichloropropene	10061-02-6	0.02	0.091
trichlorofluoromethane	75-69-4	0.05	0.280
trichloroethene	79-01-6	0.02	0.107
1,2,4-trichlorobenzene	120-82-1	0.05	0.371
vinyl acetate	108-05-4	1.00	3.50
vinyl bromide	593-60-2	0.20	0.87
vinyl chloride	75-01-4	0.02	0.051
CT RSR Additional Analytes			
1,1,1,2-tetrachloroethane	630-20-6	0.02	0.137
acrylonitrile	107-13-1	0.50	1.08
isopropyltoluene	99-87-6	0.20	1.1
n-butylbenzene	104-51-8	0.20	1.1

carbon tetrachloride	56-23-5	0.02	0.126
chlorobenzene	108-90-7	0.10	0.460
chloroethane	75-00-3	0.10	0.265
chloroform	67-66-3	0.02	0.098
chloromethane	74-87-3	0.20	0.41
cis-1,2-dichloroethene	156-59-2	0.02	0.079
cis-1,3-dichloropropene	10061-01-5	0.02	0.091
cyclohexane	110-82-7	0.2	0.69
dibromochloromethane	124-48-1	0.02	0.17
dichlorodifluoromethane	75-71-8	0.20	0.99
ethanol	64-17-5	5.0	9.42
ethyl acetate	141-78-6	0.50	1.8
ethylbenzene	100-41-4	0.02	0.087
Freon-113	76-13-1	0.05	0.383
Freon-114	76-14-2	0.05	0.349
sec-butylbenzene	135-98-8	0.20	1.1
tert-butylbenzene	98-06-6	0.20	1.1
isopropylbenzene	98-82-8	0.20	0.98
2-butanone (MEK)	78-93-3	0.50	1.48
Acetone	67-64-1	1.00	2.35
4-methyl-2-pentanone (MIBK)	108-10-1	0.50	2.05
Project & State Specific Analytes			
1,2,3-trichlorobenzene	87-61-6	0.05	0.371
1,2,3-Trichloropropane	96-18-4	0.02	0.12
acrolein	107-02-8	0.05	0.115
bromobenzene	108-86-1	0.20	1.28
Dibromomethane	74-95-3	0.20	1.42
Naphthalene	91-20-3	0.05	0.262
tertiary butyl alcohol	75-65-0	0.50	1.51
All reporting limits are subject to change.			

Appendix C

Modifications to Data Review and Case Narrative to Comply with MADEP MCP TO-15 Method

This addendum addresses modifications to this SOP required to be in compliance with the MADEP MCP TO-15 method, specifically "Quality Control Requirements and Performance Standards for the ***Analysis of Volatile Organic Compounds in Air Samples (TO-15) by Gas Chromatography/Mass Spectrometry (GC/MS)*** in Support of Response Actions under the Massachusetts Contingency Plan (MCP)" Revision No. 0, Section IX B.

1) For duplicate analyses, the 25% RPD criteria stated in Sect. 9.6 of this SOP does not need to be applied to concentrations less than 5X the reporting limit.

2) Samples cannot be analyzed if any of the target analytes if the LCS recovery criteria stated in sect. 9.2 of this SOP is below 70% recovery. For compounds listed as difficult analytes (hexachlorobutadiene, 1,2,4-trichlorobenzene, naphthalene, acetone, and 1,4-dioxane), LCS recovery cannot be less than 50%.

3) Any analyte exceeding %RSD criteria of 30% during initial calibration that is a not listed in the MCP TO-15 method, but may still be reported to the client, must be noted in the case narrative.

Appendix E

Modifications to Data Review and Case Narrative to Comply with 2014 NJDEP Technical Guidance for EPA Method TO-15

This addendum addresses modifications to this SOP required to be in compliance with the NJDEP 2014 Technical Guidance, **"NJDEP Site Remediation Program, Data of Known Quality Protocol, Version 1, April 2014**". This guidance is to be used when analyzing samples via the EPA Method TO-15.

1) Per the Data of Know Quality Protocols Technical Guidance, surrogates are not required to be reported via EPA Method TO-15.

2) A target analyte list and reporting limits are specified in Table E-1, per the Analytical Laboratory Data Generation, Assessment and Usability Technical Guidance.

3) For the analytes ethanol and isopropyl alcohol, results are allowed to be reported outside the calibration range of the instrument, per the Analytical Laboratory Data Generation, Assessment and Usability Technical Guidance. Results reported that exceed the calibration range will be designated with an "E" qualifier.

4) **Laboratory Control Sample (LCS) criteria -** Must contain all target analytes, recovery range is 70-130%. Exceptions for difficult analytes (hexachlorobutadiene, 1,2,4-trichlorobenzene, naphthalene, acetone, dichlorodifluoromethane, and 1,4-dioxane) must exhibit percent recoveries between 40-160%. In addition, the CCAL analysis cannot be reported as the LCS even if it meets LCS requirements. The LCS must be a separate analysis, analyzed after a passing CCAL standard.

5) **Duplicate analyses** - The 25% RPD criteria stated in Sect. 9.6 of this SOP does not need to be applied to concentrations less than 5X the reporting limit.

6) **Tentatively Identified Compounds (TICs)** – up to 15 TICs must be reported, if present. If a reduced target analyte list is requested by client, TICs are not reported.

Table E-1

NJDEP 2014 Target Analytes and Reporting Limits via EPA Method TO-15

Required Compound Name	CAS Number	Molecular Weight	Reporting Limit ppbV	Reporting Limit ug/m³
Acetone	67-64-1	58.08	5.0	12
Allyl chloride	107-05-1	76.53	0.2	0.6
Benzene	71-43-2	78.11	0.2	0.6
Bromodichloromethane	75-27-4	163.8	0.2	1
Bromoform	75-25-2	252.8	0.2	2
Bromomethane	74-83-9	94.94	0.2	0.8
1,3-Butadiene	106-99-0	54.09	0.2	0.4
Chlorobenzene	108-90-7	112.6	0.2	0.9
Chloroethane	75-00-3	64.52	0.5	1
Chloroform	67-66-3	119.4	0.2	1
Chloromethane	74-87-3	50.49	0.5	1
Carbon disulfide	75-15-0	76.14	0.5	2
Carbon tetrachloride	56-23-5	153.8	0.2	1
2-Chlorotoluene	95-49-8	126.6	0.2	1
Cyclohexane	110-82-7	84.16	0.2	0.7
Dibromochloromethane	124-48-1	208.3	0.2	2
1,2-Dibromoethane	106-93-4	187.9	0.2	2
1,2-Dichlorobenzene	95-50-1	147.0	0.2	1
1,3-Dichlorobenzene	541-73-1	147.0	0.2	1
1,4-Dichlorobenzene	106-46-7	147.0	0.2	1
Dichlorodifluoromethane	75-71-8	120.9	0.5	2
1,1-Dichloroethane	75-34-3	98.96	0.2	0.8
1,2-Dichloroethane	107-06-2	98.96	0.2	0.8
1,1-Dichloroethene	75-35-4	96.94	0.2	0.8
1,2-Dichloroethene (cis)	156-59-2	96.94	0.2	0.8
1,2-Dichloroethene (trans)	156-60-5	96.94	0.2	0.8
1,2-Dichloropropane	78-87-5	113.0	0.2	0.9
1,3-Dichloropropene (cis)	10061-01-5	111.0	0.2	0.9
1,3-Dichloropropene (trans)	10061-02-6	111.0	0.2	0.9
1,2-Dichlorotetrafluoroethane	76-14-2	170.9	0.2	1
1,4-Dioxane	123-91-1	88.12	5	18
Ethanol	64-17-5	46.07	5	9
Ethylbenzene	100-41-4	106.2	0.2	0.9
4-Ethyltoluene	622-96-8	120.2	0.2	1
n-Heptane	142-82-5	100.2	0.2	0.8
1,3-Hexachlorobutadiene	87-68-3	260.8	0.2	2
n-Hexane	110-54-3	86.17	0.2	0.7
Isopropanol	67-63-0	60.10	5	12

Table E-1 continued

Required Compound Name	CAS Number	Molecular Weight	Reporting Limit ppbV	Reporting Limit ug/m^3
Methylene chloride	75-09-2	84.94	0.5	2
Methyl ethyl ketone	78-93-3	72.11	0.5	1
Methyl isobutyl ketone	108-10-1	100.2	0.5	2
Methyl methacrylate	80-62-6	100.1	0.5	2
Methyl tert-butyl ether	1634-04-4	88.15	0.2	0.7
Styrene	100-42-5	104.1	0.2	0.9
Tert-butyl alcohol	75-65-0	74.12	5	15
1,1,2,2-Tetrachloroethane	79-34-5	167.9	0.2	1
Tetrachloroethene	127-18-4	165.8	0.2	1
Tetrahydrofuran	109-99-9	72.11	5	15
Toluene	108-88-3	92.14	0.2	0.8
1,2,4-Trichlorobenzene	120-82-1	181.5	0.5	4
1,1,1-Trichloroethane	71-55-6	133.4	0.2	1
1,1,2-Trichloroethane	79-00-5	133.4	0.2	1
Trichloroethene	79-01-6	131.4	0.2	1
Trichlorofluoromethane	75-69-4	137.4	0.2	1
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	187.4	0.2	2
1,2,4-Trimethylbenzene	95-63-6	120.2	0.2	1
1,3,5-Trimethylbenzene	108-67-8	120.2	0.2	1
2,2,4-Trimethylpentane	540-84-1	114.2	0.2	0.9
Vinyl bromide	593-60-2	106.9	0.2	0.9
Vinyl chloride	75-01-4	62.50	0.2	0.5
Xylenes (m&p)	179601-23-1	106.2	0.5	2
Xylenes (o)	95-47-6	106.2	0.2	0.9
Naphthalene (reported on request)	91-20-3	128.2	0.2	1

All reporting limits are subject to change.

Appendix F

Modifications to EPA TO-15 SOP to comply with Ohio EPA Voluntary Action Program (VAP) Requirements

This Appendix defines requirements that are necessary to perform TO-15 analysis for any samples submitted via the VAP Program. No deviations from the SOP are allowed under the VAP program.

1) Sec. 3 caveat – reporting limits defined in this SOP are subject to change.

2) Sec. 7 caveat – Equipment and supplies are subject to change.

3) Initial calibration acceptance – %RSD criteria must be as defined in the EPA TO-15 method; only 2 analytes allowed greater than 30% RSD, and must be less than 40%.

4) The Laboratory check standard (LCS) may not be used as the continuing calibration verification (CCV). A CCV and LCS must be analyzed prior to samples.

5) Tentatively Identified Compounds (TICs) may not be reported as certified values.

6) CCV-10% rule not allowed. All analytes reported must be +/- 30% D. (Criteria in sections 10.4.2.6 and 2.1 do not apply to VAP samples.) All analytes in the CCV must be less than 30% RSD for VAP samples (criteria in Section 2.1, 10.4.2.6 and 10.4.2.7 do not apply.)

7) 10% Duplicate criteria not allowed. All duplicate %RPD results must be below 25%.

8) For Ohio projects, only the analytes listed in Table F-1 or as explained in the footnote to Table F-1 will be reported as certified data.

9) Affidavits are required with each report or for a series of reports generated for a particular project.

10) Surrogates are not required and will not be added to Ohio VAP samples.

11) The analysis of a Laboratory Control Sample Duplicate (LCSD) is not required and will not be analyzed for Ohio VAP samples.

12) The LCS is evaluated at +/- 30. Criteria in section 2.1 does not apply to VAP samples.

13) Corrective actions for the method blank are required if it contains analyte concentrations at or above the RL for reportable analytes.

Table F-1

Ohio EPA VAP Program Target Analyte List *		
chloromethane	1,2-dichloropropane	1,1-Dichloropropene
vinyl chloride	1,4-dioxane	1,2,3-Trichloropropane
1,3-butadiene	trichloroethene	1,2,4-Trimethylbenzene
acetaldehyde	2,2,4-trimethylpentane	1,2-Dichlorobenzene
bromomethane	cis-1,3-dichloropropene	1,3,5-Trimethylbenzene
chloroethane	4-methyl-2-pentanone	1,3-Dichlorobenzene
vinyl bromide	1,1,2-trichloroethane	1,3-Dichloropropane
acrolein	toluene	Acetone
acetonitrile	1,2-dibromoethane	Bromodichloromethane
acrylonitrile	tetrachloroethene	Butyl acetate
1,1-dichloroethene	chlorobenzene	cis-1,2-Dichloroethene
methylene chloride	ethylbenzene	Cyclohexane
3-chloropropene	m+p-xylene	Dibromochloromethane
carbon disulfide	bromoform	Dibromomethane
1,1-dichloroethane	styrene	Dichlorodifluoromethane
MTBE	1,1,2,2-tetrachloroethane	Ethyl acetate
vinyl acetate	o-xylene	Ethyl ether
2-butanone	isopropylbenzene	Methyl alcohol (methanol)
chloroform	Benzyl Chloride	Methyl Methacrylate
1,2-dichloroethane	1,4-dichlorobenzene	Naphthalene
hexane	1,2-dibromo-3-chloropropane	Tetrahydrofuran
1,1,1-trichloroethane	1,2,4-trichlorobenzene	trans-1,2-Dichloroethene
benzene	hexachlorobutadiene	trans-1,3-Dichloropropene
carbon tetrachloride	1,1,1,2-Tetrachloroethane	Trichlorofluoromethane

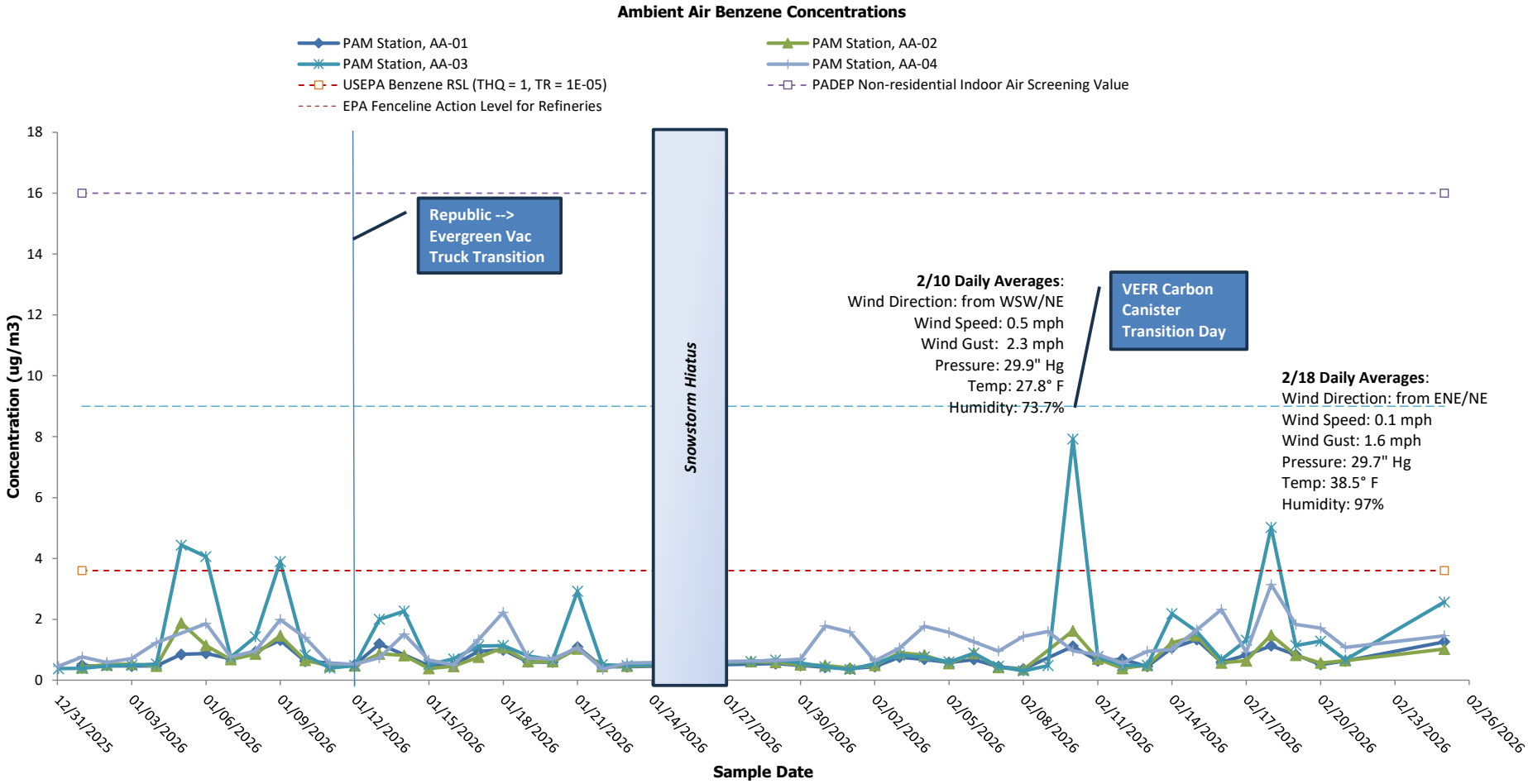
***** The analytes appearing in this table are subject to change, however, any changes will not include identification of compounds that are not included in the TO-15 method referenced at the beginning of this document. However, it is acceptable to analyze and report, as certified data, compound(s) not included in the TO-15 method referenced at the beginning of this document if the compound(s) appear on the current and valid certificate issued by VAP on the date of analysis and if the laboratory has followed all applicable VAP approved documents.

Attachment 2

Benzene Air Monitoring Trend Chart

LANGAN

Attachment 2
Benzene Trend Chart - December 31, 2025 through February 25, 2026
MIPC Chelsea Facility
920 Cherry Tree Rd, Aston, PA 19014
Langan Project No.: 220240201



LANGAN

Attachment 3

Alternative Passive Air Monitoring Plan (Method 325)

LANGAN

March 10, 2026

Fenceline Monitoring Field Sampling Plan for MIPC Chelsea Facility Remediation Program

Passive Diffusive Sampling Using Thermal Desorption Tubes

Prepared for:
MIPC Chelsea Facility
920 Cherry Tree Road
Aston Township, Pennsylvania

1.0 INTRODUCTION

This document is prepared by Langan Engineering and Environmental Services, LLC (Langan) to provide a general overview and plan for personnel responsible for conducting passive diffusive ambient air sampling as part of the remediation fence-line monitoring program at the MIPC Chelsea Facility located at 920 Cherry Tree Road, Aston Township, Delaware County, Pennsylvania.

MIPC is currently conducting investigation and remediation activities on the west side of the facility. The investigation activities consist of the excavation of monitoring/recovery wells using drill rigs, and the installation of well pipe and surface completions. The remediation activities consist of mobile product removal, product removal using a wastewater treatment unit, proposed product removal using solar activated skimmers, and proposed product/vapor recovery using dual phase extraction systems. Additional details related to the interim remedial activities are outlined below.

Onsite Investigation Activities

Ongoing investigation activities include drilling, soil sampling, well installation, well development, groundwater sampling and well evaluation tests (well slug tests and product transmissivity tests). All of the investigation activities are directed by environmental professionals who conduct breathing zone air monitoring using photoionization detectors (PIDs) and as required, benzene meters. The environmental professionals also note and report the presence of odors and have stop work authority to terminate activities if odors, monitoring, or other observations/measurements are not consistent with the requirements of the Project Health and Safety Plan.

1.1 ONSITE REMEDIATION ACTIVITIES

Several remediation technologies are currently being implemented or proposed at the MIPC Chelsea Facility to recover gasoline product and impacted groundwater identified during investigation activities on the west side of the facility. These activities include Vacuum Enhanced Fluid Recovery (VEFR) using vacuum trucks, operation of a temporary wastewater treatment unit

to separate and treat recovered groundwater and product, proposed solar-powered skimmers installed in recovery wells, and proposed dual phase vapor extraction systems for combined product and vapor recovery. The following sections describe these remediation technologies and their operation at the site.

Vacuum Enhanced Fluid Recovery (VEFR)

The interim remedial action using VEFR consists of the vacuum extraction of gasoline product in recovery wells using a vacuum truck. The truck is tied to a series of hoses connected to packers and stingers in wells containing gasoline. Up to 3 wells are extracted at one time, with the vacuum exhaust direct through 400-pound carbon canisters. The carbon canister effluent is routinely checked with a PID) for breakthrough. The exhaust hose from the carbon canisters is directed approximately 30-40 feet to the west. Environmental professionals are monitoring and observing the operation of the VEFR events and are monitoring breathing airspace and the potential for fugitive emissions with PIDs and benzene meters consistent with the requirements of the Project Health and Safety Plan. Fluids recovered in the vacuum trucks are subsequently delivered to the Monroe Refinery for Processing and/or disposal.

Wastewater Treatment Unit

A temporary wastewater treatment unit (WTU) was permitted by PADEP in September 2025 and is used to collect subsurface groundwater in a belowground vault adjacent to the former spring house structure. The system consists of pumps, controls, carbon canisters, bag filters and frac tanks to separate the gasoline and to treat the water pumped prior to discharge, consistent with the PADEP permit. Environmental professionals operating the system also oversee the removal of gasoline product from the top of the frac tanks. The gasoline product is removed by vacuum trucks using carbon canisters for the treatment of vacuum exhaust as described above. Environmental professionals also monitor the presence of odors and maintain monitoring of breathing space consistent with the requirements of the MIPC Health and Safety Program.

Solar Skimmers

Solar product skimmers are proposed for recovery wells in the Tank 708 area. The skimmers will reside in the wells at the product/groundwater interface, and pump product to a central product recovery tank. The product recovery tank will be equipped with carbon canisters for the treatment of the tank vent effluent. The tops of the wellheads will be monitored for odors/fugitive emissions using PIDs.

Dual Phase Vapor Extraction Trailers

Self-contained dual phase vapor extraction trailers and treatment systems are proposed for the remediation product recovery Phase II. The trailers will be equipped with liquid ring pumps, filters and associated controls. Effluent gas from the systems will be treated using electric catalytic oxidizers with greater than 90% destruction of volatile organic compounds.

2.0 PROPOSED AIR SAMPLING PROCEDURES

The procedures outlined herein are consistent with EPA Method 325A (Volatile Organic Compounds from Fugitive and Area Sources – Sampler Deployment and VOC Sample Collection)

and EPA Method 325B (Volatile Organic Compounds from Fugitive and Area Sources – Sampler Preparation and Analysis) and has been modified to focus on the potential air impacts from the remediation activities. The plan covers identification of sampling locations, preparation and handling of sample media, sample deployment, field documentation, sample recovery, chain-of-custody procedures, meteorological data collection, and relevant process and offsite data tracking.

This monitoring protocol is based on the EPA refinery fence-line monitoring framework described in Methods 325A and 325B, adapted for implementation at the remediation sources at the MIPC Chelsea terminal facility. The procedures described herein follow the intent of Method 325A sampler deployment requirements and Method 325B analytical requirements for benzene monitoring using passive diffusive sorbent tubes.

The objective of this monitoring program is to measure ambient concentrations of benzene and other applicable volatile organic compounds (VOCs) along the monitoring perimeter that encompasses the known VOC remediation emission sources.

2.1 IDENTIFICATION OF SAMPLE LOCATIONS

Sampling locations were selected in accordance with the requirements of EPA Method 325A using the Linear Method described in Section 8.2.3. In addition to the Method 325A placement criteria, several site-specific factors were considered in establishing the monitoring network, including the location of ongoing remediation activities, facility layout and boundary conditions, nearby residential receptors, meteorological information obtained from available sources reflecting conditions through February 2026, and observations from routine field air monitoring conducted during investigation and remediation activities.

2.2 REQUIREMENTS FOR SAMPLE LOCATIONS

Sample locations at the MIPC Chelsea Facility are established in accordance with Option 2 (Linear Method) described in Section 8.2.3 of EPA Method 325A.

The primary monitoring perimeter at the MIPC Chelsea Facility is less than 12,000 feet. Accordingly, six (6) primary sample locations are placed at approximately equal intervals along the monitoring perimeter to encompass the known VOC remediation emission sources.
A site figure illustrating the monitoring perimeter and sample locations is provided in Figure 2-1.

Guidelines for Sampling Placement

1. **Perimeter Monitoring:** Sampling points are placed primarily along the facility boundary to detect fugitive emissions from the remediation activities that could impact nearby residential areas.
2. **Upwind and Downwind Considerations:** Prevailing wind direction is considered during placement, with emphasis on downwind locations from emission sources.

Fence-Line Sampling Location Selection

Figure 2-1 shows the benzene fence-line monitoring locations established for the facility consistent with EPA Method 325A Section 8.2.3 (Linear Method).

A total of Six (6) primary sampling locations were placed at approximately equal intervals along the monitoring perimeter to provide representative fence-line coverage of potential benzene emissions from the remediation activities.

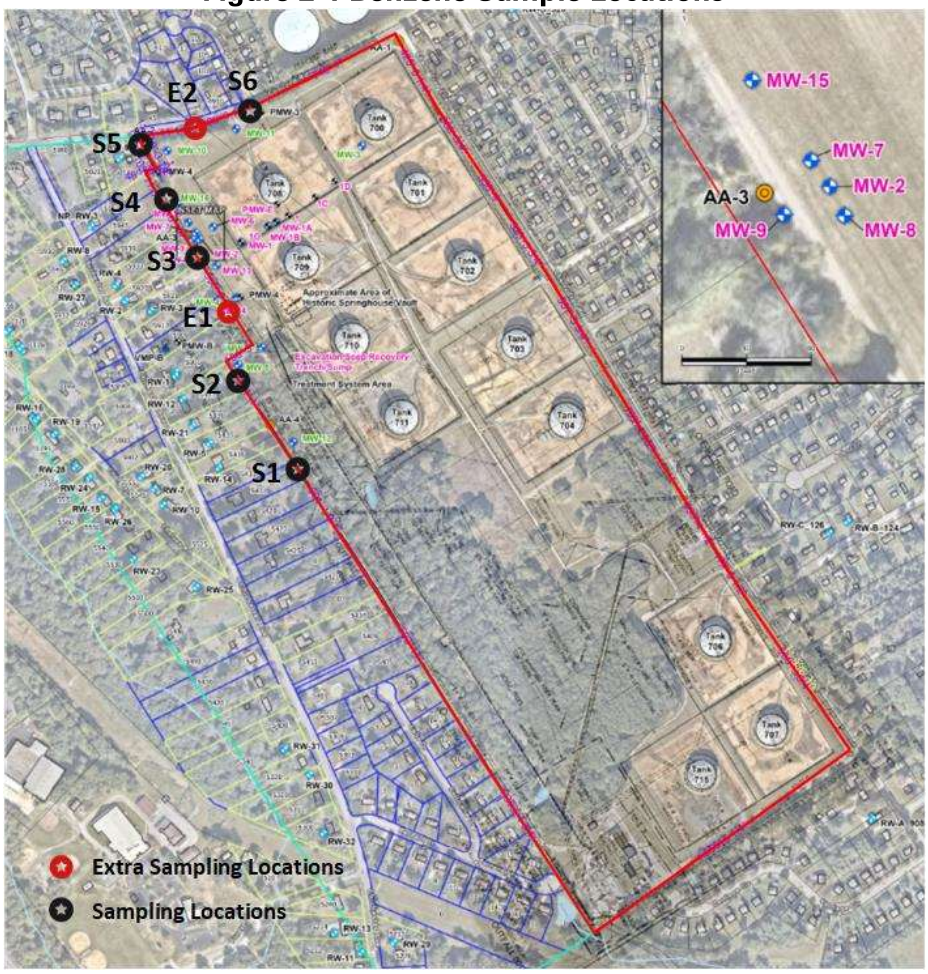
In addition, two supplemental locations were added to increase spatial resolution along boundary segments closest to the known remediation sources, consistent with Method 325A source-proximate monitoring considerations.

The final configuration includes:

- **6 primary sampling locations** (black symbols) evenly distributed along the monitoring perimeter
- **2 supplemental sampling locations** (red symbols) placed between primary locations near source-proximate boundary segments

Primary sampling locations (shown as black symbols in Figure 2-1) provide uniform monitoring-perimeter coverage around the facility. Supplemental sampling locations (shown as red symbols in Figure 2-1) provide additional spatial resolution along monitoring-perimeter segments adjacent to known remediation sources

Figure 2-1 Benzene Sample Locations



A sampling location summary table (Table 2-1) is provided documenting station ID, coordinates, mounting height, nearby structures, and siting rationale consistent with Method 325A placement considerations.

Table 2-1: Sampling Location Summary

Station ID	Latitude	Longitude	Mounting Height (m)	Nearby Structures	Siting Basis
S1	39.863032	-75.456611	2	Residential neighborhood (west of facility)	Western fenceline location representing residential receptor exposure from remediation activities
S2	39.864298	-75.457566	2	Residential properties adjacent to facility boundary	Downwind residential receptor coverage along western boundary from remediation activities
S3	39.865972	-75.458115	2	Residential homes and facility access area	Transitional zone between residential area and edge of remediation activities
S4	39.866816	-75.458787	2	Residential neighborhood and facility boundary	Northern-west fenceline coverage proximate to remediation activities
S5	39.867635	-75.459097	2	Residential area near northwest corner	Corner location capturing pollutant transport along boundary
S6	39.868011	-75.457486	2	Residential neighborhood north of facility	Northern fenceline receptor monitoring location
E1	39.865234	-75.457865	2	Residential area near western boundary	Supplemental sampling location to increase coverage near residential receptors
E2	39.867800	-75.458431	2	Residential neighborhood near northwest boundary	Supplemental/background comparison location

2.3 BLANK AND DUPLICATE SAMPLE LOCATIONS

Consistent with EPA Method 325A QA/QC guidance for monitoring networks with fewer than 19 sampling locations, **one co-located duplicate sample and one blank sample will be collected during each sampling period**.

The QA/QC samples will include:

- One co-located duplicate sampler deployed at a selected monitoring station
- One trip blank tube that remains sealed throughout handling and transport

The duplicate location will be rotated periodically among monitoring stations, with preference given to locations expected to represent downwind conditions.

One blank sample will be included during each sampling period as a **trip blank**. The trip blank tube will remain sealed with its brass storage caps throughout shipment, field handling, deployment activities, recovery, and return shipment to the laboratory. The trip blank will not be opened or exposed to ambient air and is used to evaluate potential contamination associated with sample handling, transport, and laboratory preparation.

3.0 SAMPLE MEDIA AND RECEIPT BY PARTICIPANT

Sampling tubes will be shipped from the designated analytical laboratory to the MIPC Chelsea Facility or to the consultant's office prior to each sampling round.

The sample media consists of FLM Carbopack X sorbent tubes. These tubes are ¼-inch OD stainless steel with interior coating and are approximately 3.5 inches in length. Each tube is uniquely identified with a serial number and barcode.

The Carbopack X sorbent tube and diffusion-cap configuration used for this program is laboratory-validated for benzene monitoring using passive diffusive sampling. The analytical laboratory provides compound-specific uptake rates and performs analysis in accordance with EPA Method 325B thermal desorption and gas chromatography procedures.

Brass long-term storage caps with PTFE ferrules are fitted to each end of the tube to seal the media prior to deployment and following sample recovery.

Each shipment will include:

- Individual sampling tubes in protective plastic containers (See Figure 3-1)
- Diffusion caps
- Ice packs for return shipment
- Field Data Sheets and Chain-of-Custody (COC) forms
- Return shipping label

Upon receipt:

1. Verify shipment contents against the packing list.
2. Inspect tubes for damage or missing caps.
3. Store tubes in a temperature-controlled indoor location.
4. Use tubes within 30 days of laboratory conditioning.

Unused tubes and diffusion caps must be returned to the laboratory and should not be retained for future use.

Figure 3-1. Supelco Passive Diffusive Sampling Tube

See Figure 3-2 for a photo of the cooler shipment and its contents. Spare tubes and diffusion caps are to be used only if needed (i.e. a tube or diffusion cap gets lost or damaged). Unused items should be placed in the cooler to be returned to the laboratory with each shipment (i.e., extras should be returned and not removed and "saved"). Subsequent shipments will include the same items; except they will contain only 3 diffusion caps as diffusion caps are to be reused. The sample shelters will be shipped separately.

Figure 3-2. Initial Cooler and Contents

4.0 SAMPLE PREPARATION AND PRE-DEPLOYMENT

Ice packs should be removed from the cooler and placed in a freezer until needed for return shipment.

Sample tubes must remain in their storage containers until deployment. Tubes should be allowed to equilibrate to ambient temperature prior to deployment (approximately 30 minutes to 1 hour). Field Data Sheets/COCs shall be completed as tubes are deployed. Sample IDs shall be assigned at the time of deployment.

Sample ID format:
AAAAA-BBB-C-DDDDDD

Where:
AAAAA = Facility ID (MIPC)
BBB = Sample Location ID
C = Sample Type (S, D, or B)
DDDDDD = Sample event start date

Example:
MIPC-05-S-021526

Field equipment required includes:

- GPS (required during initial setup, optional for subsequent sample periods);
- Camera (optional);
- Location map with coordinates (required during initial setup, optional for subsequent sample
- periods);

- Posts, shelters, and mounting supplies (initial setup only);
- Sample protocol;
- Pens;
- Work gloves;
- Powder-free nitrile gloves;
- Zip ties;
- Numbered zip ties for custody seal;
- Clipboard;
- 9/16" and 1/2" wrenches;
- General toolbox;
- Field Data Sheet/COC from previous deployment;
- Pre-filled Field Data Sheet/COC, printed from electronic version (optional) for deployment.

For each trip, except the first and last, you will have two coolers, one containing conditioned tubes that are ready for deployment and one to collect used tubes, ready to be returned to the laboratory for 325B analysis. Sampled tubes must never be placed in the same shipping container as clean conditioned sampling tubes.

5.0 SAMPLE LOCATION: SAMPLE SHELTER MOUNTING AND SAMPLE TUBE DEPLOYMENT

5.1 MOUNTING OF SAMPLE SHELTER

Sample shelters (Figure 5-1) shall be securely mounted at designated monitoring locations. Shelters must be mounted:

- With open end facing downward
- At a height between 1.5 and 3 meters (5 to 9.8 feet) above ground level under standard fence conditions in accordance with EPA Method 325A Section 8.5.5. Where sound barriers are present and would obstruct airflow at standard mounting height, monitoring height may be increased as necessary to maintain unobstructed airflow at the facility boundary consistent with Sections 4.1 and 8.1.2 of the EPA Method 325A perimeter monitoring guidelines.
- On a stable structure such as a post or fence

Sample shelters must be mounted securely in the locations that were previously designated for the fenceline ambient sampling program. In accordance with EPA Method 325A Section 8.2.1, passive samplers shall be placed on or inside the facility boundary as part of the established monitoring perimeter. Samplers shall be positioned so that they measure ambient air conditions at the facility boundary and are not influenced by nearby physical obstructions. Placement shall consider and avoid the influence of structures that could interfere with air parcel flow to the sampler, consistent with Sections 4.1 and 8.1.2 of Method 325A.

Where the perimeter fence coincides with the facility boundary, shelters shall be mounted immediately inside the fence line and shall not be set further back within the facility boundary. Vertical adjustments made to avoid obstructions (e.g. sound barriers) shall not alter the established horizontal position of the monitoring station at the facility boundary.

Figure 5-1. Sample Shelter

Sample shelters can be mounted as deemed appropriate by the participating facility for the specific location that has been chosen for deployment as long as it provides a secure and stable position for the sampler. Each unit must be mounted with the open end facing down, at a height of 1.5 – 3 meters (5 – 9.8 feet) above ground level (unless adjusted in accordance with the elevated installation procedures outlined in Section 5.3) using a pole or other secure structure (i.e. fence post, light post, etc.). Hardware required to secure the shelters depends on the structure to which the sample shelters are being mounted and needs to be purchased separately. It is not recommended that samplers be placed near or against solid structures such as buildings, solid fences, large tanks, etc. or anywhere where the structure itself could affect the surrounding ambient air flow to the sampler. Chain link fences are acceptable as long as they are of the open type with no privacy slats. Each sample location should be identified with a sign or other type of indicator that displays the sample location ID and, if possible, the GPS coordinates. This will provide an easy way for field personnel to identify the location and ensure that the sample locations are not mixed up on the Field Data Sheet/COC during sample tube deployment.

Sound barriers may be installed along portions of the facility boundary. During installation, field personnel shall evaluate whether such barriers could interfere with air parcel flow to the sampler. Shelters shall not be mounted directly against obstructions such as solid panels. Where barriers are present, the sampler inlet shall not be positioned below the top of the barrier. Final mounting height and presence of barrier conditions should be documented on the Field Data Sheet.

5.2 SAMPLE TUBE DEPLOYMENT

Once all sample shelters are securely mounted in place at the designated locations, the sample tubes can be deployed. A sequence of deployment for the sample locations should be determined. This sequence should be followed for the duration of the sampling program. This will maintain consistency in the sample times and will help to ensure the proper exposure time for each sampler.

The following steps describe the procedures for sample tube deployment at each location:

1. Upon arrival at the sample location, fill in the Field Test Data Sheet and Chain of Custody (COC) (Attachment A) with all of the required facility information. You may also pre-fill this information in an electronic version and print it out before each trip to deploy/collect samples.
2. Check the sample shelter and ensure that it is secure and stable and has not become loose or dislodged.
3. Note any unusual activities in the vicinity of the sample location and detail them on the Field Data Sheet/COC.
4. Select a sample tube from the lot.
5. Generate the sample ID in the format as described in Section 4.0 and record this on the field data sheet.
6. Wearing nitrile gloves, remove the sample tube from the plastic storage tube.
7. Move to a position directly next to the sample shelter where the tube will be placed prior to opening the inlet side of the tube. This is done to ensure that once the tube is opened up to the ambient air that it will only sample the surrounding air. For example if the tube is opened up in the sampler's field truck or somewhere other than the actual sampling location the tube will initially sample ambient air at a location other than where it was intended to which could potentially bias the results.
8. The arrow points to the non-sampling side. This side can also be identified by the absence of a groove (Figure 5-2). This side will remain sealed with a brass fitting during the entire sample period. Ensure this that the brass fitting on this end is tight. Do not over tighten the brass fittings as this could damage the PTFE ferrule inside the fitting and compromise the seal.
9. Remove the brass fitting from the inlet end of the sampling tube. The arrow points away from the inlet end. The inlet end is also identified by a groove on the outside of the tube (Figure 5-2). The brass plug does not have to be fully separated from the nut, only loosen the nut and it will slide off the tube. This will retain the PTFE ferrule inside the sealing fitting so it is not misplaced. Place the removed brass fitting back into the storage tube and replace the lid. Return the storage tube back to the cooler. All samples will be returned to the storage tubes for transport to the laboratory. If black powder comes out when the sample end is opened, the tube is leaking. Do not use a tube if it is leaking, has loose or missing storage cap(s), or if the tube is bent, crimped, or damaged. Return unusable tubes to the lab with a notification of the problem and use a different tube.
10. The upper plate of the tube carriage has 3 holes and a slip, plus 2 notches in the edge. The lower plate has 3 holes with red plugs, plus a gated slip. Slide the sample tube through the top plate of the tube carrier and then through the bottom plate, inlet end first.
11. Obtain one diffusion cap. These will be gray plastic caps that slide over the end of the sample tube. During initial deployment, diffusion caps will be in the cooler but during subsequent deployments, diffusion caps will be removed from the collected samples and reused.
12. Slide the diffusion cap over the inlet end of the sample tube. The diffusion cap has two o-rings that seal against the sample tube. Slide the sample tube until both o-rings have sealed against the tube and the inlet end of the tube is just against the diffusion cap screen. The diffusion cap must be pushed on far enough to seal both o-rings. It may take some force with a twisting action to slide the tube far enough into the diffusion cap to seal properly. Improper installation of the diffusion cap can affect the established diffusion rate so proper installation is crucial.
13. The tube is now ready for sampling and should look like the example in Figure 5-3. Note, the location of the groove located on the sample tube with respect to the diffusion cap

location. This can be used as a check to ensure that the diffusion cap is installed properly on the tube. THE ARROW SHOULD ALWAYS BE POINTING UP AND THE DIFFUSION CAP SHOULD ALWAYS BE AT THE BOTTOM OF THE TUBE.

14. Record the start date and start time on the Field Data Sheet/COC. Record any other data such as surrounding conditions or any other abnormal conditions near the sampling location. The average temperature and pressure for the entire 2-week period will be provided from meteorological data, so these parameters do not need to be collected in the field.
15. Collect at least one co-located duplicate sample per sampling period. For locations with a duplicate, deploy 2 tubes under the sample shelter. To add a second tube, remove a red plug and insert the tube under the shelter according to the instructions above. The red plugs in the lower plate prevent insects from getting inside the sample shelter and should be left in place for any unused tube sites.
16. Collect at least one field blank per sampling period. For locations with a field blank, deploy 2 tubes under the sample shelter. One of the tubes should be inserted with a diffusion cap according to the instructions above. The other tube, the field blank, must be inserted in the slip so that the storage cap does not need to be removed. Slide back the hinged gate, insert the tube with the brass nut still in place, and close the gate.
17. After all required tubes are in place, hold the handle on the bottom side of the lower plate and align the notches in the top plate with the posts inside the sample shelter (Figure 5-4). Push the carriage into the shelter so that the upper plate is above the posts and turn the carriage 90 degrees to secure the carriage in place.
18. Each carriage can hold up to four tubes but no more than 2 should be located at a sample location for this study. This procedure is repeated for each monitoring station.

Figure 5-2. Inlet End of Supelco Passive Diffusive Sampling Tube

Figure 5-3. Sample tube secured inside tube carriage

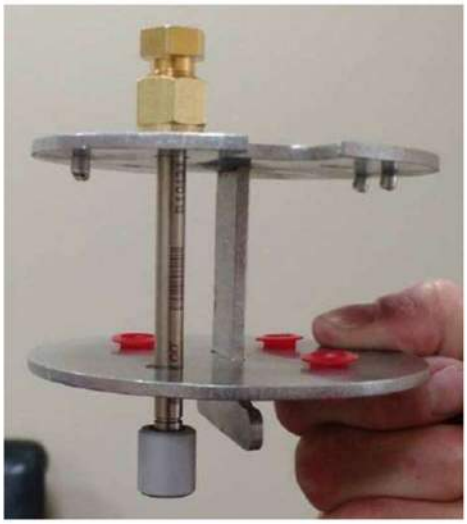


Figure 5-4. Mechanism to lock tube carriage into sample shelter

5.3 ELEVATED INSTALLATION PROCEDURES

Elevated installations shall be designed to:

- Maintain vertical orientation of the sampler
- Ensure unobstructed airflow to the inlet
- Allow safe and repeatable deployment and recovery at 14-day intervals
- Preserve the established monitoring perimeter

Where installation height exceeds the standard 1.5 to 3-meter range due to the presence of sound barriers or other airflow obstructions, shelters may be mounted at heights up to approximately 12 feet above ground surface.

Potential mounting configurations include:

- Extendable mast assemblies designed for environmental monitoring applications

  A vertically extending mast system capable of being raised to the required monitoring height and secured in a fixed, rigid upright position during the sampling period. For deployment and recovery, the mast is lowered to ground level, allowing safe tube deployment without requiring personnel to climb. Mast assemblies are widely used in perimeter air monitoring systems.

- Retractable pole assembly with platform

  A fixed elevated pole system equipped with an integrated or adjacent stabilized platform that allows personnel to access the sampler at the mounted height for sample deployment and recovery. The pole remains stationary during the sampling period and the platform provides controlled access while maintaining the sampler in a secure upright position.

- Hinged-base pole systems for ground-level access

  A rigid vertical pole mounted to a hinged based plate that allows the entire assembly to pivot downward for deployment and recovery. These systems are widely used in regulatory meteorological monitoring towers. During the sampling period, the pole is secured in a fixed upright position with locking hardware to maintain vertical alignment and stability.

Ladder-only access should be avoided. If ladders are required, OSHA-compliant ladder safety procedures shall be followed and deployment and recovery activities shall be performed in two-person field teams. The mounting method used at each station shall be document on the Field Data Sheet.

6.0 SAMPLE RECOVERY AND SHIPPING

6.1 SAMPLE RECOVERY AND RE-DEPLOYMENT

Samples shall be recovered on Day 14 (±1 day). The rule allows for +/- 1 day but stresses that refineries should strive for a 14-day sample period. Sample recovery should be conducted in the same location sequence as deployment and ideally at the same time of day. Return to each station with 2 kits, the empty one from the prior deployment and the new one that contains clean tubes. When recovering samples and re-deploying new tubes, take the following steps: Recovery shall follow the same sequence as deployment.

Where shelters are installed at elevated heights (e.g., up to approximately 12 feet above ground surface due to sound barrier adjustments), deployment and recovery shall be conducted using the controlled access methods described in Section 5.3.

Upon recovery:

1. Remove carriage.
2. Remove diffusion cap.
3. Replace brass fitting.
4. Seal the end of the used sample tube with the brass fitting that came with the tube. Tighten the fitting finger tight and then give it a ¼ turn using the wrenches. Do not over tighten as this could damage the ferrule inside the fitting and compromise the seal.
5. Verify the tube ID and location against the Field Data Sheet/COC. Record the date and stop time.
6. Place the tube back inside a glass storage jar, replace the lid, and place the jar in the original cooler. Do not put used tubes into the cooler with unused tubes or unused tubes into the cooler with used tubes.
7. Ensure the diffusion cap is not unusually dirty. It is unlikely, but, if necessary, replace the diffusion cap with a new one. Three extras will be provided with each shipment.
8. Deploy a clean tube, as well as blanks or duplicates as necessary, at the station following the deployment procedures in section 5.2.

6.2 FIELD QA/QC

Once the samples from all locations have been recovered and new samples have been deployed, before leaving the facility, the following quality assurance/quality control (QA/QC) checks should be completed:

1. Check the sample tube serial numbers of newly deployed tubes on the COC against the shipment log to ensure that all ID's have been correctly transcribed. If any tubes do not match the provided shipment log, check against the prior round's log to ensure that no tubes were mistakenly re-deployed. If any samples were mistakenly re-deployed, return to the sampling site and replace with a fresh tube noting on the prior log the time which the collected tube was re-deployed along with its location.
2. Check collected sample tube serial numbers against the COC ensuring that all samples have been collected for analysis.

When checks for both rounds of sampling have been completed, proceed to sample packaging and shipping procedures in section 6.3.

6.3 SAMPLE PACKAGING AND SHIPPING

Once the samples from all locations have been recovered and new samples have been deployed, recovered samples should be shipped to the analytical laboratory as soon as possible. If shipping is not done on the same day as sample recovery, place the samples into a refrigerator for storage and ensure the ice packs are frozen before being placed into the shipping cooler. Observe the following shipping instructions:
Recovered samples shall be shipped to the analytical laboratory as soon as practicable.

1. Place frozen ice packs into cooler.
2. Select a green tamper seal (Figure 6-1) and record the seal number on the Field Data Sheet/COC. Sign the document in the "Relinquished By" box and enter the date and time. Indicate the selected shipping agency in the "Received by" section.
3. Make a copy of the document and keep in a project file. Put the original in a Ziploc (or equivalent) plastic back and place it on top of the jars inside the cooler.
4. Close and lock the cooler lid and fasten the tamper seal through the metal eye on the front of the cooler.
5. Since the sample coolers will be sealed and the Field Data Sheet/COC will be within the cooler, it will not be possible for the shipping agency to physically sign the document. Therefore, simply indicating the shipping agency name in this section is acceptable.
6. The shipment shall include one sample tube from each monitoring location, one duplicate sample tube, and one trip blank tube. Affix return shipping label that arrived with in the sample kit to outside of case. Ship the samples via FedEx priority overnight shipping (i.e. delivery by 10am) to the LAB address, which will be printed on the included shipping label:

Shipment shall include:
• One tube per monitoring location
• One duplicate
• One blank

6.4 LABORATORY QUALITY ASSURANCE

The analytical laboratory performing analysis under EPA Method 325B shall maintain current laboratory accreditation (e.g., ISO/IEC 17025 or equivalent).

The laboratory will provide reporting limits for benzene consistent with Method 325B analytical requirements and appropriate for ambient fence-line monitoring applications. Laboratory QA/QC documentation will include trip blank results, duplicate sample evaluation, and any applicable data qualification flags. Monitoring data will be reviewed by the project team for completeness, QA/QC consistency, and conformance with Method 325A/325B requirements prior to reporting.

The laboratory shall provide:

- Method detection limits and reporting limits for benzene
- Laboratory QA/QC results
- Blank evaluation results
- Duplicate precision evaluation
- Data flags where applicable

Data will be reviewed for completeness, QA/QC conformance, and consistency prior to reporting.

7.0 METEOROLOGICAL DATA COLLECTION

Meteorological data will be obtained from a properly sited near-site meteorological station or the nearest representative National Weather Service station (USEPA station is present near airport). Wind data will be used to support interpretation of fence-line monitoring results and potential source attribution.

Hourly meteorological data must be collected for each sample period. Temperature and barometric pressure must be submitted to the laboratory to be used as part of the 325B analysis. Wind data, including wind speed and direction, is not required unless a facility uses a site-specific plan or an alternative test method, but it can provide useful information and is thus recommended. Meteorological data may be collected from a US Weather Service meteorological station within 25 miles of the facility or an onsite station. An onsite station must follow the siting requirements in Section 8.3 of Method 325A and the calibration and standardization procedures for meteorological measurements in EPA–454/B–08–002.

Figure 6-1. Tamper Seal

7.1 METEOROLOGICAL STATION LOCATION

The meteorological station shall be located at or near the MIPC Chelsea Facility and shall meet EPA sitting guidelines.

Section 8.1.4 of Method 325A states:
Identify the closest available meteorological station. Identify potential locations for one or more on-site or near-site meteorological station(s) following the guidance in EPA-454/B-08-002. The meteorological station sensors should satisfy EPA siting guidelines to the extent possible regarding distance away from structures or other potential interferences.

A brief summary of siting requirements is outlined in Section 8.3 of Method 325A.
A meteorological station is required at or near the facility you are monitoring. A number of commercially available meteorological stations can be used. Information on meteorological instruments can be found in EPA-454/R-99-005. Some important considerations for siting of meteorological stations are detailed below.

- Place meteorological stations in locations to represent conditions affecting the transport and dispersion of pollutants in the area of interest. Complex terrain may require the use of more than one meteorological station.

- Deploy wind instruments over level, open terrain at a height of 10 meters (33 feet). If possible, locate wind instruments at a distance away from nearby structures that is equal to at least 10 times the height of the structure.
- Protect meteorological instruments from thermal radiation and adequately ventilate them using aspirated shields. The temperature sensor must be located at a distance away from any nearby structures that is equal to at least four times the height of the structure. Temperature sensors must be located at least 30 meters (98 feet) from large paved areas.
- Collect and record meteorological data, including wind speed, wind direction, temperature and barometric pressure on an hourly basis. Calculate average unit vector wind direction, sigma theta, temperature and barometric pressure per sampling period to enable calculation of concentrations at standard conditions.
- Identify and record the location of the Meteorological Station by its GPS coordinate.

Wind instruments shall be installed at approximately 10 meters height where feasible and located away from obstructions. Temperature sensors must be shielded and adequately ventilated. The meteorological station location shall be recorded by GPS coordinates.

7.2 METEOROLOGICAL DATA SUBMITTAL AND ANALYSES

At the conclusion of each sampling period:

- Temperature and pressure data shall be provided to the laboratory for Method 325B analysis.
- Wind data shall be used to generate wind roses and support data interpretation.

8.0 RELEVANT PROCESS AND OFFSITE DATA COLLECTION

In order to estimate if elevated concentrations are due to operations on the facility or situations that occur offsite (see Section 12.3 of Method 325A), relevant process data and information related to offsite situations will be collected and analyzed for the study period. While a detailed site-by-site analysis of operating conditions and offsite situations relative to observed benzene concentrations will not be conducted, the collection of relevant data will support identification of any general correlation(s) between process conditions, operations, and event occurrences relevant to survey results. Supporting information may include daily field activity checklists, routine field screening data (e.g., PID and benzene meter readings), facility records, and other operational logs maintained during investigation and remediation activities.

8.1 PROCESS AND OFFSITE DATA COLLECTION

The facility shall provide:

- A general description of the facility process units present, along with a description of other processes at the site (especially if they may emit benzene).
- A list of the emission points along with location and estimated benzene emission levels (e.g. data from 2015 TRI).
- A list of periods of process downtime and duration of downtime during study period.
- Maintenance events
- Startup and shutdown records

Offsite sources of benzene shall also be documented where known.

Attachment A - EPA Method 325A

ATTACHMENT – A

EPA Method 325A

Method 325A—Volatile Organic Compounds from Fugitive and Area Sources:

Sampler Deployment and VOC Sample Collection

1.0 Scope and Application

1.1 This method describes collection of volatile organic compounds (VOCs) at or inside a facility property boundary or from fugitive and area emission sources using passive (diffusive) tube samplers (PS). The concentration of airborne VOCs at or near these potential fugitive- or area-emission sources may be determined using this method in combination with Method 325B. Companion Method 325B (Sampler Preparation and Analysis) describes preparation of sampling tubes, shipment and storage of exposed sampling tubes, and analysis of sampling tubes collected using either this passive sampling procedure or alternative active (pumped) sampling methods.

1.2 This method may be used to determine the average concentration of the select VOCs using the corresponding uptake rates listed in Method 325B, Table 12.1. Additional compounds or

alternative sorbents must be evaluated as described in Addendum A of Method 325B or by one of the following national/ international standard methods: ISO 16017-2:2003(E), ASTM D6196-03 (Reapproved 2009), or BS EN 14662-4:2005 (all incorporated by reference—see §63.14), or reported in the peer-reviewed open literature.

1.3 Methods 325A and 325B are valid for the measurement of benzene. Supporting literature (References 1-8) indicates that benzene can be measured by flame ionization detection or mass spectrometry over a concentration range of approximately 0.5 micrograms per cubic meter (µg/m^3) to at least 500 µg/m^3 when industry standard (3.5 inch long x 0.25 inch outside diameter (o.d.) x 5 mm inner diameter (i.d.)) inert-coated stainless steel sorbent tubes packed with Carbograph™ 1 TD, Carbopack™ B, or Carbopack™ X or equivalent are used and when samples are accumulated over a period of 14 days.

1.4 This method may be applied to screening average airborne VOC concentrations at facility property boundaries or monitoring perimeters over an extended period of time using multiple sampling periods (e.g., 26 x 14-day sampling periods). The duration of each sampling period is normally 14 days.

1.5 This method requires the collection of local meteorological data (wind speed and direction, temperature, and barometric pressure). Although local meteorology is a component

of this method, non-regulatory applications of this method may use regional meteorological data. Such applications risk that the results may not identify the precise source of the emissions.

2.0 Summary of the Method

2.1 Principle of the Method. The diffusive passive sampler collects VOC from air for a measured time period at a rate that is proportional to the concentration of vapor in the air at that location.

2.1.1 This method describes the deployment of prepared passive samplers, including determination of the number of passive samplers needed for each survey and placement of samplers along or inside the facility property boundary depending on the size and shape of the site or linear length of the boundary.

2.1.2 The rate of sampling is specific to each compound and depends on the diffusion constants of that VOC and the sampler dimensions/characteristics as determined by prior calibration in a standard atmosphere (Reference 1).

2.1.3 The gaseous VOC target compounds migrate through a constant diffusion barrier (e.g., an air gap of fixed dimensions) at the sampling end of the diffusion sampling tube and adsorb onto the sorbent.

2.1.4 Heat and a flow of inert carrier gas are then used

to extract (desorb) the retained VOCs back from the sampling end of the tube and transport/transfer them to a gas chromatograph (GC) equipped with a chromatographic column to separate the VOCs and a detector to determine the quantity of target VOCs.

2.1.5 Gaseous or liquid calibration standards loaded onto the sampling ends of clean sorbent tubes must be used to calibrate the analytical equipment.

2.1.6 This method requires the use of field blanks to ensure sample integrity associated with shipment, collection, and storage of the passive samples. It also requires the use of field duplicates to validate the sampling process.

2.1.7 At the end of each sampling period, the passive samples are collected, sealed, and shipped to a laboratory for analysis of target VOCs by thermal desorption gas chromatography, as described in Method 325B.

2.2 Application of Diffusive Sampling.

2.2.1 This method requires deployment of passive sampling tubes on a monitoring perimeter encompassing all known emission sources at a facility and collection of local meteorological data. It may be used to determine average concentration of VOC at a facility's "fenceline" using time integrated passive sampling (Reference 2).

2.2.2 Collecting samples and meteorological data at progressively higher frequencies may be employed to resolve

shorter term concentration fluctuations and wind conditions that could introduce interfering emissions from other sources.

2.2.3 This passive sampling method provides a low cost approach to screening of fugitive or area emissions compared to active sampling methods that are based on pumped sorbent tubes or time weighted average canister sampling.

2.2.3.1 Additional passive sampling tubes may be deployed at different distances from the facility property boundary or from the geometric center of the fugitive emission source.

2.2.3.2 Additional meteorological measurements may also be collected as needed to perform preliminary gradient-based assessment of the extent of the pollution plume at ground level and the effect of “background” sources contributing to airborne VOC concentrations at the location.

2.2.4 Time-resolved concentration measurements coupled with time-resolved meteorological monitoring may be used to generate data needed for source apportionment procedures and mass flux calculations.

3.0 Definitions

(See also Section 3.0 of Method 325B.)

3.1 Fenceline means the property boundary of a facility or internal monitoring perimeter established in accordance with the requirements in Section 8.2 of this method.

3.2 Passive sampler (PS) means a specific type of sorbent

tube (defined in this method) that has a fixed dimension air (diffusion) gap at the sampling end and is sealed at the other end.

3.3 Passive sampling refers to the activity of quantitatively collecting VOC on sorbent tubes using the process of diffusion.

3.4 PS_i is the annual average for all PS concentration results from location i.

3.5 PS_{i3} is the set of annual average concentration results for PS_i and two sorbent tubes nearest to the PS location i.

3.6 PS_{ip} is the concentration from the sorbent tube at location i for the test period or episode p.

3.7 Sampling period is the length of time each passive sampler is exposed during field monitoring. The sampling period for this method is 14 days.

3.8 Sorbent tube (Also referred to as tube, PS tube, adsorbent tube, and sampling tube) is an inert coated stainless steel tube. Standard PS tube dimensions for this method are 3.5-inch (89 mm) long x 0.25-inch (6.4 mm) o.d. with an i.d. of 5 mm, a cross-sectional area of 19.6 mm^2 and an air gap of 15 mm. The central portion of the tube is packed with solid adsorbent material contained between 2 x 100-mesh stainless steel gauzes and terminated with a diffusion cap at the sampling end of the tube. These axial passive samplers are installed under a

protective hood during field deployment.

Note: Glass and glass- (or fused silica-) lined stainless steel sorbent tubes (typically 4 mm i.d.) are also available in various lengths to suit different makes of thermal desorption equipment, but these are rarely used for passive sampling because it is more difficult to adequately define the diffusive air gap in glass or glass-line tubing. Such tubes are not recommended for this method.

4.0 Sampling Interferences

4.1 General Interferences. Passive tube samplers should be sited at a distance beyond the influence of possible obstructions such as trees, walls, or buildings at the monitoring site. Complex topography and physical site obstructions, such as bodies of water, hills, buildings, and other structures that may prevent access to a planned PS location must be taken into consideration. You must document and report siting interference with the results of this method.

4.2 Background Interference. Nearby or upwind sources of target emissions outside the facility being tested can contribute to background concentrations. Moreover, because passive samplers measure continuously, changes in wind direction can cause variation in the level of background concentrations from interfering sources during the monitoring period. This is why local meteorological information, particularly wind

direction and speed, is required to be collected throughout the monitoring period. Interfering sources can include neighboring industrial facilities, transportation facilities, fueling operations, combustion sources, short-term transient sources, residential sources, and nearby highways or roads. As PS data are evaluated, the location of potential interferences with respect to PS locations and local wind conditions should be considered, especially when high PS concentration values are observed.

4.3 Tube Handling. You must protect the PS tubes from gross external contamination during field sampling. Analytical thermal desorption equipment used to analyze PS tubes must desorb organic compounds from the interior of PS tubes and exclude contamination from external sampler surfaces in the analytical/sample flow path. If the analytical equipment does not comply with this requirement, you must wear clean, white, cotton or powder-free nitrile gloves to handle sampling tubes to prevent contamination of the external sampler surfaces. Sampling tubes must be capped with two-piece, brass, 0.25 inch, long-term storage caps fitted with combined polytetrafluoroethylene ferrules (see Section 6.1 and Method 325B) to prevent ingress of airborne contaminants outside the sampling period. When not being used for field monitoring, the capped tubes must be stored in a clean, air-tight, shipping container to prevent the

collection of VOCs (see Section 6.4.2 of Method 325B).

4.4 Local Weather Conditions and Airborne Particulates. Although air speeds are a constraint for many forms of passive samplers, axial tube PS devices have such a slow inherent uptake rate that they are largely immune to these effects (References 4,5). Passive samplers must nevertheless be deployed under non-emitting weatherproof hoods to moderate the effect of local weather conditions such as solar heating and rain. The cover must not impede the ingress of ambient air. Sampling tubes should also be orientated vertically and pointing downwards, to minimize accumulation of particulates.

4.5 Temperature. The normal working range for field sampling for sorbent packing is 0 – 40°C (References 6,7). Note that most published passive uptake rate data for sorbent tubes is quoted at 20 °C. Note also that, as a rough guide, an increase in temperature of 10 °C will reduce the collection capacity for a given analyte on a given sorbent packing by a factor of 2, but the uptake rate will not change significantly (Reference 4).

5.0 Safety

This method does not purport to include all safety issues or procedures needed when deploying or collecting passive sampling tubes. Precautions typical of field air sampling projects are required. Tripping, falling, electrical, and

weather safety considerations must all be included in plans to deploy and collect passive sampling tubes.

6.0 Sampling Equipment and Supplies, and Pre-Deployment Planning

This section describes the equipment and supplies needed to deploy passive sampling monitoring equipment at a facility property boundary. Details of the passive sampling tubes themselves and equipment required for subsequent analysis are described in Method 325B.

6.1 Passive Sampling Tubes. The industry standard PS tubes used in this method must meet the specific configuration and preparation requirements described in Section 3.0 of this method and Section 6.1 of Method 325B.

Note: The use of PS tubes packed with various sorbent materials for monitoring a wide variety of organic compounds in ambient air has been documented in the literature (References 4-10). Other sorbents may be used in standard passive sampling tubes for monitoring additional target compound(s) once their uptake rate and performance has been demonstrated following procedures in Addendum A to Method 325B. Guidance on sorbent selection can also be obtained from relevant national and international standard methods such as ASTM D6196-03 (Reapproved 2009) (Reference 14) and ISO 16017-2:2003(E) (Reference 13) (both incorporated by reference—see §63.14).

6.2 Passive or Diffusive Sampling Cap. One diffusive sampling cap is required per PS tube. The cap fits onto the sampling end of the tube during air monitoring. The other end of the tube remains sealed with the long-term storage cap. Each diffusive sampling cap is fitted with a stainless steel gauze, which defines the outer limit of the diffusion air gap.

6.3 Sorbent Tube Protection Cover. A simple weatherproof hood, suitable for protecting passive sampling tubes from the worst of the weather (see Section 4.4) consists of an inverted cone/funnel constructed of an inert, non-outgassing material that fits over the diffusive tube, with the open (sampling) end of the tube projecting just below the cone opening. An example is shown in Figure 6.1 (Adapted from Reference 13).

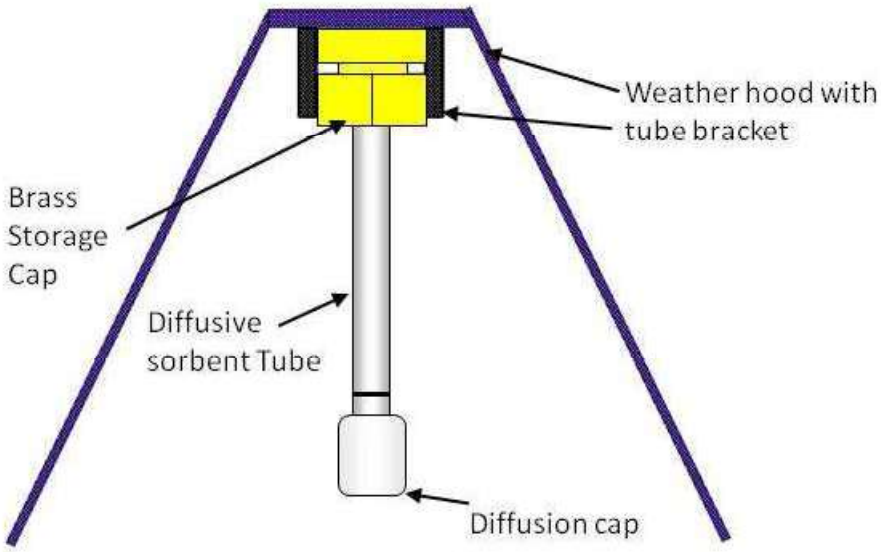


Figure 6.1. PS Tube with Weather Protector

6.4 Thermal Desorption Apparatus. If the analytical thermal desorber that will subsequently be used to analyze the passive sampling tubes does not meet the requirement to exclude outer surface contaminants from the sample flow path (see Section 6.6 of Method 325B), then clean, white, cotton or powder-free nitrile gloves must be used for handling the passive sampling tubes during field deployment.

6.5 Sorbent Selection. Sorbent tube configurations, sorbents or other VOC not listed in this method must be evaluated according to Method 325B, Addendum A or ISO 16017-2:2003(E) (Reference 13) (incorporated by reference—see §63.14). The supporting evaluation and verification data described in Method 325B, Addendum A for configurations or compounds different from the ones described in this method must meet the performance requirements of Method 325A/B and must be submitted with the test plan for your measurement program.

7.0 Reagents and Standards

No reagents or standards are needed for the field deployment and collection of passive sampling tubes. Specifications for sorbents, gas and liquid phase standards, preloaded standard tubes, and carrier gases are covered in Section 7 of Method 325B.

8.0 Sample Deployment, Recovery, and Storage

Pre-deployment and planning steps are required before field deployment of passive sampling tubes. These activities include but are not limited to conducting a site visit, determining suitable and required monitoring locations, and determining the monitoring frequency to be used.

8.1 Conducting the Site Visit.

8.1.1 Determine the size and shape of the facility footprint in order to determine the required number of monitoring locations.

8.1.2 Identify obstacles or obstructions (buildings, roads, fences), hills and other terrain issues (e.g., bodies of water or swamp land) that could interfere with air parcel flow to the sampler or that prevent reasonable access to the location. You may use the general guidance in Section 4.1 of this method during the site visit to identify sampling locations. You must evaluate the placement of each passive sampler to determine if the conditions in this section are met.

8.1.3 Identify to the extent possible and record potential off-site source interferences (e.g., neighboring industrial facilities, transportation facilities, fueling operations, combustion sources, short-term transient sources, residential sources, nearby highways).

8.1.4 Identify the closest available meteorological station. Identify potential locations for one or more on-site or

near-site meteorological station(s) following the guidance in EPA-454/B-08-002 (Reference 11) (incorporated by reference—see §63.14).

8.2 Determining Sampling Locations (References 2, 3).

8.2.1 The number and placement of the passive samplers depends on the size, the shape of the facility footprint or the linear distance around the facility, and the proximity of emission sources near the property boundaries. Aerial photographs or site maps may be used to determine the size (acreage) and shape of the facility or the length of the monitoring perimeter. Place passive samplers on an internal monitoring perimeter on or inside the facility boundary encompassing all emission sources at the facility at different angles circling the geometric center of the facility or at different distances based on the monitoring perimeter length of the facility.

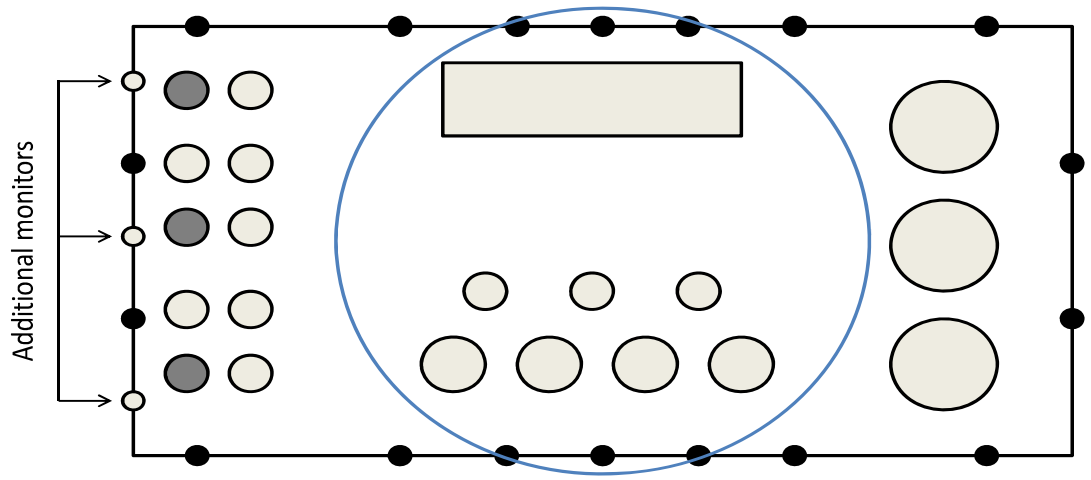
Note: In some instances, permanent air monitoring stations may already be located in close proximity to the facility. These stations may be operated and maintained by the site, or local or state regulatory agencies. If access to the station is possible, a PS may be deployed adjacent to other air monitoring instrumentation. A comparison of the pollutant concentrations measured with the PS to concentrations measured by site instrumentation may be used as an optional data quality

indicator to assess the accuracy of PS results.

8.2.1.1 The monitoring perimeter may be located between the property boundary and any potential emission source near the property boundary, as long as the distance from the source to the monitoring perimeter is at least 50 meters (162 feet). If a potential emissions source is within 50 meters (162 feet) of the property boundary, the property boundary shall be used as the monitoring perimeter near that source.

8.2.1.2 Samplers need only be placed around the monitoring perimeter and not along internal roads or other right of ways that may bisect the facility.

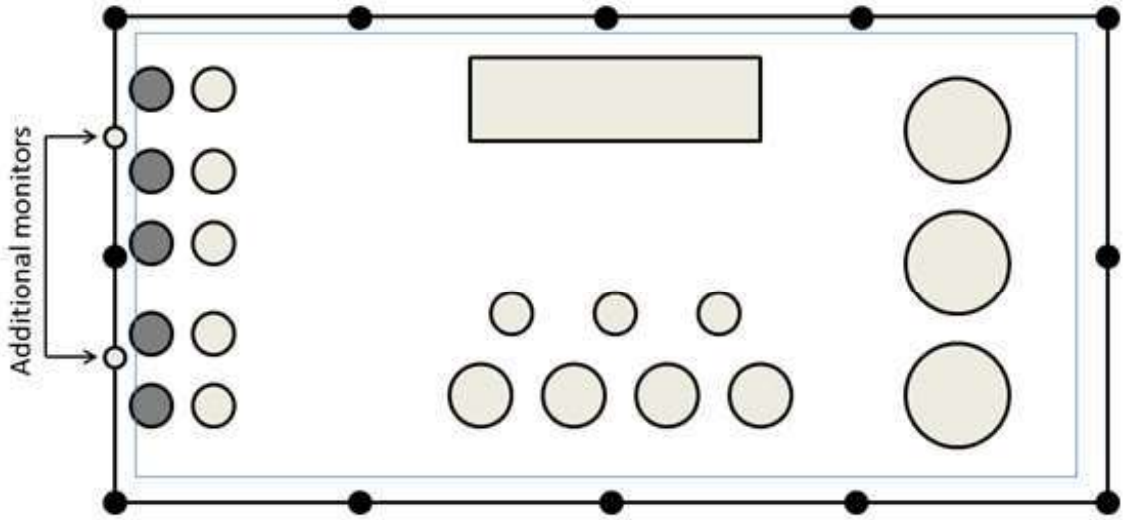
8.2.1.3 Extra samplers must be placed near known sources of VOCs if the potential emission source is within 50 meters (162 feet) of the boundary and the source location is between two monitors. Measure the distance (x) between the two monitors and place another monitor halfway between (x/2) the two monitors. For example, in Figure 8.1, the facility added three additional monitors (i.e., light shaded sampler locations) and in Figure 8.2, the facility added two additional monitors to provide sufficient coverage of all area sources.



Refinery (20% Angle)

Note: Shaded sources are within 50 meters of the property boundary and are located between two monitors. Additional coverage required by this method was accomplished by placing the monitors halfway between two existing monitors.

Figure 8.1. Facility with a Regular Shape Between 750 and 1,500 Acres in Area



Refinery (24,000 Feet Perimeter)

Note: Shaded sources are within 50 meters of the property boundary and are located between two monitors. Additional coverage required by this method was accomplished by placing the monitors halfway between two existing monitors.

Figure 8.2. Facility with a Boundary Length of 24,000 feet

8.2.2 Option 1 for Determining Sampling Locations.

8.2.2.1 For facilities with a regular (circular, triangular, rectangular, or square) shape, determine the geographic center of the facility.

8.2.2.1.1 For facilities with an area of less than or equal to 750 acres, measure angles of 30 degrees from the center point for a total of twelve 30 degree measurements evenly spaced (±1 degree).

8.2.2.1.2 For facilities covering an area greater than 750 acres but less than or equal to 1,500 acres, measure angles of 20 degrees from the center point for a total of eighteen 20 degree measurements evenly spaced (±1 degree). Figure 8.1 shows the monitor placement around the property boundary of a facility with an area between 750 and 1,500 acres. Monitor placements are represented with black dots along the property boundary.

8.2.2.1.3 For facilities covering an area greater than 1,500 acres, measure angles of 15 degrees from the center point for a total of twenty-four 15 degree measurements evenly spaced (±1 degree).

8.2.2.1.4 Locate each sampling point where the measured angle intersects the outer monitoring perimeter.

8.2.2.2 For irregularly shaped facilities, divide the area into a set of connecting subarea circles, triangles or rectangles to determine sampling locations. The subareas must be

defined such that a circle can reasonably encompass the subarea. Then determine the geometric center point of each of the subareas.

8.2.2.2.1 If a subarea is less than or equal to 750 acres (e.g., Figure 8.3), measure angles of 30 degrees from the center point for a total of twelve 30 degree measurements (±1 degree).

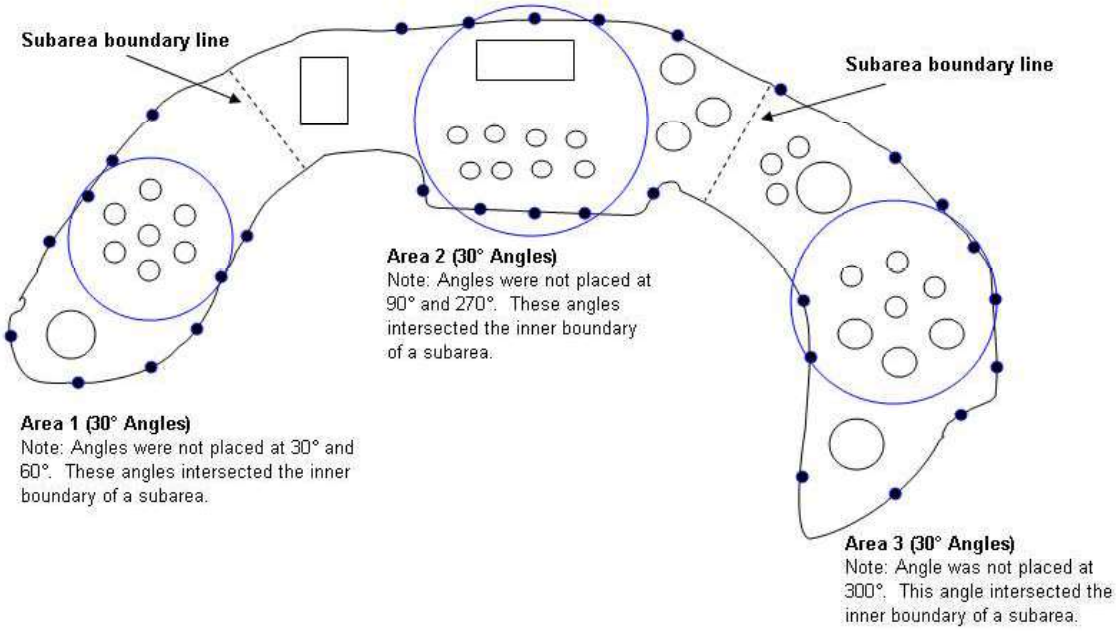


Figure 8.3. Facility Divided into Three Subareas

8.2.2.2.2 If a subarea is greater than 750 acres but less than or equal to 1,500 acres (e.g., Figure 8.4), measure angles of 20 degrees from the center point for a total of eighteen 20 degree measurements (±1 degree).

8.2.2.2.3 If a subarea is greater than 1,500 acres, measure angles of 15 degrees from the center for a total of twenty-four 15 degree measurements (±1 degree).

8.2.2.2.4 Locate each sampling point where the measured angle intersects the outer monitoring perimeter. Sampling points need not be placed closer than 152 meters (500 feet) apart (or 76 meters (250 feet) if known sources are within 50 meters (162 feet) of the monitoring perimeter), as long as a minimum of 3 monitoring locations are used for each subarea.

8.2.2.2.5 Sampling sites are not needed at the intersection of an inner boundary with an adjacent subarea. The sampling location must be sited where the measured angle intersects the subarea's outer monitoring perimeter.

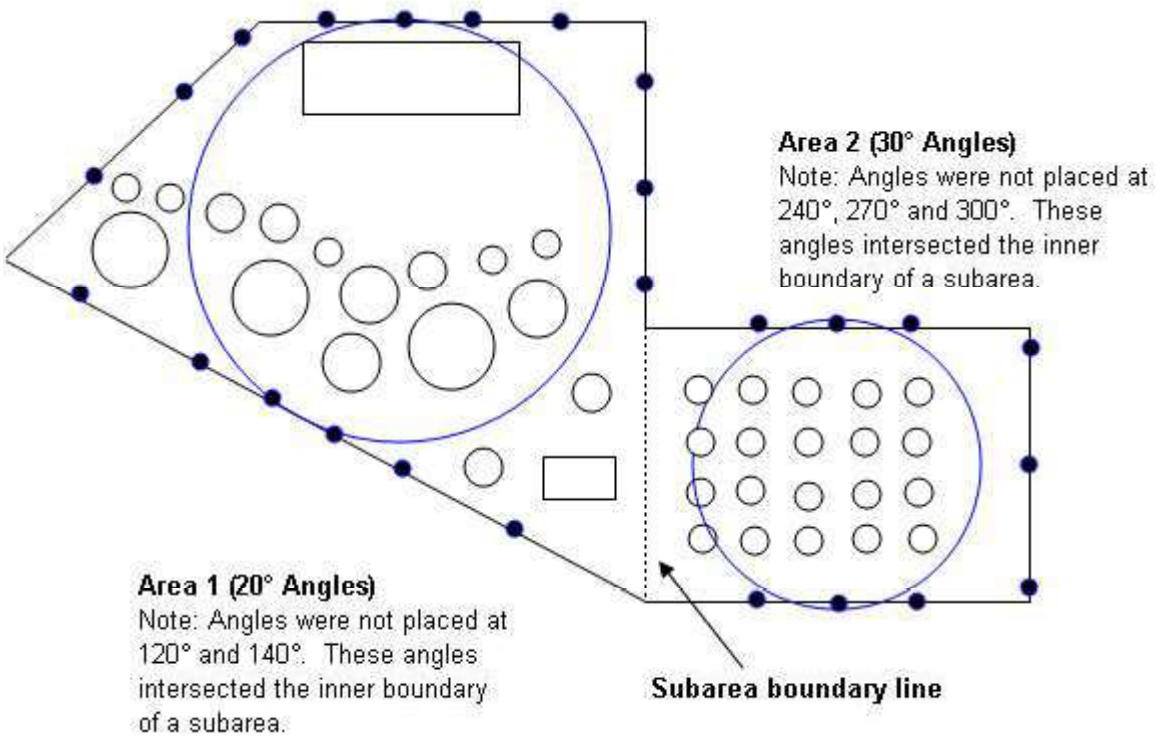


Figure 8.4. Facility Divided into Two Subareas

8.2.3 Option 2 for Determining Sampling Locations.

8.2.3.1 For facilities with a monitoring perimeter length

of less than 7,315 meters (24,000 feet), a minimum of twelve sampling locations evenly spaced ± 10 percent of the location interval is required.

8.2.3.2 For facilities with a monitoring perimeter length greater than 7,315 meters (24,000 feet), sampling locations are spaced 610 ± 76 meters (2,000 ± 250 feet) apart.

8.3 Siting a Meteorological Station. A meteorological station is required at or near the facility you are monitoring. A number of commercially available meteorological stations can be used. Information on meteorological instruments can be found in EPA-454/R-99-005 (Reference 11) (incorporated by reference—see §63.14). Some important considerations for siting of meteorological stations are detailed below.

8.3.1 Place meteorological stations in locations that represent conditions affecting the transport and dispersion of pollutants in the area of interest. Complex terrain may require the use of more than one meteorological station.

8.3.2 Deploy wind instruments over level, open terrain at a height of 10 meters (33 feet). If possible, locate wind instruments at a distance away from nearby structures that is equal to at least 10 times the height of the structure.

8.3.3 Protect meteorological instruments from thermal radiation and adequately ventilate them using aspirated shields. The temperature sensor must be located at a distance away from

any nearby structures that is equal to at least four times the height of the structure. Temperature sensors must be located at least 30 meters (98 feet) from large paved areas.

8.3.4 Collect and record meteorological data, including wind speed, wind direction, temperature and barometric pressure on an hourly basis. Calculate average unit vector wind direction, sigma theta, temperature and barometric pressure per sampling period to enable calculation of concentrations at standard conditions. Supply this information to the laboratory.

8.3.5 Identify and record the location of the meteorological station by its GPS coordinate.

8.4 Monitoring Frequency.

8.4.1 Sample collection may be performed for periods up to 14 days.

8.4.2 A site screening protocol that meets method requirements may be performed by collecting samples for a year where each PS accumulates VOC for a 14-day sampling period. Study results are accumulated for the sampling periods (typically 26) over the course of one calendar year. To the extent practical, sampling tubes should be changed at approximately the same time of day at each of the monitoring sites.

8.5 Passive Sampler Deployment.

8.5.1 Clean (conditioned) sorbent tubes must be prepared

and packaged by the laboratory as described in Method 325B and must be deployed for sampling within 30 days of conditioning.

8.5.2 Allow the tubes to equilibrate with ambient temperature (approximately 30 minutes to 1 hour) at the monitoring location before removing them from their storage/shipping container for sample collection.

8.5.3 If there is any risk that the analytical equipment will not meet the requirement to exclude contamination on outer tube surfaces from the sample flow path (see Section 6.6 of Method 325B), sample handlers must wear clean, white, cotton or powder-free nitrile gloves during PS deployment and collection and throughout any other tube handling operations.

8.5.4 Inspect the sampling tubes immediately prior to deployment. Ensure that they are intact, securely capped, and in good condition. Any suspect tubes (e.g., tubes that appear to have leaked sorbent) should be removed from the sampling set.

8.5.5 Secure passive samplers so the bottom of the diffusive sampling cap is 1.5 to 3 meters (4.9 to 9.8 feet) above ground using a pole or other secure structure at each sampling location. Orient the PS vertically and with the sampling end pointing downward to avoid ingress of particulates.

Note: Duplicate sampling assemblies must be deployed in at least one monitoring location for every 10 monitoring locations during each field monitoring period.

8.5.6 Protect the PS from rain and excessive wind velocity by placing them under the type of protective hood described in Section 6.1.3 or equivalent.

8.5.7 Remove the storage cap on the sampling end of the tube and replace it with a diffusive sampling cap at the start of the sampling period. Make sure the diffusion cap is properly seated and store the removed storage caps in the empty tube shipping container.

8.5.8 Record the start time and location details for each sampler on the field sample data sheet (see example in Section 17.0.).

8.5.9 Expose the sampling tubes for the required sampling period-normally 14-days.

8.5.10 Field blank tubes (see Section 9.3 of Method 325B) are stored outside the shipping container at representative sampling locations around the site, but with both long-term storage caps kept in place throughout the monitoring exercise. Collect at least two field blanks sorbent samples per sampling period to ensure sample integrity associated with shipment, collection, and storage.

8.6 Sorbent Tube Recovery and Meteorological Data Collection. Recover deployed sampling tubes and field blanks as follows:

8.6.1 After the sampling period is complete, immediately

replace the diffusion end cap on each sampled tube with a long-term storage end cap. Tighten the seal securely by hand and then tighten an additional quarter turn with an appropriate tool. Record the stop date and time and any additional relevant information on the sample data sheet.

8.6.2 Place the sampled tubes, together with the field blanks, in the storage/shipping container. Label the storage container, but do not use paints, markers, or adhesive labels to identify the tubes. TD-compatible electronic (radio frequency identification (RFID)) tube labels are available commercially and are compatible with some brands of thermal desorber. If used, these may be programmed with relevant tube and sample information, which can be read and automatically transcribed into the sequence report by the TD system.

Note: Sampled tubes must not be placed in the same shipping container as clean conditioned sampling tubes.

8.6.3 Sampled tubes may be shipped at ambient temperature to a laboratory for sample analysis.

8.6.4 Specify whether the tubes are field blanks or were used for sampling and document relevant information for each tube using a Chain of Custody form (see example in Section 17.0) that accompanies the samples from preparation of the tubes through receipt for analysis, including the following information: Unique tube identification numbers for each sampled

tube; the date, time, and location code for each PS placement; the date, time, and location code for each PS recovery; the GPS reference for each sampling location; the unique identification number of the duplicate sample (if applicable); and problems or anomalies encountered.

8.6.5 If the sorbent tubes are supplied with electronic (e.g., RFID) tags, it is also possible to allocate a sample identifier to each PS tube. In this case, the recommended format for the identification number of each sampled tube is AA-BB-CC-DD-VOC, where:

AA = Sequence number of placement on route (01, 02, 03. . .)

BB = Sampling location code (01, 02, 03 . . .)

CC = 14-day sample period number (01 to 26)

DD = Sample code (SA = sample, DU = duplicate, FB = field blank)

VOC = 3-letter code for target compound(s) (e.g., BNZ for benzene or BTX for benzene, toluene, and xylenes)

Note: Sampling start and end times/dates can also be logged using RFID tube tags.

9.0 Quality Control

9.1 Most quality control checks are carried out by the laboratory and associated requirements are in Section 9.0 of Method 325B, including requirements for laboratory blanks, field blanks, and duplicate samples.

9.2 Evaluate for potential outliers the laboratory results

for neighboring sampling tubes collected over the same time period. A potential outlier is a result for which one or more PS tube does not agree with the trend in results shown by neighboring PS tubes—particularly when data from those locations have been more consistent during previous sampling periods. Accidental contamination by the sample handler must be documented before any result can be eliminated as an outlier. Rare but possible examples of contamination include loose or missing storage caps or contaminated storage/shipping containers. Review data from the same and neighboring monitoring locations for the subsequent sampling periods. If the anomalous result is not repeated for that monitoring location, the episode can be ascribed to transient contamination and the data in question must be flagged for potential elimination from the dataset.

9.3 Duplicates and Field Blanks.

9.3.1 Collect at least one co-located/duplicate sample for every 10 field samples to determine precision of the measurements.

9.3.2 Collect at least two field blanks sorbent samples per sampling period to ensure sample integrity associated with shipment, collection, and storage. You must use the entire sampling apparatus for field blanks including unopened sorbent tubes mounted in protective sampling hoods. The tube closures

must not be removed. Field blanks must be placed in two different quadrants (e.g., 90° and 270°) and remain at the sampling location for the sampling period.

10.0 Calibration and Standardization

Follow the calibration and standardization procedures for meteorological measurements in EPA-454/B-08-002 March 2008 (Reference 11) (incorporated by reference—see §63.14). Refer to Method 325B for calibration and standardization procedures for analysis of the passive sampling tubes.

11.0 Analytical Procedures

Refer to Method 325B, which provides details for the preparation and analysis of sampled passive monitoring tubes (preparation of sampling tubes, shipment and storage of exposed sampling tubes, and analysis of sampling tubes).

12.0 Data Analysis, Calculations and Documentation

12.1 Calculate Annual Average Fenceline Concentration. After a year's worth of sampling at the facility fenceline (for example, 26 14-day samples), the average (PS_i) may be calculated for any specified period at each PS location using Equation 12.1.

$$PS_i = \frac{\sum PS_{ip}}{N} \qquad \text{Eq. 12.1}$$

Where:

PS_i = Annual average for location i.

PS_{ip} = Sampling period specific concentration from Method 325B.

i = Location of passive sampler (0 to 360°).

p = The sampling period.

N = The number of sampling periods in the year (e.g., for 14-day sampling periods, from 1 to 26).

Note: PS_{ip} is a function of sampling location-specific factors such as the contribution from facility sources, unusual localized meteorological conditions, contribution from nearby interfering sources, the background caused by integrated far-field sources and measurement error due to deployment, handling, siting, or analytical errors.

12.2 Identify Sampling Locations of Interest. If data from neighboring sampling locations are significantly different, then you may add extra sampling points to isolate background contributions or identify facility-specific "hot spots."

12.3 Evaluate Trends. You may evaluate trends and patterns in the PS data over multiple sampling periods to determine if elevated concentrations of target compounds are due to operations on the facility or if contributions from background sources are significant.

12.3.1 Obtain meteorological data including wind speed and wind direction or unit vector wind data from the on-site meteorological station. Use this meteorological data to determine the prevailing wind direction and speed during the periods of elevated concentrations.

12.3.2 As an option you may perform preliminary back trajectory calculations (http://ready.arl.noaa.gov/HYSPLIT.php) to aid in identifying the source of the background contribution to elevated target compound concentrations.

12.3.3 Information on published or documented events on- and off-site may also be included in the associated sampling period report to explain elevated concentrations if relevant. For example, you would describe if there was a chemical spill on site, or an accident on an adjacent road.

12.3.4 Additional monitoring for shorter periods (See section 8.4) may be necessary to allow better discrimination/resolution of contributing emission sources if the measured trends and associated meteorology do not provide a clear assessment of facility contribution to the measured fenceline concentration.

12.3.5 Additional records necessary to calculate sampling period average target compound concentration can be found in Section 12.1 of Method 325B.

13.0 Method Performance

Method performance requirements are described in Method 325B.

14.0 Pollution Prevention

[Reserved]

15.0 Waste Management

[Reserved]

16.0 References

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17.0 Tables, Diagrams, Flowcharts and Validation Data

Method 325 A/B

EXAMPLE FIELD TEST DATA SHEET (FTDS)
AND
CHAIN OF CUSTODY

I. GENERAL INFORMATION

SITE NAME:
_____
SITE LOCATION ADDRESS:
_____
CITY: _____STATE: _____ ZIP: _____

II. SAMPLING DATA

Sample ID (Tube) #	Sorbent	Sample or blank	Start Date	Start Time	Stop Date	Stop Time	Location (gps)	Ambient Temp. (°F)	Barometric Pressure (in. Hg)

III. CUSTODY INFORMATION

COLLECTED BY: _____
Relinquished to Shipper -
Name: _____ Date: _____ Time _____
Received by Laboratory -
Name _____ Date: _____ Time _____
Sample condition upon receipt:
_____
Analysis Required:
_____
_____
Comments:
_____
_____
_____

Figure 17.1. Example Field Data Form and Chain of Custody