

SECTION 4 MEASUREMENT METHODS FOR THE NATTS PROGRAM

4.0 INTRODUCTION

Section 4 presents information, guidelines, and specifications pertaining to 5 sample collection and analysis methods that will be applied to determination of the compounds of interest and meteorological parameters specifically for the NATTS Program. Also presented are other air toxics methods that are not specifically applicable to the NATTS program at present, but have the potential for future or complementary applications. To accomplish consistency in the data generated across the entire nation, adherence to the MQOs presented in Section 3 of this document is mandatory. The information below presents specific configurations and approaches to accepted and emerging methods with the intent of standardizing sampling and analysis across the NATTS Program. This level of specification could limit flexibility of approach but is expected to elevate data consistency, a primary goal of the NATTS Program. NATTS participants wishing to use alternate configurations and/or approaches other than those specified in this TAD may do so only with Regional EPA approval, provided that the alternate configurations and/or approaches meet the program MQOs. It is the responsibility of the NATTS participant to demonstrate equivalent performance to the corresponding methodology presented in this TAD prior to the initiation of monitoring. The approval process is performance based, with the onus of proof of data consistency the responsibility of the applying agency.

The following methods are discussed in this section:

- 4.1 Method TO-15 (NATTS Specific)
- 4.2 Method TO-11A (NATTS Specific)
- 4.3 Method IO-3.5 (NATTS Specific)
- 4.4 Hexavalent Chromium Method (NATTS Specific)
- 4.5 Method TO-13A

- 4.6 Method TO-9A
- 4.7 Aethalometer Method
- 4.8 Methods for Meteorological Monitoring (NATTS Specific)
- 4.9 Innovative Methods for Ambient Air Monitoring

4.1 OVERVIEW OF EPA COMPENDIUM METHOD TO-15

EPA Compendium Method TO-15¹ is the method used for sampling and analytical procedures for the measurement of subsets of the 97 VOCs that are included in the 188 HAPs listed in Title III of the Clean Air Act Amendments of 1990. The approach presented here includes Acrolein as one of the target compounds. These VOCs are defined as organic compounds having a vapor pressure greater than 10^{-1} Torr at 25 °C and 760 millimeters (mm) of mercury (Hg). This method addresses most conditions encountered in the sampling of ambient air into passivated canisters.

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4.1.1 General Description of Sampling Method and Analytical Method Requirements/Capabilities

The atmosphere is sampled by introduction of air into a specially prepared stainless steel canister. A sample of air is drawn through a sampling train comprising components that regulate the rate and duration of sampling into the preevacuated and passivated canister. After the air sample is collected, the canister valve is closed, the chain of custody (COC) sheet is filled out, and both are transported to the laboratory. Upon receipt, the canister arrival is recorded and the

canister is stored until it is analyzed. Storage times of up to 30 days without significant compound concentration losses have been demonstrated for many of the VOCs.

To analyze the sample, a known volume is directed from the canister through a mass flow controller to a solid multisorbent concentrator. As a whole air sample, ambient humidity (i.e., water vapor) levels will be present. This water vapor can complicate the analysis processes. A portion of the water vapor will pass through the concentrator during sample concentration. The water vapor content of the concentrated sample can be reduced by dry purging the concentrator with dry helium. After the concentration and drying steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, and then focused in a small volume by trapping on a reduced temperature trap or small volume multisorbent trap. The VOCs are then released from the trap by thermal desorption and swept by the carrier gas onto a gas chromatographic column for separation.

The analytical strategy for using Compendium TO-15 for NATTS Program analysis involves using a high resolution gas chromatograph (HRGC) coupled to a mass spectrometer (MS) operated by selective ion monitoring (SIM) mode. The fragmentation pattern from interaction of individual molecules with the MS ionization source (electron beam) is compared with stored spectra taken under similar conditions in order to calibrate for and identify the compounds. For any given compound, the intensity of the given fragment is compared with the system response to the given fragment for known amounts of the compound to establish the compound concentration that exists in the sample.

4.1.2 Contamination

Canisters should be manufactured using high quality welding and cleaning techniques, and new or reconditioned canisters should be filled with humidified zero air and then analyzed after 24 hours to evaluate cleanliness. Although the 24-hour period is not a method requirement, new and reconditioned canisters have a higher potential for contamination due to the manufacturing processes, and it is therefore prudent to allow the humidified zero air to remain in the canister for a longer period to ensure that contaminants are desorbed from active sites. The

cleaning apparatus, sampling system and analytical system should be assembled from clean, high quality components, and each system should be demonstrated to be free of contamination.

Impurities in the calibration, internal/tuning standard dilution and carrier gases, organic compounds outgassing from the system components ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by analyzing humidified zero air blanks. Nonchromatographic-grade stainless steel tubing, non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with Buna-N[®] rubber components are potential contamination sources and must be avoided.

Significant contamination of the analytical equipment can occur whenever samples containing high levels of VOCs are analyzed, resulting in carryover contamination in subsequent analyses. Whenever a sample with high concentrations of VOCs is encountered, this sample should be followed by an analysis of humid zero air to check for carryover contamination.

4.1.3 Precision

Precision refers to the agreement between independent measurements performed according to identical protocols and procedures. Replicate analysis of duplicate samples is used to quantify “sampling and analytical precision specific to a single sampling system” (i.e., how precisely the sampling and analytical methods measure ambient air concentrations). A duplicate sample is a sample collected simultaneously with a primary sample (i.e., in two separate canisters through the same sampling system at the same time). This simultaneous collection is typically achieved by teeing the line from the sampler to each of the two canisters and doubling the flow rate applied to achieve integration over the 24-hour collection period. Duplicate samples allow intrasystem precision to be evaluated. The difference between duplicate samples and collocated samples is that the duplicate samples are collected in two canisters using one collection system, whereas collocated samples are collected at the same time but using two completely separate collection systems, each with a separate canister. Replicate analysis of collocated samples is used to quantify precision between different sampling systems or

intersystem precision. Although collocated samples are highly desirable, the cost of an additional sampling system is usually prohibitive because collocated data would have to be acquired at every site. However, any NATTS site that is able should conduct both duplicate and collocated sampling.

Precision is a measurement of random errors associated with sampling and analysis of environmental samples. These errors may result from various factors but typically originate from random “noise” inherent to analytical instruments. Laboratories can easily evaluate analytical precision by comparing concentrations measured during replicate analysis of the same ambient air samples.

- Average concentration difference quantifies the difference between replicate analytical results for each compound. When interpreting central tendency estimates for the specific compounds sampled, central tendencies should be compared to the average concentration differences. If the average concentration difference of a compound exceeds or nearly equals its central tendency, the analytical method may not be capable of precisely characterizing annual concentrations. Therefore, data interpretations for these compounds should be made with caution.
- RPD expresses average concentration differences relative to the average concentrations detected during replicate analyses. The RPD is calculated as follows:

$$RPD = \frac{|X_1 - X_2|}{\bar{X}} \times 100 \quad (4.1-1)$$

where:

X_1 = Ambient air concentration of a given compound measured in one sample;

X_2 = Concentration of the same compound measured during replicate analysis;

\bar{X} = Arithmetic mean of X_1 and X_2 .

Replicate analyses with low variability have lower RPDs (and better precision), whereas replicate analyses with high variability have higher RPDs (and poorer precision).

4.1.4 Sampling Procedure and Issues Associated with EPA Compendium Method TO-15

EPA Compendium Method TO-15¹ deals with sampling and analysis of VOCs—defined as organic compounds having a vapor pressure greater than 10^{-1} Torr at 25 °C and 760 mm Hg (standard conditions). Sampling using the EPA Compendium Method TO-15 configuration and approach for NATTS entails integrated subambient pressure collection of these VOCs in precleaned, evacuated passivated stainless steel canisters (i.e., a whole air sample)².

4.1.4.1 Sample Inlet and Manifold

A sample inlet and manifold assembly should be used to provide a representative air sample for collection and subsequent analysis. Glass sample inlet and manifold assemblies are commercially available. Alternatively, custom-made inlets and manifolds constructed of chromatographic-grade stainless steel may be designed and fabricated. Examples of a typical glass sample probe and manifold assembly are presented below. If automated calibration techniques that periodically flood the manifold with calibration standards are to be applied for the criteria pollutants, a separate manifold would be required to support the VOC and carbonyl components of the NATTS Program network.

The sample inlet is constructed of glass that is approximately 1 in. o.d. The entrance of the sample inlet is configured with an inverted funnel approximately 4 in. o.d. The sample manifold is constructed of glass approximately 1.5 in. o.d. The manifold has ports for sample distribution; the number of ports must be equal to or greater than the total number of sampling systems to which sample will be delivered. To reduce the potential for bias, the port nearest to the entrance of the manifold should be reserved for VOC sampling.

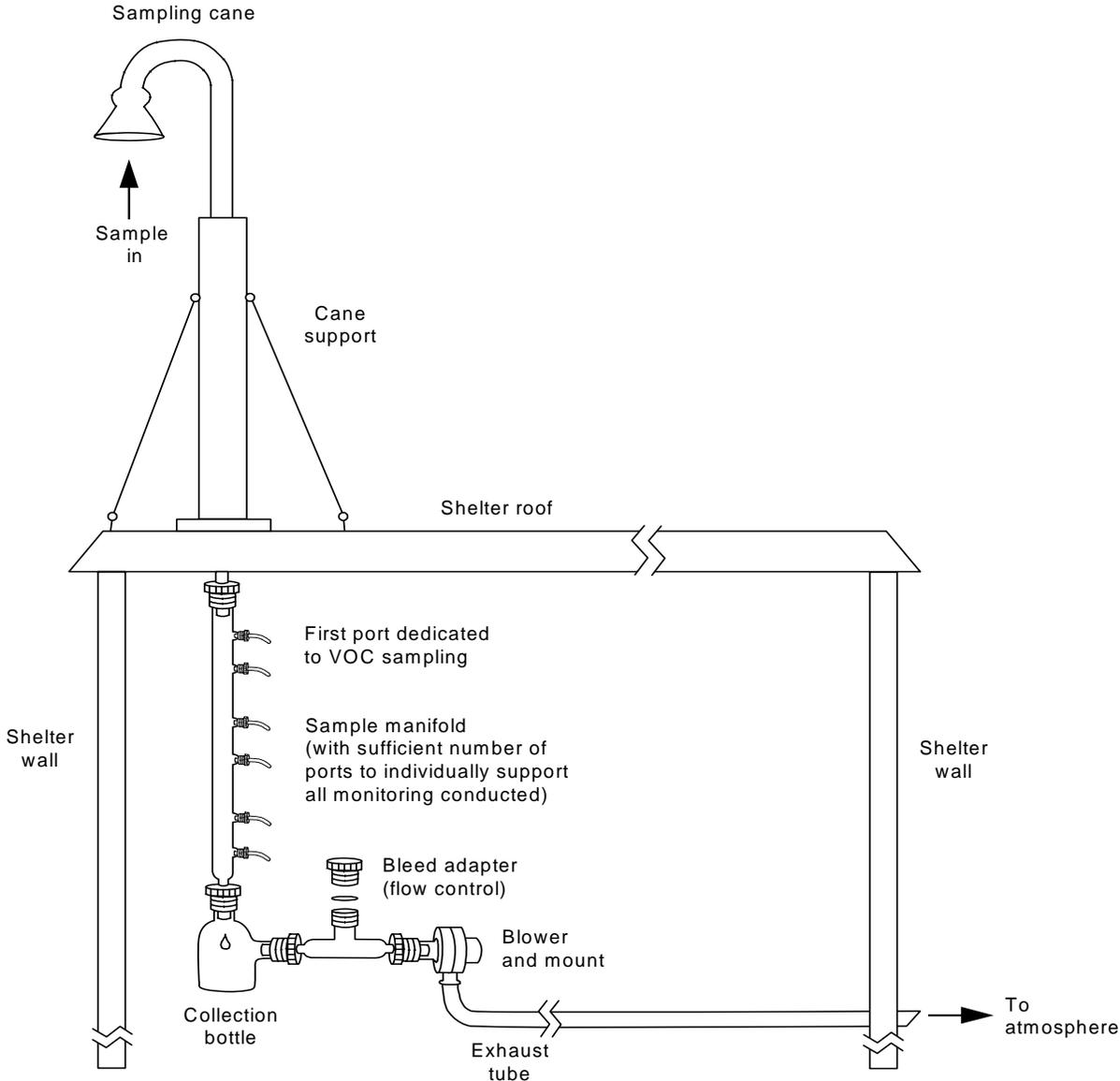
Teflon bushings are used to connect sample lines to the manifold. Because the manifold and ports are constructed of glass, care must be taken not to place excessive stress on the assembly to avoid breakage. For VOC sampling, the sample lines should be constructed of 1/8-in. o.d. stainless steel tubing—tubing that is flexible and will accommodate the flow rates

typically associated with VOC sample collection. The sample lines should be kept as short as possible to reduce sample transfer time.

A blower and bleed adapter are located at the exit end of the sample manifold. The blower is used to pull sample air through the inlet and manifold, and the bleed adapter is used to control the rate at which the sample air is pulled through the manifold. An excess of sample air is pulled through the sample inlet and manifold to reduce residence time and prevent back diffusion of room air into the manifold and to ensure that the sample air is representative of outside ambient air. Sample airflow through the sample inlet and manifold should be at least two times greater than the total airflow being removed for collection and analysis by all systems on the manifold.

The vertical placement of the sample inlet and inlet funnel should be in the breathing zone at a height of approximately 2 to 4 m above ground level. In addition, the inlet funnel should be positioned more than 1 m, both vertically and horizontally, away from the housing structure. The inlet funnel should be positioned away from nearby obstructions such as a forest canopy or building. The vertical distance between the inlet funnel and any obstacle should be at least two times the height difference between the obstacle and the inlet funnel. Unrestricted airflow across the inlet funnel should occur within an arc of at least 270 degrees. The predominant and second most predominant wind directions must be included in this arc. If the inlet funnel is positioned on the side of a building, a 180-degree clearance is required. The glass inlet should be reinforced or supported along the straight vertical axis of the assembly. Typically, this support is provided by routing the inlet shaft through a rigid section of metal or plastic tubing secured to the housing structure.

The manifold can be positioned in either a horizontal or vertical configuration. Figure 4.1-1 presents the manifold assembly in the vertical configuration. Figure 4.1-2 presents the manifold assembly in the horizontal configuration. If the horizontal configuration is used, the sample ports must point upward so material that may be present in the manifold will not be transferred into the sample lines.



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Figure 4.1-1. Vertical Configuration

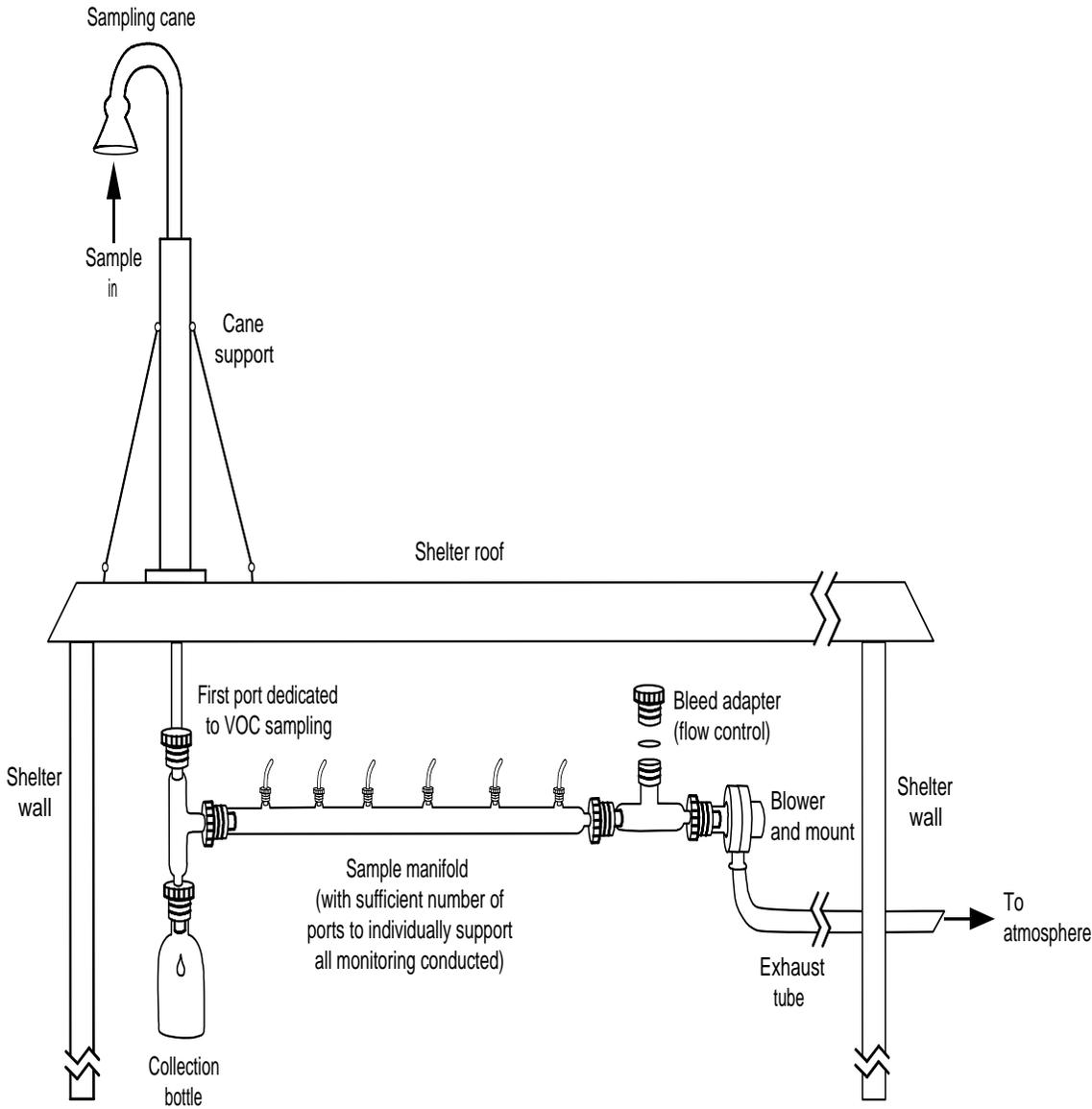


Figure 4.1-2. Horizontal Configuration

With continuous use, the sample inlet and manifold can accumulate deposits of particulate material and other potential contaminants. The sample inlet and manifold should be cleaned to remove these materials at a recommended quarterly frequency. To clean the assembly, the sample lines and blower should be disconnected from the manifold. For safety, electric power to the blower should be terminated until the cleaning process is completed. The individual components are disassembled by disconnecting the inlet, manifold, collection bottle, and coupling devices from each other. The individual components should then be cleaned using heated, high purity distilled water (i.e., only high purity distilled water, no organic solvents or soaps) and a long-handled bottle brush. The components should then be rinsed with the distilled water and allowed to dry completely before reassembling.

4.1.4.2 Sampling Equipment

Canister samples are collected using a specific configuration of an automated sample collection system as presented in Section 4.1.5.3. Water vapor in the sample can condense on the canister surface under certain conditions and provide a sink for water-soluble compounds. One circumstance where this condensation can occur is when the canister is pressurized with sample air to levels above atmospheric pressure. In this case, water vapor accumulates in the canister until the partial pressure of the water exceeds the equilibrium vapor pressure at the canister temperature. To avoid losses of VOCs to condensed water in the canisters, the pressure of the air sample in the canister must not exceed atmospheric pressure. Under conditions of normal usage for sampling of ambient air to a subambient final pressure in canisters, most VOCs can be recovered from canisters near their original concentrations after storage times of at least 30 days.

EPA Compendium Method TO-15 makes provision for the collection of either negative or positive final pressure samples. However, because consistency of data is a paramount consideration for the NATTS Program, standardization on one approach is strongly recommended. Based on inhouse research preformed by EPA/OAQPS (McClenny, et. al.) canister sampling systems used to collect samples for the NATTS Program should meet the following specifications:

- The sampling system will yield a **subambient final sample pressure** (i.e., approximately 2 to 10 in. Hg). **Note:** if positive pressure sample collection is advocated by a specific agency, approval of this approach must be obtained from the associated EPA Region.
- Integration of the sample collection will ideally be achieved using **electronic mass flow control**. Use of a critical orifice or vacuum regulator will be acceptable but considered a second choice. Sample sequencing, or collecting sample for only a portion of each hour, is not acceptable.
- The sample collection system will perform a **24-hour purge** with local ambient air before each sampling episode.
- The sampling system must incorporate either a latching solenoid valve or a solenoid valve with a **low temperature rise coil** (i.e., temperature rise of no more than 10 °F when activated) to prevent excessive elevation of the sample gas temperature prior to collection.
- The sampling system will be configured so that the sample gas **does not pass through a pump** prior to collection in the canister.

Note that canister sampling systems can be made to be very complex. However, these complexities very frequently fail when the sampling system is required to operate for extended periods in the field without attendance. Consequently, sampling systems should remain as simple as possible and still accomplish representative integrated sample collection during the specified time period. A sampling system that will be used in the NATTS network is shown in Figure 4.1-3.

Canister sampling requires the collection and analysis of a large number of canister samples to achieve a completion rate of 85% for 1-in-6 day sampling. The magnitude and success of the monitoring program depends on the quantity of canisters available, the capabilities and reliability of the sample collection system used and the availability and skill of field staff to address the sampling needs of the NATTS Program. Users of the canister sample collection methodology are responsible for the selection, setup and optimization of their systems and for the preparation of SOPs that delineate the details of all operations.

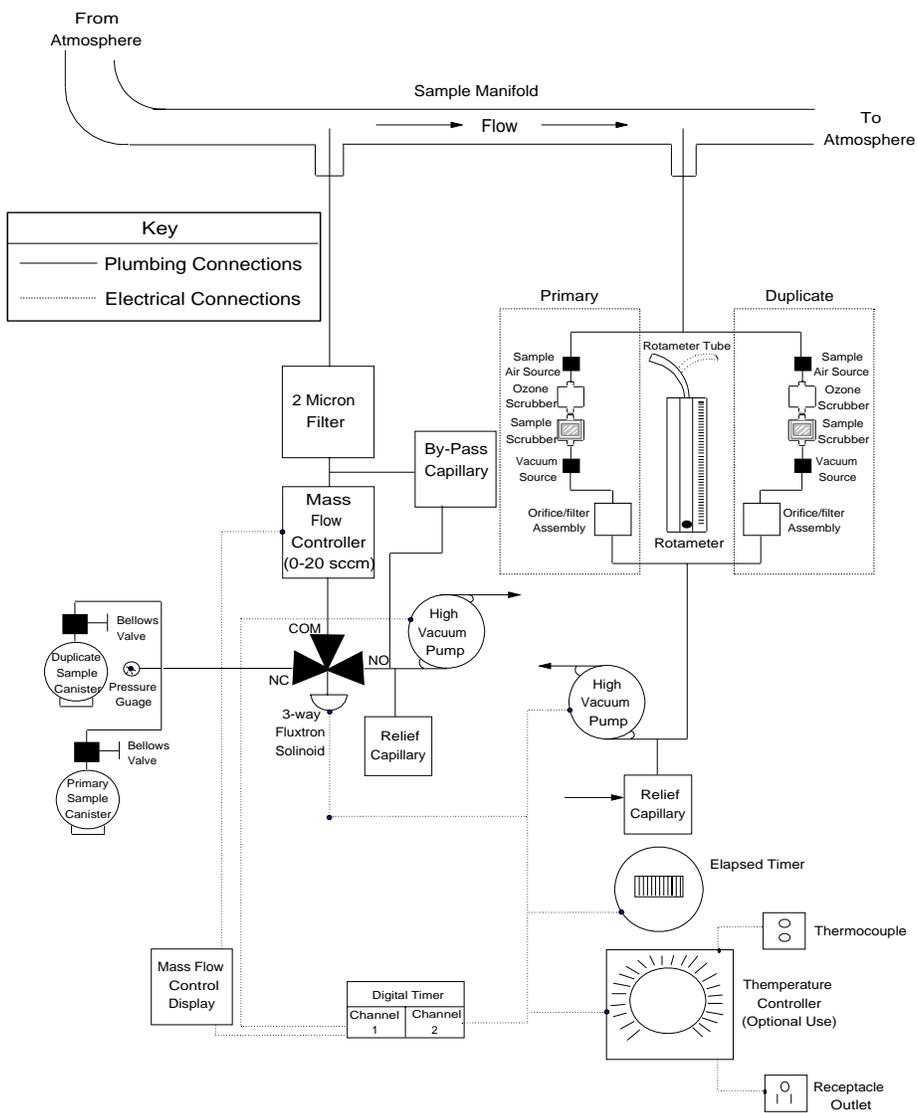


Figure. 4.1-3. A Typical NATTS Sample Collection System

The specified canister sample collection system consists of the following primary components:

- Inlet probe and manifold assembly. Constructed of glass or stainless steel. Used as a conduit to transport sample air from the atmosphere at the required sampling height and distribute sample air for collection by a variety of collection media.
- Bypass pump. A single- or double-headed diaphragm pump or a caged rotary blower. Used to continuously draw sample air through the inlet probe and manifold assembly at a rate in excess of the sampling system total uptake. All excess sample air is exhausted back to the atmosphere.
- Sample inlet line. Chromatographic-grade stainless steel tubing. Used to connect the sampler to the manifold assembly.
- Sample canisters. Passivated stainless steel sample vessels of desired internal volume with a bellows valve attached at the inlet of each unit. Used to contain the collected sample air for transportation and analysis.
- Stainless steel vacuum gauge (or optional electronic pressure sensor). A pressure measurement device capable of measuring vacuum (0 to 30 in. Hg). Used to measure initial and final sample canister pressures.
- Adjustable electronic mass flow controller. An indicating mass flow control device (or devices). Used to maintain a constant flow rate ($\pm 10\%$) over a specific sampling period under conditions of changing temperature (20 to 40 °C) and humidity (0 to 100% relative).
- Particulate filter. Two-micron, sintered stainless steel in-line filter. Used to remove particulate material larger than 2 microns from the sample air being collected.
- Electronic timer (or optional microprocessor). An event control device. Used to allow unattended operation (activation and deactivation) of the collection system.
- Solenoid valve. An electric-pulse-operated or low temperature rise coil, stainless steel body, solenoid valve, with Viton[®] plunger seat and O-ring. Used to provide access to or isolation of the sample canister(s).
- Elapsed time indicator. A time measurement device used to measure the duration of the sampling episode.

- Stainless steel tubing and fittings. Isolation and interconnection hardware. Used to complete system interconnections. All tubing in contact with the sample prior to analysis should be chromatographic-grade stainless steel, and all fittings should be 316-grade stainless steel.

4.1.5 Canister Sampling System Certification

Canister sampling systems must exhibit nonbiasing characteristics before being used to collect samples. These sampling systems must be subjected to laboratory certification to quantify any additive or subtractive biases that may be attributed directly to the sampling system. The following procedure is required to certify canister sampling systems.

A challenge sample, consisting of a certified standard blend of organic compounds that span the analytical chromatographic range at a known concentration in clean, humidified zero air, is collected through the sampling system into a canister (over a 24-hour period). Typical challenge gas concentrations are approximately 10 ppbv per compound. A reference sample is concurrently collected using a dedicated electronic mass flow controller that has been characterized prior to each use. The samples are then analyzed using a gas chromatograph (GC)/MS system that is the primary analytical system used to analyze field samples or an alternate system that is equivalent to the primary system. The percent recoveries for target challenge compounds are calculated based on the concentrations determined for the reference sample. Recoveries of each of the challenge compounds should be in the range of 85 to 115% of the concentrations determined for the reference sample. A system-specific overall recovery should also be calculated. The overall recovery is the average of the individual compound recoveries. Each sampling system should have an overall recovery of 85 to 115%. The challenge sample percent recoveries are used to gauge potential additive and/or subtractive bias characteristics for each specific sampling system.

In addition to characterizing the sampling system with a blend of VOCs, the system should also be characterized using humidified zero air. A humidified zero air blank sample is collected through the sampling system to further gauge the potential for additive bias. The blank samples are analyzed for the specific NATTS Program VOC target analytes. The criterion

applied to the blank portion of the certification process requires that the determined concentration for each target analyte species be 0.2 ppbv or less.

Sampling is accomplished using dedicated manifolds for both the zero and challenge phases of the certification procedure (Figures 4.1-4 and 4.1-5). Zero air supplied to the zero manifold should be hydrocarbon-free and humidified to approximately 70% RH. The zero air should be supplied from a canister cleaning system similar to the one described below or an alternate system that is equivalent.

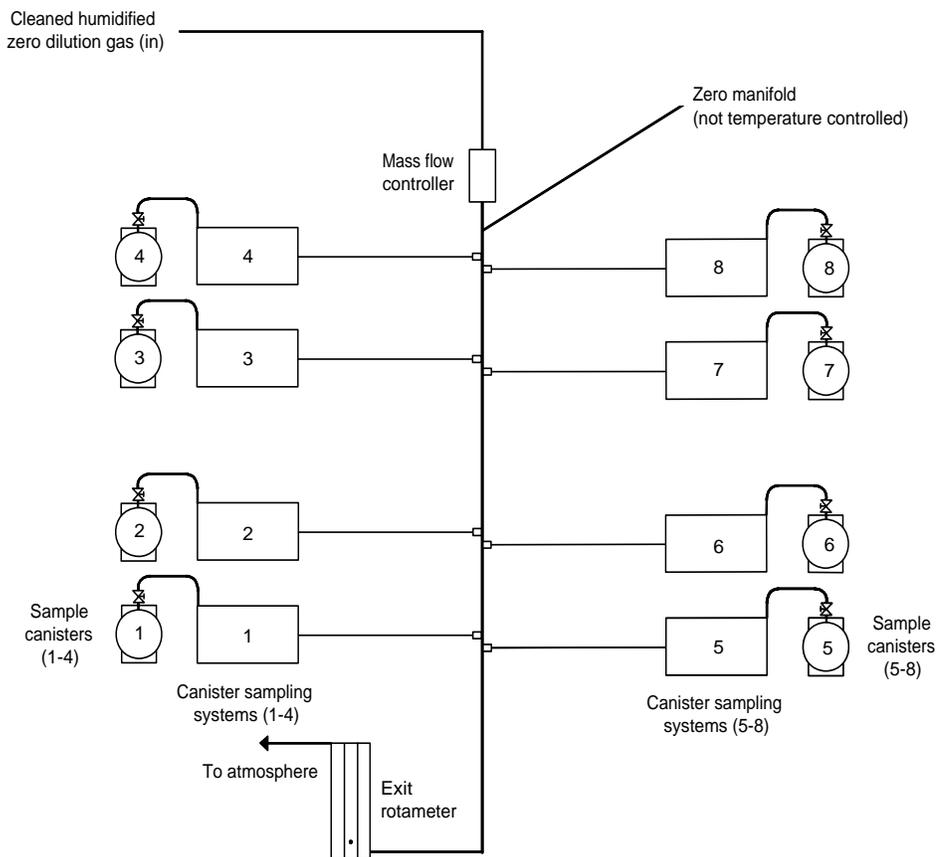


Figure 4.1-4. Dedicated Manifold for Zero Gas Certification

4.1.5.1 Certification Equipment

The equipment required to perform canister sampling system certification is described below. The equipment listed is consistent with the systems presented in Figures 4.1-4 and 4.1-5.

- Mass flow controllers. Mass flow controllers located at the inlets to the manifolds. Mass flow controllers are used to regulate the certification pollutant, diluent, and zero airflow rates.
- Zero air manifold. A zero air manifold (Figure 4.1-4) constructed of 1/4-in. o.d. chromatographic-grade stainless steel tubing and 1/4-in. fittings. The zero manifold is used to distribute zero air to the individual sampling systems being certified. The number of sample ports provided on the zero air manifold is determined by the number of sampling systems to be certified simultaneously.
- Exit rotameter. An exit rotameter located at the outlet of both the challenge gas and zero air manifolds. The exit rotameter is used to visually indicate that an excess of challenge gas or zero air is present in the respective manifolds during certification sample collection.
- Cord heater. A cord heater rated at 80 watts spiraled around the outside of the challenge manifold. The cord heater is used to heat the challenge manifold to 80 °C. Heating the challenge manifold helps to reduce the potential for loss of challenge gas compounds to the walls of the challenge manifold. The zero manifold is not heated.
- Temperature controller. A temperature controller used in conjunction with the cord heater to actively regulate the challenge manifold temperature at 80 °C.

4.1.5.2 Certification Procedure

The procedure used to perform canister sampling system certification is presented below.

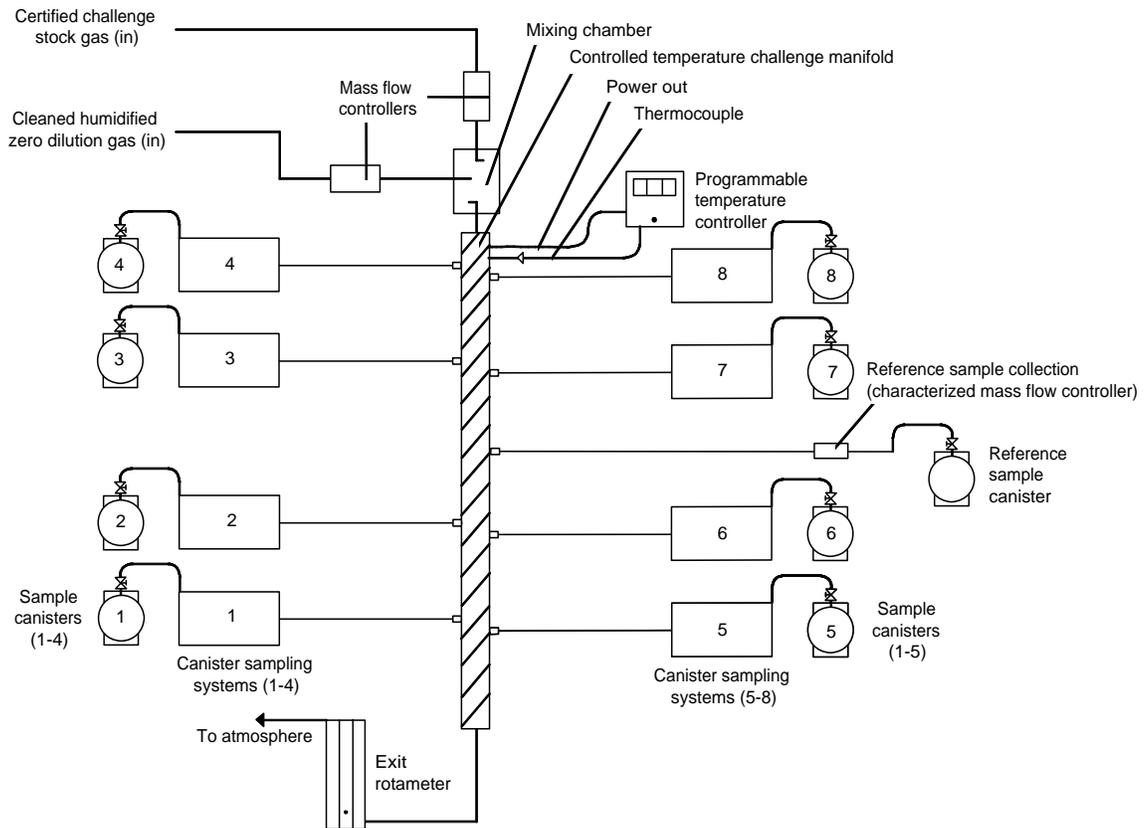


Figure 4.1-5. Dedicated Manifold for Challenge Gas Certification

1. Perform a negative pressure leak check. Attach an evacuated canister to the exit of the sampling system. Open the canister bellows valve and record the initial vacuum indicated by the sample pressure gauge. Close the canister bellows valve, view the sample pressure gauge and determine whether the vacuum is maintained (i.e., no change over a 10-minute (min) period). The system is leak free if the vacuum is maintained. If the vacuum is not maintained, the system is not leak free. Repair leaks and retest the system.
2. Connect the sampling systems and the reference sample flow controller to the zero manifold and purge them with humidified zero air for 48 hours. The purge air should simultaneously be routed to the challenge manifold to clean and prepare the challenge manifold for challenge sample collection. Terminate the humidified zero airflow at the end of the 48-hour period.
3. Purge the sampling systems, reference system, and manifold with dry zero air for 1 hour to remove accumulated moisture. During the dry purge, determine the certification flow requirements using the following equation:

$$Q_t = [(Q_s \times N_1) + (Q_R \times N_2)] \times F_1 \quad (4.1-2)$$

where:

Q_t = Total required flow rate (mL/min)

Q_s = Individual sampling system collection flow rate (mL/min)

N_1 = Number of sampling systems

Q_R = Reference system collection flow rate (mL/min)

N_2 = Number of reference systems

F_1 = Excess flow factor = 2.0.

4. Determine the pollutant and diluent flows required to generate the desired concentration of challenge gas using the following equations:

$$F_2 = \frac{C_1}{C_2} \quad (4.1.3)$$

where:

F_2 = Dilution factor (for use in next equation)

C_1 = Desired challenge gas concentration (ppbv)

C_2 = Concentration of the stock cylinder (ppbv)

$$Q_P = F_2 \times Q_T \quad (4.1-4)$$

where:

Q_P = Pollutant flow rate (mL/min)

Q_T = Total required flow rate

$$Q_D = Q_T - Q_P \quad (4.1-5)$$

where:

Q_D = Diluent flow rate (mL/min)

1. Generate and deliver the challenge gas to the challenge manifold and sampling systems. Condition the challenge manifold with the challenge gas for 10 min with the sampling systems off. Condition the challenge manifold an additional 90 min with the sampling systems on and in the bypass mode. Connect a clean, evacuated canister to each sampling system.
2. Collect the challenge and reference samples. Conduct challenge sample collection according to the normal specified operation of the sampling system (for NATTS, 24-hour integrated collection at a flow rate that yields a subambient final pressure consistent with normal NATTS sampling).
3. Connect the sampling systems to the zero manifold and purge with zero air humidified to 100% RH, for 48 hours. Dry the manifold and samplers with dry zero air for 1 hour. Adjust the zero air stream to 70% RH. Condition the zero manifold for 10 min with the sampling systems off. Condition the zero manifold an additional 10 min with the sampling systems on and in the bypass mode. Connect a clean, evacuated canister to each sampling system.
4. Collect the humidified zero air blank samples. Conduct the blank sample collections using the same sampling system operating procedures used during the challenge sample collection.
5. Analyze the zero and challenge samples and calculate the percent recoveries.

The sampling system must be challenged with a known concentration of selected analytes prior to deployment and annually thereafter. Operator/analyst judgment is critical: a challenge should be performed whenever the operation of the sampling system is questioned for any reason.

4.1.6 Canister Cleaning

The canister cleaning procedure and equipment described in this section are recommended when obtaining integrated whole ambient air samples for subsequent analysis of VOCs³. The cleaning procedure involves purging the canisters with cleaned humidified air and then subjecting them to high vacuum. The purpose of canister cleaning is to ensure that the interior canister surfaces are free of contaminants and that the canister meets the TO-15 cleanliness criteria (0.2 ppbv for all compounds of interest). This level of cleanliness minimizes

the potential for carryover of organic pollutants from one sample to the next and helps to ensure that the samples collected are representative.

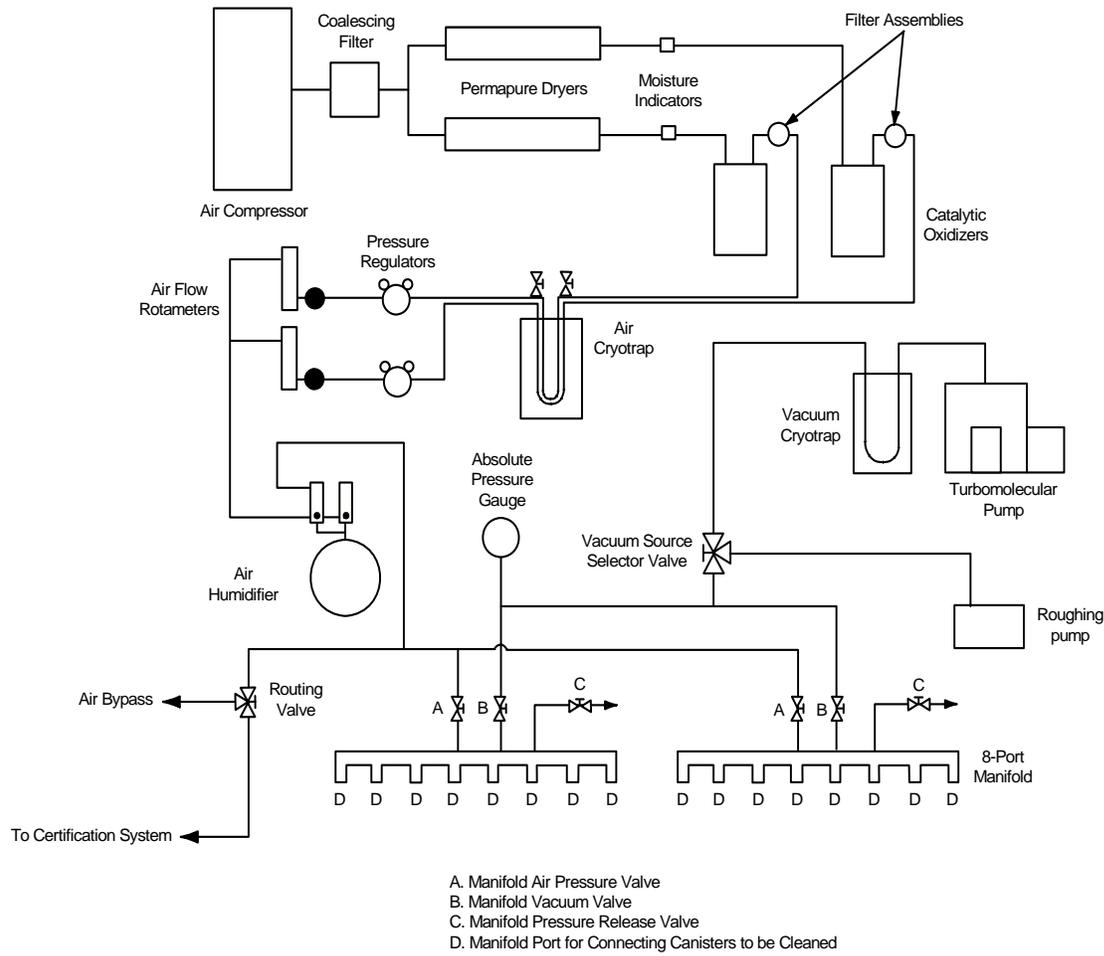
4.1.6.1 Canister Cleaning Equipment

The equipment required to clean canisters includes a source of clean, humidified air to pressurize the canisters to 20 pounds per square inch gauge (psig) and a vacuum system to evacuate the canisters to 5.0 mm Hg absolute pressure. Air from a standard, oil-free air compressor will contain pollutants from the ambient air. In addition, various VOCs will be found in the compressed air because of the lubricants used in the air compressor. Canister sampling programs typically require the cleaning and preparation of large numbers of canisters. Consequently, an efficient cleanup system capable of handling large numbers of canisters is essential. Figure 4.1-6 presents the schematic of a canister cleanup system suitable for cleaning up to 16 canisters concurrently. This and any alternative system must include a vacuum pump capable of evacuating the canisters to an absolute pressure of 0.5 mm Hg. The equipment is designed so that one manifold of eight canisters is undergoing the pressurization portion of the cleaning cycle while the other manifold of eight canisters is undergoing the vacuum portion of the cleaning cycle.

The following equipment is incorporated in a typical canister cleaning system:

- Air compressor. A shop or laboratory oil-free air compressor used to provide the air supply for the canister cleanup apparatus.
- Coalescing filter. A coalescing filter designed to remove condensed moisture or hydrocarbon contaminants present in the air supplied from the air compressor.
- Permeation driers. Permeation driers used to dry the air prior to introduction into the catalytic oxidizers. Two permeation driers are installed in parallel. (Note: Chilled air moisture removal systems may be substituted for permeation driers.)
- Filter assemblies. A 5-micron sintered stainless steel filter installed in the filter housing assembly downstream of each catalytic oxidizer to trap any particulate material that may be present in the airstream leaving the catalyst bed of the oxidizer.

- Air cryotrap and purge valves. The air cryotrap (i.e., liquid argon only) allows the cleaned air supply lines to be subjected to cryogenic temperatures to condense water formed during the oxidation of hydrocarbons, any remaining unoxidized hydrocarbons, and other condensables. Air cryotrap purge valves are used to purge these condensed components from the air cryotrap, as described in the operating procedure below.
- Pressure regulators. A high purity, dual stage pressure regulator is installed in each branch of the air supply line so that the maximum pressure attained during the cleanup procedure is controlled at 20 psig.
- Flow controllers. The flow control devices shown in the canister cleanup schematic (Figure 4.1-6) are metering valves. The flow rates are set not to exceed the maximum recommended flow rate through the catalytic oxidizers.
- Airflow rotameters. Rotameters are installed in the air supply lines to allow monitoring of the flow rates through the catalytic oxidizers.
- Air humidifier. The air humidifier shown in Figure 4.1-6 is a passivated, double-valve stainless steel canister with an inlet dip tube that projects to the bottom of the sphere. HPLC grade water is placed in the canister prior to use. Two rotameters are connected to control airflow so that about 80% of the flow rate can be directed to the humidifier (to bubble through the water to become saturated) while the other 20% bypasses the humidifier. This procedure allows the humidification apparatus to supply cleaned, dried air that has been humidified to an RH of ~80%.
- Manifold air pressure valves. Manifold air pressure valves are used to isolate the air supply system from the manifold or to make the pressurized air available to the manifold.



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Figure 4.1-6. Schematic of a Canister Cleanup System

- Eight-port manifolds. Eight-port manifolds are designed to allow up to eight canisters at a time to be connected. Fewer canisters may be connected to the manifold if the vacant ports are sealed off with a plug fitting.
- Roughing pump. The roughing pump shown in Figure 4.1-6 is a high capacity diaphragm vacuum pump used to remove the moist cleaning air from the canisters while evacuating the canisters to about 100 mm Hg absolute. The high moisture content of the cleaning air contained in the canisters will not impede the function of this diaphragm-style pump but will impede the performance of the high vacuum pump.
- High vacuum pump. A high vacuum pump capable of reducing the pressure in the canisters to 0.5 mm Hg absolute. High moisture content will impede the performance of the high vacuum pump.
- Vacuum cryotrap. A U-shaped trap located in the vacuum manifold that is sized to fit inside a Dewar flask filled with cryogen. The purpose of this trap is to condense water vapor from the air that is pulled from the canisters during the vacuum cycle and prevent back diffusion of organic vapors from the high vacuum pump into the canisters during the vacuum cycle of the cleaning procedure.
- Vacuum source selector valve. The vacuum source selector valve is a multiposition valve used to route either the roughing pump or the high vacuum pump to the eight-port manifold assemblies or to isolate both pumps from the manifold assemblies.
- Compound absolute pressure gauge. An absolute pressure gauge is used to measure the pressure attained in the canisters during the vacuum and pressurization cycles of the cleaning procedure. The absolute pressure gauge must be able to measure absolute pressures from 40 psig down to 0.5 mm Hg absolute.
- Air bypass valve. The air bypass valve is used to allow a 1.0-Lpm flow of air to be maintained through the catalytic oxidizers when the cleaning system is not in use. This flow prevents the oxidizers from overheating when the cleaning system is not in use.
- Manifold valves. The manifold vacuum valve and the manifold pressure valve are used to apply vacuum or pressure to the canisters, as required during the cleaning procedure.
- Manifold ports. The manifold ports permit connection of the canisters to the manifold. Fittings that mate directly with the canister valve fittings are used. These connections will not leak during the pressurization portion or the vacuum portion of the cleaning procedure.

4.1.6.2 Canister Cleaning Procedure

The cleaning system is prepared for use by checking the position of all the valves. All valves should be closed initially with the exception of the air bypass valve. Both the air source and vacuum pump vacuum flasks should be filled with cryogen, and the high vacuum pump should be actuated. These vacuum flasks must remain filled with cryogen throughout all cleanup activities. The inlet bellows valve on the humidifier is opened and the valve on the wet air rotameter is also opened. The valve on the dry air (bypass) rotameter should be closed to allow the air to become humidified. The system should stabilize for 10 min. After preparing the cleanup system, canister cleaning is performed using the following procedure.

1. Connect the canisters to be cleaned to the cleaning manifolds. Record the canister numbers and precleanup concentrations, if available, as determined by the last analysis, in the appropriate cleanup and canister history logbook. Record data pertinent to the vacuum and pressure cleanup cycles as they are completed.
2. Remove collected moisture from the air cryotrap by opening and immediately closing the air cryotrap purge valves. Removal of the collected moisture should be performed at the beginning of each pressure cycle so the cryotrap does not plug with ice.
3. Release pressure from the canisters by opening all the canister bellows valves and then opening the manifold pressure release valve. When venting is complete, leave the canister bellows valves open and close the manifold pressure release valve.
4. Begin the first vacuum cycle by actuating the roughing pump, placing the vacuum source selector valve in the roughing pump position, and opening the manifold vacuum valve.
5. Evacuate the canisters to approximately 100 mm Hg, as indicated by the absolute pressure gauge.
6. Position the vacuum source selector valve in the high vacuum pump position.
7. Evacuate the canisters to 0.5 mm Hg absolute pressure (or less) and maintain the vacuum for 30 min.

8. Close the manifold vacuum valve after the 30-min, high vacuum period has been completed.
9. Begin the first pressure cycle by purging the air cryotrap (refer to Step 2) and then closing the air bypass valve. Open the manifold air pressure valve. Using the airflow control valves, adjust the airflow rate to the manufacturer's recommended optimum flow rate for the oxidizers, as indicated by the air rotameters.
10. Check the pressure regulators to verify that they are set to deliver a final pressure of 20 psig. Fill the canisters to 20 psig. As the final pressure is attained, the flow rates indicated on the air rotameters will drop to zero regardless of the setting on the flow controllers because the pressure in the canisters and the pressure at the exit of the regulators reach equilibrium.
11. Close the manifold air pressure valve when filling is complete. Open the air bypass valve and adjust the airflow meters to 1.0 Lpm.
12. Release the pressure from the canisters after they have been under a 20-psig pressure for 30 min by opening the manifold pressure release valve.
13. Repeat Steps 4, 5, 6, 7, and 8 for Vacuum Cycle 2.
14. Repeat Steps 9, 10, 11, and 12 for Pressure Cycle 2.
15. Repeat Steps 4, 5, 6, 7, and 8 for Vacuum Cycle 3.
16. Repeat Steps 9, 10, and 11 for Pressure Cycle 3.
17. Close the bellows valves on all of the canisters.

4.1.6.3 Determination of Canister Cleanliness

Prior to deployment for use in sample collection, the cleanliness of canisters is determined. One canister out of every cleaned batch of canisters (i.e., one canister per eight cleaned) is analyzed by GC/MS following EPA Compendium Method TO-15¹ and must contain less than 0.2 ppbv of any NATTS Program target air toxics VOC. After the cleaned canister passes this test, the whole batch of cleaned canisters associated with the analyzed canister can be prepared for sample collection. If the cleaned canister does not pass the test, the whole batch of canisters (eight) associated with the analyzed canister, including the analyzed canister, must be recleaned and checked again.

4.1.7 Sample Collection Procedure

A detailed SOP must be prepared for sample collection. During the sample collection process, a vacuum pump draws in ambient air from the sampling inlet and manifold assembly at a constant flow rate of approximately 100 cubic centimeter (cc)/min or greater. A mass flow control device is used to maintain a constant sample flow rate into the canister over a specific sampling period. Displacement of the vacuum in the canister with sample air is the mechanism that facilitates sample collection. The flow rate used is a function of the final desired sample pressure, the internal volume of the canister used, and the specified sampling period. A starting pressure of 5.0 mm Hg absolute for the canisters is assumed.

During operation, the timer is programmed to activate and deactivate the sample collection system at specified times that are consistent with the beginning and end of a sample collection period. The flow rate into the canister should remain constant over the entire sampling period.

Prior to field use, each sample collection system must be certified as nonbiasing. After the initial certification, samplers must be recertified on an annual basis. Sampler certification is discussed in Section 4.1.5. The canisters must also be demonstrated to be clean before each use. Canister cleaning is discussed in Section 4.1.6.

The following generic steps are provided for the operation of a sample collection system while collecting a single sample:

1. Activate the sample collection system and verify that the correct sample flow rate has been input into the mass flow controller. Allow the system to equilibrate for 2 min.
2. Deactivate the sample collection system and reset the elapsed time indicator to show no elapsed time.
3. Open the canister bellows valve.

4. Record the initial vacuum in the canister, as indicated by the sample collection system vacuum gauge, on the canister sampling field data sheet.
5. Record the time of day and elapsed time indicator reading on the canister sampling field data sheet.
6. Set the electronic timer to start and stop sampling at the appropriate times.
7. After sample collection, record the final sample pressure on the sampling field data sheet. Final sample pressure should be close to the desired calculated final pressure. Time of day and elapsed time indicator readings should also be recorded.
8. Close the canister bellows valve. Disconnect and remove the canister from the sample collection system.
9. Attach a field data form/airflow form to document the canister serial number, sample number, sample type, location, and collection date.

Calculation of method precision for the NATTS Program is determined by repeated analysis of duplicate samples. Consequently, 10% of all sample collections will be duplicate or collocated samples. A duplicate sample is a sample collected simultaneously with a primary sample (i.e., in two separate canisters through the same sampling system at the same time). This simultaneous collection is typically achieved by teeing the line from the sampler to each of the two canisters and doubling the flow rate applied to achieve integration over the 24-hour collection period. The difference between duplicate samples and collocated samples is that the duplicate samples are collected from two canisters using one collection system, whereas collocated samples are collected at the same time but using two completely separate collection systems. Although collocated samples are highly desirable, the cost of an additional sampling system is usually prohibitive because collocated data would have to be acquired at every site. However, any NATTS site that is able should conduct both duplicate and collocated sampling.

4.1.7.1 Specifications for the Sampling System

To ensure that the sample collection system meets the needs of the NATTS Program, the following system specifications should be presented to and addressed by the candidate vendor(s) prior to procurement:

- An in-depth, detailed manual covering all aspects of the sample collection system (i.e., operation, maintenance, etc.) must be provided by the vendor.
- The overall size of the sampling system should still be kept as compact as possible.
- The sampling system should meet all applicable electrical and safety codes, operate on standard 110-volt AC power, and incorporate a main power fuse or circuit breaker. Specific potential electrical hazards and/or other safety considerations should be detailed in a supplied user's manual.
- The overall configuration, and the components comprising that configuration, should allow simple operation, maintenance, and service of the sample collection system, with the emphasis on simplicity. Materials used in the construction of components of the sample collection system should exhibit nonbiasing characteristics. All surfaces that will come in direct contact with sampled air should be constructed of glass, stainless steel, or Viton[®]. The use of Teflon or other plastics or polymers should be avoided because the absorption/desorption characteristics of these materials increase the potential for sample bias.
- The sample collection system must be certified as nonbiasing. The user must be able to document that the sample collection system design/configuration being considered can be or has been certified according to the prescribed procedures in Compendium Method TO-15¹, as described below.
- The sample collection system must be able to perform mass flow controlled time integration of the canister sample collections and allow for variable collection flow rates so canisters of different volume may be used.
- Expedient and responsive vendor support should be a mandatory requirement and primary consideration when procuring a canister sample collection system. Missed sample collections seriously impair the ability of the NATTS Program to meet DQOs. The user should specify that the vendor maintain an adequate supply of replacement parts and qualified service technicians to ensure that the absolute minimal number of sampling events is missed should a sample collection system failure occur. The user should specify that the vendor guarantee that parts/components be delivered to the sampling site within two working days of

order placement. The user should also specify that a sample collection system delivered to the vendor for repair or for other problems be serviced and returned to the user expeditiously. A vendor's ability to meet these requirements should be a primary consideration in the selection of instrumentation.

4.1.8 Analysis Procedures and Issues

A detailed SOP must be prepared to encompass all the procedures involved in the analysis of field canister samples^{1,2}.

4.1.8.1 Interferences

Interferences can confound the analysis by affecting the ability to identify the mass spectra, obtain accurate peak areas, or obtain an accurate retention time. Interferences can be introduced through the sample matrix, the sample canisters, the analytical system, or the canister cleaning system. In the case of a coeluting compound, the mass spectrum can still generally be interpreted unless the coeluting compound is an isomer of the compound of interest and the masses are the same or approximately the same. Very volatile compounds can display peak broadening and coelution with other species if the compounds are not delivered to the GC column in a very small volume of carrier gas. Refocusing of the sample after collection on the primary trap, either on a separate focusing trap or at the head of the GC column under subambient temperature conditions, mitigates this problem.

Sample moisture can lead to retention time shifts and poor peak shape; both retention time shifts and poor peak shape can result in peak misidentification. Carbon dioxide can be present as a large peak that causes retention time shifts and loss of nearby smaller peaks; the presence of a large carbon dioxide peak can therefore result in peak misidentification. Moisture and carbon dioxide can be removed from the analytical system with the moisture management subsystem in the preconcentrator. The analysis of blanks will prove that the analytical system is free from interferences.

4.1.8.2 Chromatography Issues

The MS provides advantages over nonspecific systems using multiple detectors. These advantages include positive compound identification supported by spectral libraries, identification of non-target compounds without the use of standards, and interpretation of coeluting compounds. An FID can be added to specifically quantitate a wide range of hydrocarbons at a high sensitivity.

Table 4.1-1 presents the VOCs analyzed by EPA Compendium Method TO-15¹, including the NATTS compounds. In general, polar compounds and, to a lesser extent, non-aromatic compounds do not consistently chromatograph well. Also, these compounds, especially the polar compounds, are not easily quantitated at low concentrations due to low detector response at the parameters mentioned in the analytical procedure section of this document. In the past, acrolein has been difficult to quantitate. However, using GC/MS SIM mode, it can be accurately quantitated, even at low concentrations. Studies and NATTS acrolein audits have been performed to validate Method TO-15 using GC/MS SIM mode as an effective method.^{4, 5, 6}

Table 4.1-1. Characteristic Masses Used for Quantitation of VOCs

Compound	CAS#	Primary Ion	Secondary Ion
acetylene	74-86-2	26	25
propylene	115-07-1	41	39, 42
dichlorodifluoromethane	75-71-8	85	87, 101
chloromethane	74-87-3	50	52
dichlorotetrafluoroethane	1320-37-2	85	135, 87
vinyl chloride	75-01-4	62	64
1,3-butadiene	106-99-0	54	53, 39
bromomethane	74-83-9	94	96
chloroethane	75-00-3	64	66
acetonitrile	75-05-8	41	40
acrolein	107-02-8	56	26, 27, 29, 55

Table 4.1-1. Characteristic Masses Used for Quantitation of VOCs

Compound	CAS#	Primary Ion	Secondary Ion
acetone	67-64-1	43	58
trichlorofluoromethane	75-69-4	101	103, 105
acrylonitrile	107-13-1	53	52
1,1-dichloroethene	75-35-4	96	98, 61
methylene chloride	75-09-2	84	49
Carbon disulfide	75-15-0	76	44, 78
trichlorotrifluoroethane	26523-64-8	101	151, 103
<i>trans</i> -1,2-dichloroethylene	56-60-5	96	98, 61
1,1-dichloroethane	75-34-3	63	65
methyl <i>tert</i> -butyl ether	1634-04-1	73	57
methyl ethyl ketone	78-93-3	43	72
chloroprene	126-99-8	53	88, 90
<i>cis</i> -1,2-dichloroethylene	56-60-5	96	61, 98
bromochloromethane	74-97-5	128	130, 49
chloroform	67-66-3	83	85
ethyl <i>tert</i> -butyl ether	637-92-3	59	87, 57
1,2-dichloroethane	107-06-2	62	64
1,1,1-trichloroethane	71-55-6	97	99, 61
benzene	71-43-2	78	77
carbon tetrachloride	56-23-5	117	119
<i>tert</i> -amyl methyl ether	994-05-8	73	87
1,2-dichloropropane	78-87-5	63	62, 41
ethyl acrylate	140-88-5	55	99
bromodichloromethane	75-27-4	83	85, 129
trichloroethylene	79-01-6	130	132, 95
methyl methacrylate	80-62-6	41	69, 100
<i>cis</i> -1,3-dichloropropene	10061-01-5	75	39, 77
methyl isobutyl ketone	108-10-1	43	58, 100
<i>trans</i> -1,3-dichloropropene	10061-02-6	75	39, 77

Table 4.1-1. Characteristic Masses Used for Quantitation of VOCs

Compound	CAS#	Primary Ion	Secondary Ion
1,1,2-trichloroethane	79-00-5	97	83, 61
toluene	108-88-3	91	92
dibromochloromethane	124-48-1	129	127, 131
1,2-dibromoethane	106-93-4	107	109
<i>n</i> -octane	111-65-9	85	57, 71
tetrachloroethylene	127-18-4	166	164, 131
chlorobenzene	108-90-7	112	77, 114
ethylbenzene	100-41-4	91	106
<i>m</i> -, <i>p</i> -xylene	108-38-3/106-42-3	91	106
bromoform	75-25-2	173	171, 175, 252
styrene	100-42-5	104	78, 103
1,1,2,2-tetrachloroethane	79-34-5	83	85
<i>o</i> -xylene	95-47-6	91	106
1,3,5-trimethylbenzene	108-67-8	105	120
1,2,4-trimethylbenzene	95-63-6	105	1220
<i>m</i> -dichlorobenzene	541-73-1	146	148, 111
chloromethylbenzene	100-44-7	91	126
<i>p</i> -dichlorobenzene	106-46-7	146	148, 111
<i>o</i> -dichlorobenzene	95-50-1	146	148, 111
1,2,4-trichlorobenzene	120-82-1	180	182, 184
hexachloro-1,3-butadiene	87-68-3	225	227, 223

Compounds required for NATTS are indicated in bold print. Shading indicates the other compounds that will ultimately be required for NATTS.

4.1.8.3 Humidity

Humidity in canister samples can present some chromatography problems ranging from poor reproducibility to column degradation⁷. Some moisture from the sample invariably is

delivered with the sample onto the chromatography column. This water is more easily tolerated by the analytical system when it is spread out over a longer time instead of injected all at once with the sample. Polar compounds have an affinity for water and can be difficult to chromatograph (i.e., peaks often become broad and/or tailing). The polar compounds may even shift retention times, depending on the delivery method of the moisture onto the column.

Reducing sample size can reduce the moisture that is collected and injected. Alternatively, an active moisture management subsystem can be incorporated in the preconcentrator to reduce moisture from the sample prior to injection onto the analytical system. Moisture removal should be done cautiously because some methods of removing water from the sample may also remove some of the compounds of interest, especially the polar compounds.

4.1.8.4 Equipment and Materials for VOC Analysis

The following equipment and materials are required for performing successful analysis of field canister samples^{1,6}.

- Automated preconcentrator and autosampler. This instrument is designed to interface between the sample contained in a canister and the chromatographic analytical system. A concentrator is used to concentrate the condensable (organic) portion of an air sample. The system is equipped with two traps, a hybrid 60/80 Tenax[®]/deactivated glass bead trap and a secondary Tenax[®] trap.
- GC/MS system. A gas chromatograph is an analytical system complete with a temperature-programmable gas chromatograph having subambient capabilities and with a DB-1 60 m × 0.32 mm, 1- μ m film thickness fused silica capillary column or equivalent.
- MS. This instrument is capable of scanning from 23 to 350 atomic mass unit (amu) every 1 second or less. It uses 70 volts (nominal) of electron energy in the electron ionization mode and produces a mass spectrum that meets all criteria for the manufacturer's specifications for BFB tuning.
- Data acquisition and processing software. The data system software includes programs to calibrate and tune the MS, acquire data, and process data, as well as utilities for file management and editing. Tuning programs can adjust voltages in the ion source, calibrate mass assignments, and control the scanning of the mass

analyzer. Data acquisition programs monitor the total ion current, automatically storing the mass spectra of GC peaks as they elute (scanning mode) or, alternatively, monitor the concentrations of particular ions (selected ion monitoring mode). The data system also includes a mass spectral reference library for identification of mass spectra.

- Calibration manifold. A dynamic flow dilution system can be assembled by the laboratory or obtained commercially.
- Calibration stock standard. The calibration stock(s) should be traceable to an NIST SRM and include the VOCs of interest in one or more cylinders.
- Laboratory control standard. The calibration stock(s) should be traceable to an NIST SRM and include VOCs to use as a second source standard daily calibration check. It does not have to include all of the VOCs of interest and can include other VOCs.
- Internal standards. These are commercially available or can be prepared by the laboratory with humidified air containing d₁₄-hexane, 1,4-difluorobenzene, and d₅-dichlorobenzene at a nominal concentration of 30 ppbv. The internal standard should be sampled directly from the vendor-supplied cylinder and not diluted.
- Tuning standard. A 30-ppbv BFB commercially available gas standard that can also be prepared by the laboratory by injecting neat liquid BFB into a cleaned and evacuated canister and filling with clean humidified air. The BFB standard can be prepared or purchased in the same cylinder as the internal standards gas mixture. Tuning criteria are shown in Table 4.1-2.
- Sample canisters. These canisters are stainless steel (typically 6 L internal volume), with valve and passivated inner lining (i.e., SUMMA[®] and Silco Steel[®]), available from a variety of manufacturers.

Table 4.1-2. 4-Bromofluorobenzene (BFB) Tuning Criteria

Target Mass	Relative to Mass	Lower Limit %	Upper Limit %
50	95	8	40
75	95	30	66
95	95	100	100
96	95	5	9
173	174	0	2
174	95	50	120
175	174	4	9
176	174	93	101
177	176	5	9

4.1.8.5 Analytical Procedure

Preparation of the Analytical Standards

Stock gas mixtures certified traceable to an NIST SRM are preferred. For the best economy, the stock gas mixtures should be about 500 ppbv per compound. Lower concentration stock standards can be used, but preparation/certification of lower concentration standards tends to cost more. The calibration standards are prepared by dynamic flow dilution of the stock gas with clean humidified air using a manifold and calibrated mass flow controllers. Although other methods can be used to prepare standards (i.e., syringe injection, pressure methods), the inherent reproducibility/accuracy of the alternative methods of standard preparation is not sufficient to meet requirements for data consistency. It is important to note that to avoid the potential for calibration error due to errors in loading sample volume, standards and humidified zeros should be prepared to have the same approximate final pressure as the samples that will be analyzed (i.e., if samples will typically have a final pressure that is atmospheric pressure or lower, standards should be prepared at atmospheric). Humidified zero air is used as the diluent. The diluted stock gas is allowed to mix in the dilution system reservoir and is then introduced into a clean and evacuated canister. One standard canister should be prepared for each of the six calibration concentrations, 0.25 ppbv, 0.50 ppbv, 1.0 ppbv, 5.0 ppbv, 10.0 ppbv and 15.0 ppbv. Each standard must be assigned a unique standard identification number, and the preparation of each standard should be documented in the dilution system notebook. The prepared standards should be allowed at least 24 hours to reach equilibrium prior to analysis. A diagram of a dynamic flow dilution system is included in Section 9.2 of EPA Compendium Method TO-15¹. The mass flow controllers of the dilution system should be recalibrated annually, and the calibration should be documented in the dilution system notebook.

To calculate the final diluted compound concentration:

$$\text{Diluted Conc.} = (\text{Original Conc.})(\text{Stock gas flow rate})/(\text{Airflow rate} + \text{Stock gas flow rate})$$

A certified cylinder (commercially available) of BFB and internal standards as a gaseous mixture should be attached to the preconcentrator system with stainless steel tubing. A known volume from a BFB/internal standard gas mixture in a cylinder is loaded through the preconcentrator system along with the sample to introduce the internal standards and BFB to the sample analysis. The same amount of the BFB/internal standard gas mixture is loaded with each analysis, whether sample, blank, or standard. Table 4.1-3 shows the internal standard compounds and their characteristic masses.

Table 4.1-3. Internal Standards and BFB: Characteristic Masses

Internal Standard Compounds	CAS No.	Primary Ion	Secondary Ion
d ₁₄ -hexane	21666-38-6	66	50, 100
1,4-difluorobenzene	540-36-3	114	63, 88
d ₅ -dichlorobenzene	2199-69-1	117	82, 54

Typical GC/MS Analytical System Operating Conditions

The information below provides a set of typical operating conditions for the GC/MS system in performing analysis of canister samples.

MS Information

Solvent Delay: 4.80 min
EM Absolute: True
Resulting Voltage: 1800 (Usually set approximately 200 above the autotune)

[SIM Parameters]

GROUP 1
Group ID: 1
Resolution: Low
Plot 1 Ion: 26.00
Ions In Group: 26.00

GROUP 2

Group ID: 2
Resolution: Low
Group Start Time: 7.80
Plot 1 Ion: 39.00
Ions In Group: 39.00, 41.00, 42.00

GROUP 3

Group ID: 3
Resolution: Low
Group Start Time: 8.60
Plot 1 Ion: 52.00
Ions In Group: 50.00, 52.00, 62.00, 64.00, 85.00, 87.00, 101.00, 135.00

GROUP 4

Group ID: 4
Resolution: Low
Group Start Time: 11.80
Plot 1 Ion: 54.00
Ions In Group: 39.00, 54.00, 64.00, 66.00, 94.00, 96.00

GROUP 5

Group ID: 5
Resolution: Low
Group Start Time: 14.30
Plot 1 Ion: 41.00
Ions In Group: 29.00, 40.00, 41.00, 49.00, 50.00, 52.00, 53.00, 55.00, 56.00, 61.00, 76.00, 78.00, 84.00, 86.00, 96.00, 98.00, 101.00, 103.00, 151.00

GROUP 6

Group ID: 6
Resolution: Low
Group Start Time: 18.40
Plot 1 Ion: 61.00
Ions In Group: 41.00, 43.00, 49.00, 53.00, 57.00, 61.00, 63.00, 64.00, 65.00, 66.00, 72.00, 73.00, 83.00, 85.00, 87.00, 88.00, 90.00, 96.00, 98.00, 128.00, 130.00

GROUP 7

Group ID: 7
Resolution: Low
Group Start Time: 21.20
Plot 1 Ion: 62.00

Ions In Group: 57.00, 59.00, 61.00, 62.00, 77.00, 78.00, 79.00,
87.00, 97.00, 98.00, 100.00, 114.00, 117.00,
119.00, 121.00

GROUP 8

Group ID: 8
Resolution: Low
Group Start Time: 23.40
Plot 1 Ion: 55.00
Ions In Group: 41.00, 55.00, 63.00, 69.00, 73.00, 76.00, 83.00,
85.00, 87.00, 95.00, 97.00, 99.00, 100.00, 114.00,
129.00, 130.00

GROUP 9

Group ID: 9
Resolution: Low
Group Start Time: 25.50
Plot 1 Ion: 39.00
Ions In Group: 39.00, 43.00, 58.00, 61.00, 75.00, 79.00, 83.00,
85.00, 91.00, 92.00, 93.00, 97.00, 100.00, 110.00

GROUP 10

Group ID: 10
Resolution: Low
Group Start Time: 27.80
Plot 1 Ion: 127.00
Ions In Group: 43.00, 85.00, 94.00, 107.00, 109.00, 114.00, 127.00,
129.00, 131.00, 166.00

GROUP 11

Group ID: 11
Resolution: Low
Group Start Time: 30.20
Plot 1 Ion: 51.00
Ions In Group: 51.00, 77.00, 78.00, 82.00, 83.00, 85.00, 91.00,
104.00, 106.00, 112.00, 117.00, 171.00, 173.00,
175.00

GROUP 12

Group ID: BFB
Resolution: Low
Group Start Time: 33.20
Plot 1 Ion: 50.00
Ions In Group: 50.00, 75.00, 95.00, 96.00, 173.00, 174.00, 175.00,
176.00, 177.00

GROUP 13

Group ID: 12
Resolution: Low
Group Start Time: 35.00
Plot 1 Ion: 105.00
Ions In Group: 91.00, 105.00, 111.00, 120.00, 126.00, 146.00, 148.00

GROUP 14

Group ID: 13
Resolution: Low
Group Start Time: 40.00
Plot 1 Ion: 180.00
Ions In Group: 180.00, 182.00, 184.00, 223.00, 225.00, 227.00

Timed MS Detector Entries

Time (min): 44.00
State (MS on/off): Off

GC Temperature Information

Column: Restek Rxi-lms, 60 m, 0.32 i.d., 1- μ m film thickness
Injector Oven Temperature: 250 °C
Oven Initial Temperature: -50 °C
Initial Time Temperature: 5.00 min
MS Quad: 150 °C
MS Source: 230 °C

<u>Level</u>	<u>Rate (°C/min)</u>	<u>Final Temp (°C)</u>	<u>Final Time (min)</u>
1	15.00	0	0.00
2	5.00	150	0.00
3	25.00	275	5.20

Next Run Time: 48.53 min

Preconcentrator Interface Conditions

	<u>Initial Temperature</u>	<u>Desorption Temperature</u>
Trap 1: Glass Bead/Tenax [®] Trap	-155 °C	10 °C
Trap 2: Tenax [®] Trap	-55 °C	200 °C
Cryofocuser	-185 °C	100 °C

	<u>Volumes (mL)</u>	<u>Flow (mL/min)</u>
Internal Standard	100	50
Sample	400	50
Final Flush	75	25
Trap1-Trap2 Transfer	40	10

4.1.8.6 Preparation of the GC/MS Analytical System

The analytical system must be characterized and optimized prior to operation. Such parameters as retention times, relative retention times, existence and identification (ID) of coeluting peaks, internal standard retention times, and method detection limits should be established prior to sample analysis.

The use of RRT ID is incorporated in some data processing software and will compensate for any retention time variations. Separation of the internal standard from the target compounds must be achieved prior to analysis. The use of internal standards can help minimize the influence of analytical system variability.

To interface the preconcentrator system to the analytical system, megabore size (0.53 mm) stainless steel (Silco Steel[®]) tubing housed in a heated transfer line is used. The tubing is connected to the column at the injector port with a zero dead volume union. The column (helium) carrier flow is set to deliver about 1 mL/min (EPC @ 18 psi @ 100 °C) to the MS. Flow from the end of the column is verified before making the connection to the MS by inserting the end of the column into methanol and observing bubbles. After flow is verified, the end of the column is connected to the MS with the MS transfer nut. The GC is allowed time to purge the ambient air from the instrument before the GC oven temperature is ramped above 100 °C. The certified cylinder of BFB and internal standards gas mixture is attached to the preconcentrator system with stainless steel tubing to allow the BFB and the internal standards to be concentrated with the sample prior to injection. Any changes or maintenance to the system should be documented in a maintenance logbook dedicated to that system.

4.1.8.7 Initial Calibration

An initial multipoint calibration curve must be performed during setup of the analytical system and then once per quarter (three months), after any major instrument change, or if the daily calibration check acceptance criteria have not been met. The system must be recalibrated if the daily QC sample will not meet acceptance criteria. The calibration range is approximately 0.25, 0.5, 1, 5, 10, and 15 ppbv for each compound. The lowest calibration point, 0.25 ppbv, is intended to be near (but not at) experimentally determined MDLs at a level for which the standard can be prepared accurately and reproducibly. Each calibration standard must be analyzed once and the data processing software must be used to create a data base with the calibration responses for all of the compounds and generate a complete response factor report that includes the percent RSD. The percent RSD for each compound must be within $\pm 30\%$ with up to two compounds allowed to be within $\pm 40\%$. The RRTs for each compound must be within 0.06 RRT units of the mean relative retention time (MRRT) for the compound. At the time of calibration, the analyst should record the expected due date (three months from the date of calibration) for the next calibration in the analysis logbook.

The RRF is calculated as follows:

$$RRF = (A_t)(C_{is}) / (A_{is})(C_t) \quad (4.1-6)$$

where:

A_t = area count of the primary ion for the target compound to be measured

A_{is} = area count of the primary ion for the internal standard

C_t = concentration of the target compound (ppbv)

C_{is} = concentration of the internal standard (ppbv).

The RRTs are calculated as follows:

$$RRT = \frac{RT_t}{RT_{is}} \quad (4.1-7)$$

where:

RT_t = retention time for the target compound (seconds)

RT_{is} = retention time for the internal standard (seconds).

The MRRTs are calculated as follows:

$$MRRT = \sum_{i=1}^n \frac{RRT}{n} \quad (4.1-8)$$

where:

RRT = Relative retention time for each compound at each calibration level.

4.1.8.8 Analytical Sequence

Sample analysis can begin after the daily system performance check, continuing calibration (or initial calibration), laboratory control standard, and daily system blank criteria have met acceptance criteria. Daily QC criteria are presented in Section 4.1.8.

- Instrument performance check (BFB tune). Use BFB to verify instrument tune at the beginning of each 24-hour GC/MS analysis time period to demonstrate that the tuning performance criteria have been met before any sample analyses. The mass spectral ion abundance criteria for the instrument performance check standard are shown in Table 4.1-2. If the criteria are not met, the MS must be retuned. Some MS software acquires the mass spectrum automatically and gives the user a pass or fail report. Alternately, the analyst should take the average spectrum of the entire peak and subtract the background spectrum at a point well away from the BFB peak.
- Daily calibration check standard. A mid-level calibration check standard must be analyzed daily before sample analysis to ensure that the initial calibration is still valid. A valid daily calibration must have a RPD for each response factor less than $\pm 30\%$ from the mean response factor of the initial calibration for all compounds. If the daily calibration is not valid, analysis of the calibration check sample should be repeated. If still not valid, system maintenance and/or recalibration with new standards is required.

$$RPD = \frac{RRF_t - MRRF_i}{MRRF_i} \times 100 \quad (4.1-9)$$

where:

RRF_t = RRF of the target compound in the daily calibration check.

$MRRF_i$ = mean RRF of the target compound in the most recent initial calibration.

A second source calibration check should be analyzed daily as a laboratory control standard (LCS). The second source gas mixture can be attached directly to the preconcentrator system if it is at a low concentration, such as 15.0 ppbv. The recoveries for the LCS should be from 70 to 130% of expected concentration. If the daily LCS does not meet criteria, it should be reanalyzed. If acceptance criteria are still not achieved, recalibration is required.

$$\% \text{ Recovery} = \frac{\text{observed value}}{\text{expected value}} \times 100 \quad (4.1-10)$$

- Daily system blank. Analyze a zero air canister containing purified, humidified air after the calibration standard and before the samples to prove that the analytical system is clean. The acceptance criterion for a blank is <0.2 ppbv for any target compound or 3 times the detection limit of the compound, whichever is higher. If the system blank does not meet criteria, analysis must be repeated with a different zero air canister. If still not valid, the preconcentrator/GC/MS system must be checked for leaks and/or contamination. Canister cleaning batch blanks can be used for clean zero air blanks since one canister of each cleaned batch must be analyzed by GC/MS for the batch to be certified as clean.

4.1.8.9 Sample Tracking

Each sample canister received is entered into the LIMS and assigned a unique laboratory identification number. The pressure of the canister is compared against the pressure recorded at the site to ensure the canister remained airtight during transport. If any leaks are detected, the sample is invalidated. The sample canister is then tagged with the laboratory identification number, site location, collection date, and canister pressure. The sample airflow COC is completed with the same information. Canister samples must be analyzed within 30 days of the

sample collection date. If canister hold time requirements are not met, the data for that sample should be flagged.

4.1.8.10 Sample Analysis

Sample canisters are connected to the autosampler inlet ports and the canister valves are opened. While the GC oven is cooled to $-50\text{ }^{\circ}\text{C}$, the autosampler preconcentrator collects the specified volume of a single sample out of a canister along with the specified volume of the BFB/internal standard (IS) mixture and concentrates the sample volume in cryogenically cooled traps. The trapped sample is then thermally desorbed onto the head of the subambient GC column, and the GC begins the temperature program. Each analysis should be recorded in the analysis logbook for that system, including such information as sample name, laboratory identification number, collection date, analysis date, analysis file name, calibration method used, canister number, dilution factor, and volume of sample loaded.

The IS peak areas for each analysis completed in the 24-hour GC/MS analysis period must be compared to the mean area response for each IS in the most recent calibration. The responses of each IS in the sample must be within $\pm 40\%$ of the mean area response for each of the ISs in the multipoint calibration and the retention time of each IS must be within 0.06 RRT units of the retention time of the ISs in the calibration or the samples must be reanalyzed. If the area response for any IS changes by more than $\pm 40\%$ between the sample and the most recent calibration, the GC/MS system must be inspected for malfunction and corrections made as appropriate. When corrections are made, a calibration check sample must be analyzed to determine whether the multipoint calibration is valid. If acceptance criteria are not met, recalibration is necessary. Reanalysis of samples analyzed while the GC/MS system was malfunctioning is necessary.

The ID of each compound in the sample must be verified by retention time and relative abundances of the primary and secondary ions. See Table 4.1-1 for characteristic masses. Each compound spectrum is compared against a reference spectrum from the spectral library. It may

be helpful to subtract the background noise from the compound spectrum to aid in verification of the identification of that compound. Target compound concentrations in units of ppbv are calculated using the RRFs obtained in the initial calibration. The abundance of the primary ion is used for quantitation unless there is an interference with the primary ion; in case of interference with the primary ion, a secondary ion can be used. The calculation is shown below (Eq. 4.1-11). After the data results have been verified and quantitated by the analyst, the data are reviewed by a second person, who verifies the compound IDs and quantitation and summarizes the data into spreadsheet tables. The tables are then reviewed by a third person to identify and investigate any apparent anomalies and to ensure that all calculations are correct. All analysis data and data reports are saved in the LIMS and archived electronically.

$$C_t = \frac{(A_t)(C_{is})(DF)}{(A_{is})(MRRF)} \quad (4.1-11)$$

where:

A_t = area count of the primary ion for the target compound to be measured

A_{is} = area count of the primary ion for the IS

C_t = concentration of the target compound (ppbv)

C_{is} = concentration of the internal standard (ppbv)

$MRRF$ = mean RRF from initial calibration

DF = dilution factor. $DF = 1$, if no dilution.

4.1.8.11 Sample Dilution

Samples with analyte concentrations greater than the calibration range should be diluted either by reducing the 400 mL sample volume or (in the canister) by adding clean, pressurized nitrogen or air. Samples diluted with nitrogen or air should be allowed 24 hours for equilibration before analysis. A dilution factor must be applied to the data for either a volume dilution or dilution by nitrogen or air. For samples loaded at a lower volume, the dilution factor can be calculated dividing the usual sample volume by the dilution sample volume.

4.1.9 Requirements for Demonstrating Method Acceptability for VOC Analysis

Three measurements of method acceptability are presented below.

4.1.9.1 Determination of Method Detection Limits

MDLs for the ambient air analysis are experimentally determined in accordance with 40 Code of Federal Regulations (CFR), Part 136, Appendix B, with 99% confidence level with a standard deviation estimate having n - 1 degrees of freedom. The VOC MDLs in Table 4.1-4 present the maximum acceptable MDLs allowable to ensure consistency across the NATTS Program. It is recognized and understood that the target MDLs shown in Table 4.1-4 are significantly lower than the MDLs reflected in Compendium Method TO-15¹.

Table 4.1-4. Target Method Detection Limits for GC/MS/SIM Analysis of VOCs

Compound	MDL (ppbv)	Compound	MDL (ppbv)
acetylene	0.023	<i>tert</i> -amyl methyl ether	0.012
propylene	0.009	1,2-dichloropropane	0.033
dichlorodifluoromethane	0.005	ethyl acrylate	0.011
chloromethane	0.014	bromodichloromethane	0.007
dichlorotetrafluoroethane	0.003	trichloroethylene	0.010
vinyl chloride	0.008	methyl methacrylate	0.006
1,3-butadiene	0.006	<i>cis</i> -1,3-dichloropropene	0.014
bromomethane	0.010	methyl isobutyl ketone	0.007
chloroethane	0.008	<i>trans</i> -1,3-dichloropropene	0.009
acetonitrile	0.099	1,1,2-trichloroethane	0.006
acrolein	0.080	toluene	0.005
trichlorofluoromethane	0.007	dibromochloromethane	0.010
acrylonitrile	0.057	1,2-dibromoethane	0.018
1,1-dichloroethene	0.014	octane	0.006
methylene chloride	0.017	tetrachloroethylene	0.011

Table 4.1-4. Target Method Detection Limits for GC/MS/SIM Analysis of VOCs

Compound	MDL (ppbv)	Compound	MDL (ppbv)
carbon disulfide	0.009	chlorobenzene	0.005
trichlorotrifluoroethane	0.012	ethylbenzene	0.005
<i>trans</i> -1,2-dichloroethy-lene	0.018	<i>m</i> -, <i>p</i> -xylene	0.009
1,1-dichloroethane	0.006	bromoform	0.017
methyl <i>tert</i> -butyl ether	0.002	styrene	0.010
methyl ethyl ketone	0.044	1,1,2,2-tetrachloroethane	0.013
chloroprene	0.022	<i>o</i> -xylene	0.004
<i>cis</i> -1,2-dichloroethylene	0.016	1,3,5-trimethylbenzene	0.004
bromochloromethane	0.019	1,2,4-trimethylbenzene	0.003
chloroform	0.004	<i>m</i> -dichlorobenzene	0.004
ethyl <i>tert</i> -butyl ether	0.007	chloromethylbenzene	0.005
1,2-dichloroethane	0.015	<i>p</i> -dichlorobenzene	0.006
1,1,1-trichloroethane	0.003	<i>o</i> -dichlorobenzene	0.005
benzene	0.005	1,2,4-trichlorobenzene	0.015
carbon tetrachloride	0.009	hexachloro-1,3-butadiene	0.013

At least seven (usually 7 to 10) VOC standard canisters are prepared at the same concentration. A concentration that is one to five times the expected detection limit should be chosen. Using standards at a lower concentration will not necessarily provide lower MDLs. The VOC compounds analyzed by EPA Compendium Method TO-15 generally have detection limits at or below 0.20 ppbv. Therefore, the MDL study standard should be prepared at a concentration of 0.25 ppbv or lower. Each standard should be analyzed once with an injected volume equivalent to the sample volume analyzed; the standard deviation for each compound should be calculated for all of the analyses and should be multiplied by the applicable Student's *t* value, 3.143 for seven analyses, 2.998 for eight analyses, etc., to determine the MDLs consistent with 40 CFR Part 36 Appendix B. See Table 4.1-5 for applicable Student's *t* values.

Any analyzed concentrations below the MDL values should be flagged when the data are reported. All calculated values should be reported.

Table 4.1-5. Student's t Values at the 99% Confidence Level

Number of Replicates	Degrees of Freedom	Student's t Value
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764

4.1.9.2 Replicate Precision

Analytical precision is estimated by repeated analysis of samples. Replicate analysis is performed on all duplicate or collocated samples taken in the field, (i.e., 10% of the total sample number). The RPD between the replicate analyses must be within 30%, except with compound concentrations less than five times the method detection limit for each compound. A replicate analysis that does not meet the criteria should be reanalyzed. The equation for percent difference is:

$$\text{relative percent difference} = \frac{(|X_1 - X_2|)}{X_{avg}} \times 100 \quad (4.1-11)$$

where:

X_1 = first measurement

X_2 = second measurement

X_{avg} = average of two measurements.

4.1.9.3 PE Accuracy

EPA will provide PE samples to program participants on a quarterly basis to verify the performance of the NATTS analytical systems. The equation for PE sample accuracy is:

$$\text{PE sample accuracy, \%} = \frac{[(\text{spiked value} - \text{observed value})]}{(\text{spiked value})} \times 100 \quad (4.1-12)$$

4.1.10 Quality Control Specifications

QC specifications for the NATTS VOC program are presented in Table 4.1-6. Overall MQOs for VOC sampling and analysis are shown in Section 3 (Table 3.3-1).

Table 4.1-6. Summary of Air Toxics TO-15 Quality Control Procedures

QC Check	Frequency	Acceptance Criteria	Corrective Action
BFB Instrument Tune Performance Check	Daily ¹ prior to sample analysis	Evaluation criteria in Table 4.1-2 of this document.	1) Retune 2) Clean ion source and/or quadrupoles
Multipoint (at least five) calibration bracketing the expected sample concentrations.	Following any major change, repair or maintenance if daily QC is not acceptable. Recalibration period not to exceed three months.	1) RSD of response factors ≤ .30% 2) RRT for target peaks ±0.06 RRT units from mean RRT	1) Repeat an individual standard analysis 2) Repeat calibration curve 3) Prepare new calibration standards and repeat analysis
Calibration check using midpoint of calibration curve or one other point in curve.	Daily ¹ on the days of sample analysis	Analyst verifies that the response factor ≤ 30% bias from calibration curve average response factor	1) Repeat calibration check 2) Repeat calibration curve
LCS (Second Source Standard)	Monthly	Analyst verifies that the response factor ≤ 30% bias from calibration curve average response factor	1) Repeat analysis 2) Repeat calibration
System Blank Analysis	Daily ¹ following BFB and calibration check; prior to sample analysis	1) <0.2 ppbv per analyte 2) IS area response ±40% and IS retention time ±0.33 min of most recent calibration check	1) Repeat analysis with new blank canister 2) Check system for leaks, contamination 3) Reanalyze blank
Duplicate and Replicate Analysis	All duplicate field samples	<30% RPD for compounds greater than 5 times MDL	Repeat sample analysis
Samples	All samples	IS area response ±40% of calibration mean and IS retention time ±0.33 min of calibration	Repeat analysis

¹Every 24 hours frequency

4.2 OVERVIEW OF COMPENDIUM METHOD TO-11A

EPA Compendium Method TO-11A⁸ will be applied to the determination of formaldehyde and other carbonyl compounds (aldehydes and ketones) in ambient air. EPA Compendium Method TO-11A⁸ utilizes a coated solid adsorbent for collection of carbonyl compounds from ambient air followed by HPLC analysis with UV detection.

Carbonyl compounds, especially low molecular weight aldehydes and ketones, have received increased attention in the regulatory community due in part to their effects on humans and animals. Exposure to formaldehyde and other specific aldehydes (acetaldehyde, acrolein, and crotonaldehyde), even short term, has been proven to cause irritation of the eyes, skin, and mucous membranes of the upper respiratory tract. High concentrations of carbonyls, especially formaldehyde, can injure the lungs and may contribute to eye irritation and affect other organs of the body. Aldehydes may also cause injury to plants. Sources of carbonyl compounds in ambient air range from natural occurrences to secondary formation through atmospheric photochemical reactions.

In general, natural sources of carbonyls do not appear to be important contributors to air pollution. Aldehydes are commercially manufactured by various processes, including production of alkenes, dehydrogenation of alcohols, and addition reactions between aldehydes and other compounds. Formaldehyde and other aldehyde production in the United States has shown a substantial growth over the last several years due in part to use of these compounds in a wide variety of industries, such as the chemical, rubber, tanning, paper, perfume, and food industries. The major industrial use of carbonyl compounds is as an intermediate in the syntheses of organic compounds, including alcohols, carboxylic acids, dyes, and medicinals.

A major source of carbonyl compounds in the atmosphere may be attributed to motor vehicle emissions. In particular, formaldehyde, the major carbonyl compound in automobile exhaust, accounts for 50 to 70% of the total carbonyl burden in the atmosphere. Furthermore, motor vehicles also emit reactive hydrocarbons that undergo photochemical oxidation to produce formaldehyde and other carbonyl compounds in the atmosphere.

To address the need for a measurement method that determines carbonyl compounds with the sensitivity required to perform health risk assessments (i.e., 10^{-6} risk level), a combination of wet chemistry and solid adsorbent methodology was developed. Activating or wetting the surface of an adsorbent with a chemical specific for reacting with carbonyl compounds allowed greater volumes of air to be sampled, thus enabling better sensitivity in the methodology. Various chemicals and adsorbent combinations have been utilized with various levels of success. The currently accepted technique, as applied to the NATTS Program, is based on reacting airborne carbonyls with 2,4-dinitrophenylhydrazine (DNPH) coated on a silica gel adsorbent cartridge, followed by separation and analysis of the hydrazone derivative by HPLC with UV detection. The methodology used to accomplish carbonyl compounds measurements is EPA Compendium Method TO-11A⁸ (<http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-11ar.pdf>). EPA Compendium Method TO-11A provides sensitive and accurate measurements of carbonyl compounds and includes sample collection and analysis procedures. In this method, a cartridge(s) containing a coated solid sorbent is used to capture the compounds of interest. The sampling cartridge is extracted and the extract is analyzed using HPLC with UV detection.

NATTS participants wishing to use alternate configurations and/or approaches other than those specified in this document may do so only with Regional EPA approval provided that the alternate configuration and/or approach meet the program MQOs. It is the responsibility of the NATTS participant to demonstrate equivalent performance to the methodology specified in this document, prior to the initiation of monitoring.

Organic compounds that have the same HPLC retention time and significant absorbance at 360 nanometers (nm) (the absorption of the DNPH derivative of formaldehyde) will interfere. Such interferences can often be overcome by altering the chromatographic separation conditions (e.g., using alternative HPLC columns or mobile phase compositions).

Formaldehyde may be a contaminant in DNPH reagent. The use of commercially available precoated cartridges is required for the NATTS Program. For a commercial cartridge to be acceptable, formaldehyde background concentration should be less than 0.15 microgram

(μg)/cartridge. For the enhanced carbonyl analysis, the following certification blank criteria must also be met for each lot of sampling cartridges:

- Acetaldehyde must be less than 0.10 μg /cartridge;
- Acetone must be less than 0.30 μg /cartridge; and
- All other carbonyl compound totals must be less than 0.10 μg /cartridge.

A “certification blank for formaldehyde” must be obtained for each lot of cartridges purchased.

The purity of the acetonitrile (ACN) used for the extraction of the sampling cartridges is an important consideration in the determination of allowable formaldehyde blank concentration in the reagent. Background concentrations of formaldehyde in ACN will be quantitatively converted to the hydrazone, adding a positive bias to the ambient air formaldehyde determinations.

Ozone has been identified as an interferent in the measurement of carbonyl compounds when EPA Compendium Method TO-11A⁸ is used. To eliminate this interference, removal or scrubbing of O₃ from the sample airstream in the field is mandatory. Ozone at high concentrations has been shown to interfere negatively in the sampling process by reacting with both the DNPH and its carbonyl derivatives (hydrazones) on the cartridge. The extent of interference depends on the temporal variations of both the ozone and the carbonyl compounds and the duration of sampling. Significant negative interference from O₃ has been observed at concentrations of formaldehyde and ozone typical of clean ambient air. Because of these issues, it is recommended that the ozone interference should be removed before the ambient air sample stream reaches the coated cartridge. This removal process entails constructing or purchasing an ozone denuder scrubber and placing it in front of the cartridge. The denuder scrubber is constructed using a saturated solution of potassium iodide (KI).

4.2.1 Sampling Procedure and Issues Associated with EPA Compendium Method TO-11A

Information and specifications applicable to conducting EPA Compendium Method TO-11A⁸ for NATTS Program carbonyl measurements are presented below.

4.2.1.1 O₃ Scrubbers

The EPA has determined through laboratory tests that O₃ present in ambient air interferes with the measurement of carbonyl compounds when using EPA Compendium Method TO-11A⁶. O₃ can interfere with carbonyl analyses in three ways:

- The O₃ reacts with the DNPH on the cartridge and makes the DNPH unavailable for derivatizing carbonyl compounds;
- The O₃ also degrades the carbonyl derivatives formed on the cartridge during sampling and returns the carbonyl compounds to the more volatile underivatized state and contributes to a low bias in the analytical results; and
- If the analytical separation is insufficient, the DNPH degradation products can coelute with target carbonyl derivatives.

The extent of interference depends on the temporal variations of both the ozone and the carbonyl compounds and the duration of sampling. Carbonyl compound losses have been estimated to be as great as 48% on days when the ambient O₃ concentration reaches 120 ppbv. Eliminating this measurement interference problem by removing or scrubbing O₃ from the sample ambient air stream prior to collection of the carbonyl compounds is a mandatory facet of carbonyl compounds sample collection. Two types of O₃ scrubbers, the denuder O₃ scrubber and the cartridge O₃ scrubber, have been developed. Both the denuder and cartridge O₃ scrubbers use KI as the scrubbing agent. Scrubbing is based on the reaction of O₃ with KI, specifically:



where:

O₃ = ozone (ambient)

H₂O = water (ambient)

I^S = the iodide ion from KI forming molecular iodine (I_2), oxygen (O_2), and the hydroxide ion (OH^S)

The denuder O_3 scrubber can effectively remove O_3 at sample collection flow rates up to 1 Lpm and has sufficient scrubbing capacity to meet the needs of carbonyl compounds measurement for enhanced O_3 monitoring programs; the cartridge O_3 scrubber is susceptible to plugging problems in the presence of moisture and is not applicable to the NATTS Program. Consequently, EPA has determined that, for the NATTS Program, only the denuder scrubber will be used. Details of the denuder O_3 scrubber equipment and recommended procedures for use are presented below.

4.2.1.2 Denuder O_3 Scrubber

The denuder O_3 scrubber consists of a copper tube coated internally with a saturated solution of KI. The tube is coiled and housed in a temperature-controlled chamber that is heated to and maintained at 50 to 70 °C during sample collection. Heating prevents condensation from occurring in the tube during sampling. The scrubber is connected to the inlet of the sample collection system. Sample air is extracted from a sample probe and distribution manifold (see below) and pulled through the scrubber by an oil-free vacuum pump. O_3 in the sample air is converted (i.e., scrubbed) by the chemical reaction described above.

The denuder O_3 scrubber is reusable. The copper tube should be recoated with a saturated solution of KI after each six months of use. The denuder O_3 scrubber prepared as described in EPA Compendium Method TO-11A⁸ has been found to effectively remove ozone from the air stream for up to 100,000 ppb-hours. Thus, the scrubber will last for six months of 24-hour sampling on every sixth day when sampling air with an average O_3 concentration of 120 ppbv. If sampling frequency is increased, the usable period for the O_3 scrubber is proportionately decreased.

To recoat the denuder, the copper tube is filled with a saturated solution of KI in water. The solution should remain in contact with the tube for a few minutes, and then the tube should

be drained. The tube should be dried by blowing a stream of clean air or nitrogen through it for about one hour.

An alternative to using a KI-coated copper tube is to use a modified Dasibi ozone scrubber device. The manganese-dioxide-coated screens are replaced with 15 KI-coated copper or stainless steel screens assembled in a cartridge holder. The screens are washed in pure water in a sonic bath and dried. The screens are then coated by dipping them into a saturated KI solution in water and air dried. This procedure deposits about 4 mmoles or about 700 milligrams (mg) of KI over a sandwich of 15, 2-in. diameter screens. The coated screens are assembled in the Dasibi encasement with a fiberglass filter at each end, and the encasement is closed and sealed including the O-rings with the screws. Based on this removal capacity, this scrubber will last approximately 300 days when sampling air with an average O₃ concentration of 120 ppbv at a rate of 1 Lpm.

Another alternative to using a KI-coated copper tube is the use of a commercially available KI-coated glass denuder housed in a heated compartment. Manufacturers' specifications for longevity of the denuder should be followed carefully to ensure timely recoating or replacement.

Denuder O₃ Scrubber Equipment

Figure 4.2-1 presents a cross-sectional view of the denuder O₃ scrubber. The scrubber is comprised of the following components:

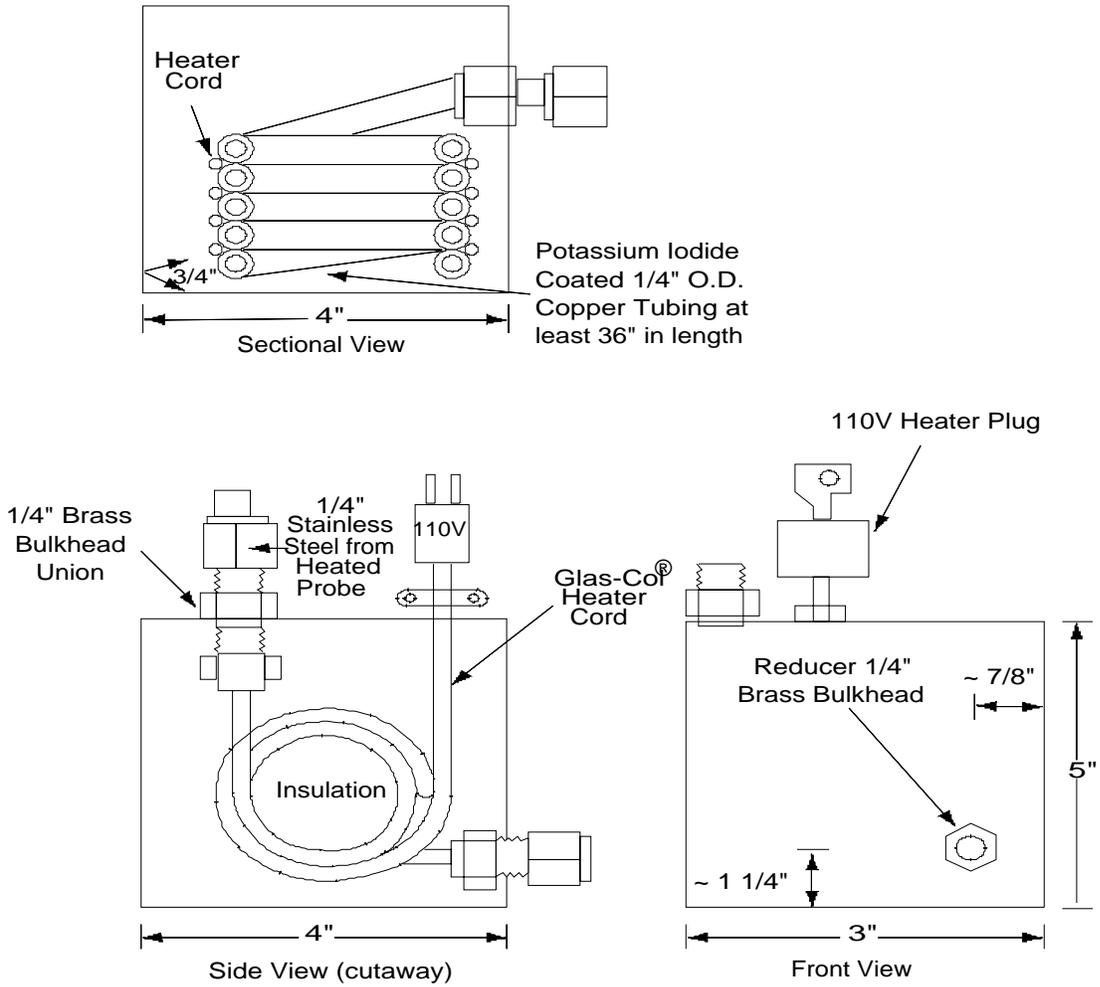


Figure 4.2-1. Cross-Sectional View of the Denuder O₃ Scrubber

- Copper tubing. 0.250 inch. copper tubing at least 36 in. length, coiled into a spiral approximately 2 to 4 in. diameter; used as the body of the O₃ scrubber.
- KI. The inside surface of the copper coil is coated with a saturated solution of ACS Reagent-Grade KI and is used to provide the O₃ scrubbing mechanism.
- Cord heater. A 2-foot long cord heater, rated at approximately 80 watts, wrapped around the outside of the copper coil is used to provide heat to prevent condensation of water or organic compounds from occurring within the coil.
- Thermocouple. This Chromel-Alumel (Type K) thermocouple is located between the surface of the copper coil and the cord heater and is used to provide accurate temperature measurement for temperature control.
- Temperature controller. This Type K active temperature controller is used to maintain the O₃ scrubber at 66 °C as referenced by the Type K thermocouple.
- Fittings. These are bulkhead unions attached to the entrance and exit of the copper coil; used to allow connection to other components of the sampling system.
- Chassis box. This box is a conveniently sized aluminum enclosure used to contain the fittings, coated copper tube, heater, and thermocouple.

4.2.1.3 Cartridge O₃ Scrubber

Although allowable under EPA Compendium Method TO-11A⁸, use of cartridge O₃ scrubbers is not allowed for NATTS.

4.2.2 Sample Collection Systems

Sample collection systems should be capable of unattended operation in order to allow for single and duplicate sample collection in a practical manner. Sampling systems are manufactured commercially or can be custom manufactured by the user for a specific application; several sampling systems are commercially available. The following sections generally describe sampling equipment, procedures, and specifications. Also, recommended system specifications applicable to the evaluation and procurement of sampling systems are presented.

4.2.2.1 Sample Collection System Equipment

The cartridge sampling system consists of the following primary components:

- Inlet probe and manifold assembly. This assembly is constructed of glass or stainless steel and is used as a conduit to extract sample air from the atmosphere at the required sampling height and distribute it for collection.
- Bypass pump. This is a single- or double-headed diaphragm pump, or a caged rotary blower, used to continuously draw sample air through the inlet probe and manifold assembly at a rate in excess of the sampling system total uptake. All excess sample air is exhausted back to the atmosphere.
- Sample pump. This is an oil-free vacuum pump capable of achieving an inlet pressure of -25 in. Hg continually that is used to extract sample air from the manifold assembly and pull it through the sample cartridges during collection.
- Sample inlet line. This line is chromatographic-grade stainless steel or Teflon tubing used to connect the sampler to the manifold assembly that should be kept as short as possible.
- O₃ scrubber. This is a temperature-controlled denuder scrubber used to remove ambient O₃ from the sample airstream prior to exposure to the sample cartridge.
- Sample cartridge. This cartridge is a plastic housing containing silica gel solid sorbent (see Section 4.4 of EPA Compendium Method TO-11A) coated with DNPH that is used to contain the collected sample for transportation and analysis.
- Adjustable orifice and mass flow meter assembly, or electronic mass flow controller. This assembly is an indicating flow control device(s) used to maintain a relatively constant flow rate ($\pm 30\%$) over a specific sampling period under conditions of changing temperature (20 to 40 °C) and humidity (0 to 100% relative).
- Digital timer or microprocessor. This is an event control device used to allow unattended operation (i.e., activation and deactivation of each sampling event) of the collection system.
- Tubing and fittings (stainless steel or Teflon). These are hardware for isolation and interconnection of components used to complete system interconnections. All stainless steel tubing in contact with the sample prior to analysis should be chromatographic-grade stainless steel, and all fittings should be 316-grade

stainless steel. Note that if the manifold is heated, stainless steel tubing should be used because of the potential of off-gassing of tubing or other materials.

4.2.2.2 Carbonyl Sampling System Certification

Carbonyl sampling systems must exhibit nonbiasing characteristics before being used to collect samples. These sampling systems must be subjected to a laboratory zero certification to quantify any additive biases that may be attributed directly to the sampling systems. The certification procedure is analogous to the zero portion of the procedures used to certify canister sampling systems (Section 4.1.6). Specifically, the sampling system is characterized using humidified zero air. A humidified zero air blank to gauge the potential for additive bias is collected through the sampling system using the same conditions that will be applied to collect field samples. The blank sample is analyzed for specific NATTS Program carbonyl target analytes. The criteria applied to the zero certification process require that the concentration determined for each target analyte species be 0.2 ppbv or less (a value consistent with a 1000-L sampling volume).

4.2.2.3 Sample Collection Procedures

Samples are collected on individual solid sorbent sample cartridges using a single pump and flow control device. An oil-free vacuum pump draws ambient air from the sampling probe and manifold assembly through the sample cartridge at a relatively constant flow rate during each specific sampling event. A flow control device(s) is used to maintain a relatively constant sample flow rate through each sample cartridge over each specific sampling period. A nominal flow rate of 600 to 900 mL/min is applied for sample collection. During operation, the control device is programmed to activate and deactivate the components of the sample collection system, consistent with the beginning and end of the sample collection period. Cartridge sampling systems can collect sample from a shared sample probe and manifold assembly or from a dedicated stainless steel sample probe, manifold assembly, and bypass pump. If a dedicated probe, manifold assembly, and bypass pump are used, a separate timer device should be incorporated to start the bypass pump several hours prior to the first sampling event of a

collection period to flush and condition the probe and manifold assembly components. The connecting lines between the manifold assembly and the sampling system should be kept as short as possible to minimize the system residence time.

The following generic steps are provided for operation of a typical collection system while collecting a sample:

1. Set the sampling system to the desired sample collection flow rate(s) (i.e., referencing the corresponding ambient calibration curve(s) and considering the desired total volume of ambient air to be sampled and the sampling period for each sampling event).
2. Program the digital timer control system to start and stop sample collection consistent with program specific collection frequency requirements.
3. Using vinyl gloves, attach the sample cartridge to the sampling system: one cartridge to collect a single sample, two cartridges for duplicate samples.
4. Record the start and end time of the collection event and the corresponding flow rate onto the sampling field data sheet and calculate an average flow rate.
5. Using vinyl gloves, remove each sample cartridge (i.e., one at a time), cap both ends, and attach an identifier to each (i.e., again, one at a time to avoid mislabeling). Sample event number, sample type, location, and collection date should be recorded on the field data sheet.
6. Place cartridges in tightly enclosed transport containers and transport the samples and corresponding information to the central laboratory for preparation and analysis.

Calculation of method precision for the NATTS Program is determined by repeated analysis of duplicate samples. Consequently, 10% of all sample collections will be duplicate samples. A duplicate sample is a sample that is collected simultaneously with a primary sample (i.e., on two separate cartridges through the same sampling system at the same time). This simultaneous collection is typically achieved by teeing the inlet line of the sampler to each of the two cartridges. Each cartridge has its own associated flow control device to achieve integration over the 24-hour collection period. A common pump pulls the sample through both collection cartridges (i.e., separately but simultaneously). Collocated sampling involves the use of two

separate sampling systems to generate two samples at the same location. The extent of collocated sampling is dictated by the availability of sampling equipment.

4.2.2.4 Collection System Specifications

Primary system specifications are presented below. However, additional system specifications and considerations may be added at the discretion of the user.

- An in-depth, detailed manual covering all aspects of the sample collection system (i.e., operation, maintenance, etc.) must be provided by the vendor.
- The overall size of the sampling system should be kept as compact as possible. The sampling systems are usually installed into existing sampling site shelters where many other parameters (i.e., criteria pollutants concentrations, meteorological conditions, etc.) are also measured. Each of the other parameters requires separate instrumentation and consequently the shelters can become very crowded.
- The sample collection system should meet all applicable electrical and safety codes, operate on standard 110 volts of AC power, and incorporate a main power fuse or circuit breaker. Specific potential electrical hazards and/or other safety considerations should be detailed in a supplied user's manual.
- The overall configuration and components comprising that configuration should allow for simple operation, maintenance, and service of the sample collection system. Materials used in the construction of components of the sample collection system should exhibit nonbiasing characteristics. The components themselves should generally conform to the descriptions presented above. All surfaces that come in direct contact with sampled air should be constructed of glass, stainless steel, Teflon, or Viton[®].
- The sampling system must incorporate or provide for removal of O₃ consistently with the denuder O₃ scrubber design detailed above.
- The sampling system should incorporate a digital timer or microprocessor event control device. At a minimum this event control device should be able to be programmed to control the start and stop times of every collection event within a given 24-hour sampling duration. The event control device should incorporate a battery backup system to address power failure situations. Incorporation of a battery backup system should result in fewer invalidated sample collections and a higher sample collection completion rate. The battery backup system would ensure that all programmed control activities and collection process data would

be retained for a predetermined interval should standard power to the system be interrupted. Retaining the programmed control activities would allow sampling to resume automatically at the next programmed event time when standard power is once again established to the sampling system. Retaining the collection process data obtained for samples collected prior to the termination of standard power would allow these samples to be qualified as valid or invalid based on sampling start and stop times and initial and flow rates. Although not absolutely necessary, the incorporation of a miniature printer that would allow for a report style listing of all sample collection process data would be advantageous.

4.2.3 Analysis Procedures and Issues

A detailed SOP must be prepared to encompass all the procedures involved in the analysis of field samples. Carbonyl compounds measured using EPA Compendium Method TO-11A⁸ for the NATTS Program are shown in Table 4.2-1.

4.2.3.1 Analytical Interferences and Contamination

Contamination and interference can occur throughout the process from sampling to analysis and must be examined closely. Pure solvents and clean laboratories can prevent interference and contamination.

Solvents used in extractions and analysis must be high purity or reagent grade. ACN must be high purity and carbonyl free. If it is not, higher concentrations of formaldehyde during analysis of samples and blanks can result. All glassware must be washed, rinsed with deionized distilled water, allowed to dry, then rinsed again with ACN and baked in a vacuum oven at 60°C for 30 min. Burdick & Jackson[®], carbonyl-free ACN meets all quality specifications of the methodology.

Table 4.2-1. Carbonyl Compounds Measured Using EPA Compendium Method TO-11A

Compound	CAS No.
formaldehyde	50-00-0
acetaldehyde	75-07-0
acetone	67-64-1
propionaldehyde	123-38-6
crotonaldehyde ¹	4170-30-3
butyr/isobutyraldehyde	123-72-8
benzaldehyde	100-52-7
isovaleraldehyde	590-86-3
valeraldehyde	110-62-3
<i>o</i> -tolualdehyde	529-20-4
<i>m</i> -tolualdehyde	620-23-5
<i>p</i> -tolualdehyde	104-87-0
hexaldehyde	66-25-1
2,5-dimethylbenzaldehyde	5779-94-2

¹Analytical problems similar to those of acrolein are encountered with crotonaldehyde. Compounds required for NATTS' first year are indicated in bold print. Shading indicates the other compounds that will ultimately be required for NATTS.

Acetone vapors found in the laboratory during extraction will also cause concentrations of compounds determined by analysis to be inaccurate. Acetone is found in many common items such as permanent markers, felt tip pens, paint, etc. It is therefore necessary to keep all acetone products out of the laboratory. Acetone is also encountered when laboratory facilities are shared; additional precautions will be required to mitigate acetone contamination during extraction.

4.2.3.2 Extraction and Chromatography Issues

Each carbonyl cartridge should be examined closely before extracting. Cartridges that are leaking silica gel must be voided. Cartridges that are dark orange or reddish contain moisture and should be firmly tapped several times before extraction. These samples must be flagged in the extraction log as they may need to be diluted. Once extraction has occurred, the extract

should also be examined. Any solution with noticeable particles must be filtered before the sample can be analyzed to prevent clogging the HPLC filters, frits and tubing.

Due to the acidity of the cartridge, the compound acrolein becomes unstable and breaks down partially or completely into other compounds; this breakdown makes quantitation based on a single peak inaccurate. Therefore, EPA Compendium Method TO-11A⁸ is presently suitable for the detection of this compound.

The chromatogram of each sample must have a DNPH peak to indicate that unreacted reagent is still available on the cartridge (i.e., the capacity of the cartridge for the collection of carbonyl compounds has not been exceeded). This DNPH peak occurs at approximately 4.4 min into the HPLC chromatogram and is usually the highest peak on the chromatogram. If there is no DNPH peak, the reagent has been expended and the sample must be voided because collection of the carbonyl compounds may not have been quantitative. Exhaustion of the derivatization reagent is an indication of high concentrations of aldehydes/ketones at the site and an insufficient amount of DNPH within the cartridge for complete derivatization. If the DNPH peak is smaller than usual and the aldehyde/ketone peak concentrations are not above the highest level of the curve, the sample is valid.

Acrolein

Method TO-11A⁸ has been determined to be an inappropriate methodology for acrolein. The reaction of DNPH with acrolein can produce at least two tautomers of the hydrazone derivative, and the proportions of the two compounds to each other and the conditions under which one interconverts to the other have not been established. Accordingly, acrolein is to be measured using EPA Compendium Method TO-15 (see Section 4.1).

In the analysis of standards under the HPLC analytical conditions commonly used for EPA Compendium Method TO-11A⁸, the two distinct acrolein peaks are readily observed (Figure 4.2-2). In this standard, the peak labeled "Acrolein Peak 2" is clearly seen to interfere

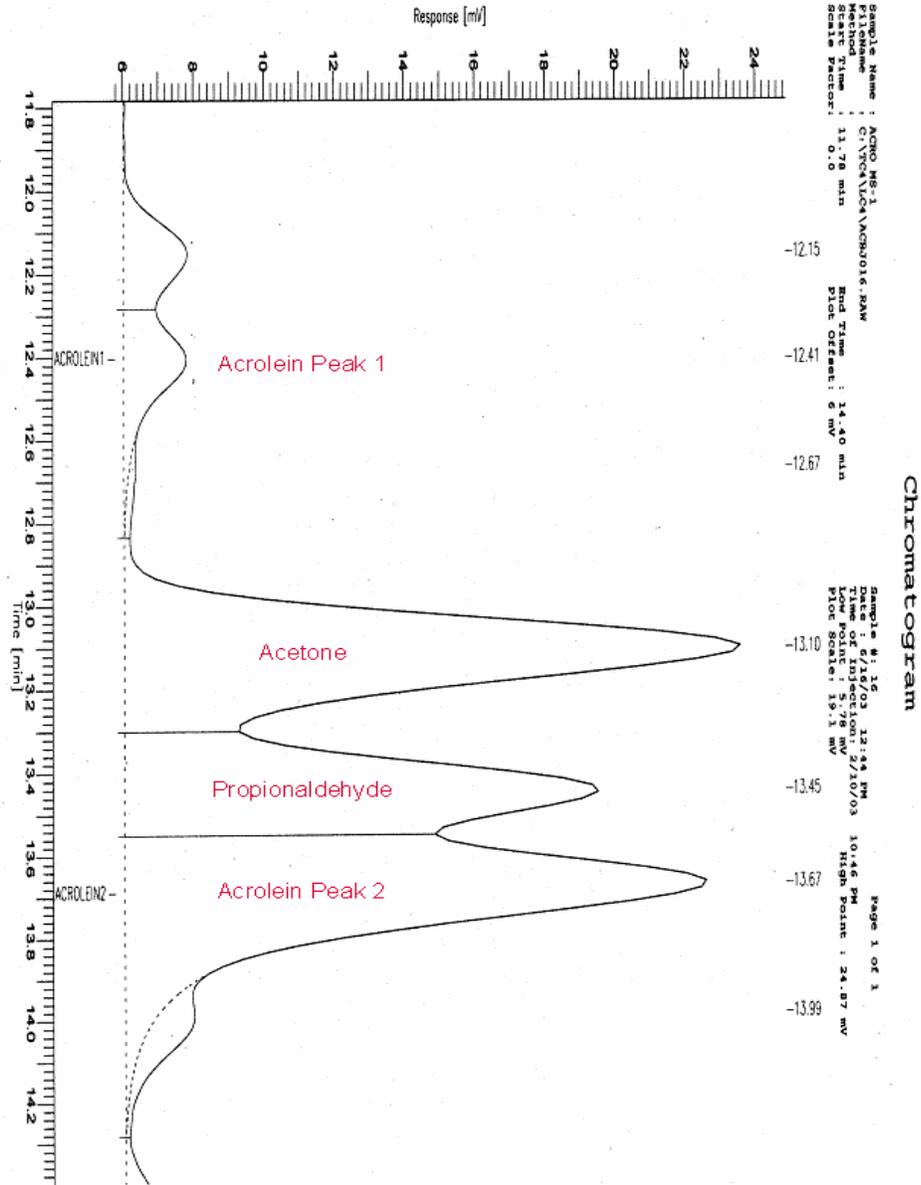


Figure 4.2-2. HPLC Chromatogram of Analysis of Derivatized Aldehyde/Ketone Standard Solution, Showing Two Acrolein Peaks as Well as the Acetone and Propionaldehyde Peaks

with the propionaldehyde peak, as the peaks do not show baseline resolution. With the computer integration as indicated, propionaldehyde would be underreported, i.e., reported values would be biased low. The reported values for acetone would likewise be biased low, although not as severely as propionaldehyde. As the labeled peaks in the chromatogram show, acetone, propionaldehyde, and the two acrolein peaks all elute within two minutes of each other. In a sample of a standard, with the three analytes all present at relatively high concentrations and all at the same concentration, the acrolein interference with propionaldehyde and propionaldehyde interference with acetone are clearly visible. A further complication in making an accurate measurement of any or all of these analytes is the nearly ubiquitous presence of large quantities of acetone in ambient air field samples.

In field samples, however, where one of the three analytes (usually acetone) may be present at levels significantly higher than the others, the chromatography is distorted and the extent of the interference of these derivatized carbonyl compounds with each other is very difficult to determine (Figures 4.2-3, 4.2-4, and 4.2-5).

Figure 4.2-3 shows peaks that represent acetone, propionaldehyde, and presumably acrolein peak No.2 (the identification of the acrolein peak No. 2 is uncertain). The acetone peak, with acetone present in the sample at a level order(s) of magnitude higher than propionaldehyde, is allowed to go off scale in this figure in order to amplify the detail in the region of the chromatogram that includes propionaldehyde. (The same chromatogram with acetone on scale is shown in Figure 4.2-4.) The integration of the propionaldehyde peak (as illustrated in Figure 4.2-3) shows propionaldehyde would be reported at a low bias due to the interference arising from the other peaks in the chromatographic elution window.

In Figure 4.2-5, a peak representing propionaldehyde cannot be reported at all. The propionaldehyde peak either is not present or is completely overshadowed by the acetone peak. In this case, no value can be reported for propionaldehyde.

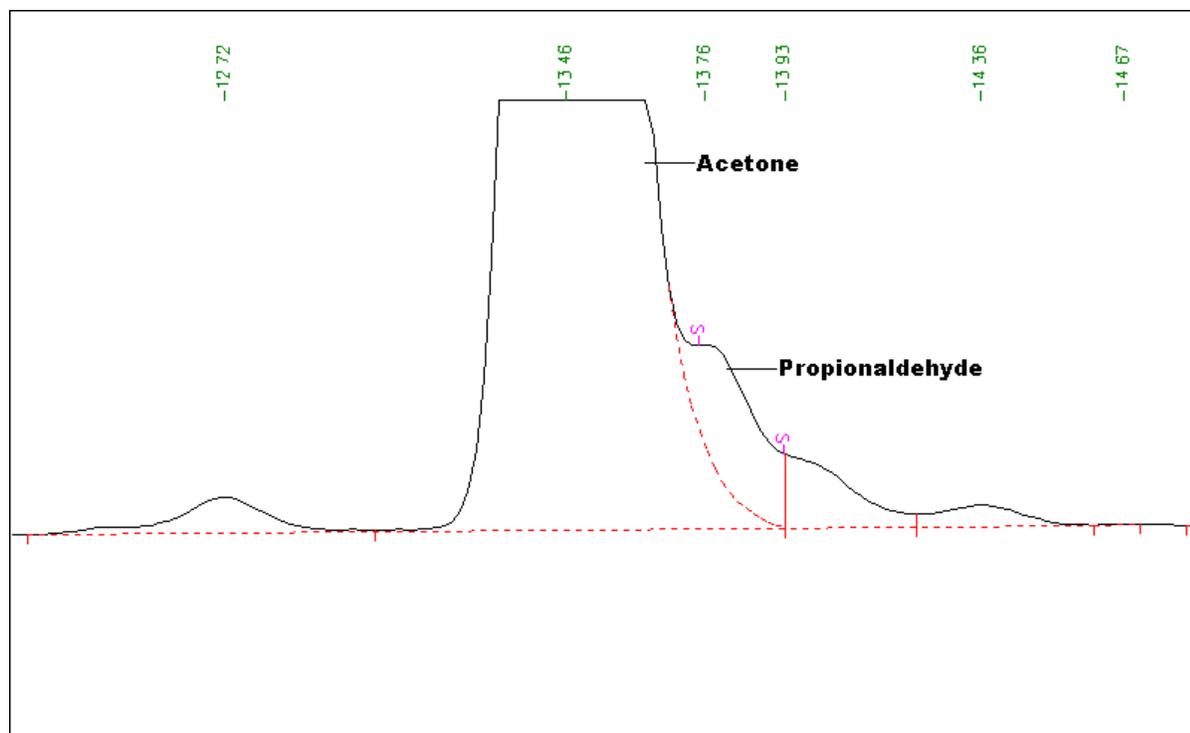


Figure 4.2-3. Chromatogram Showing Elution of Acetone, Propionaldehyde, and Acrolein Hvdrazones

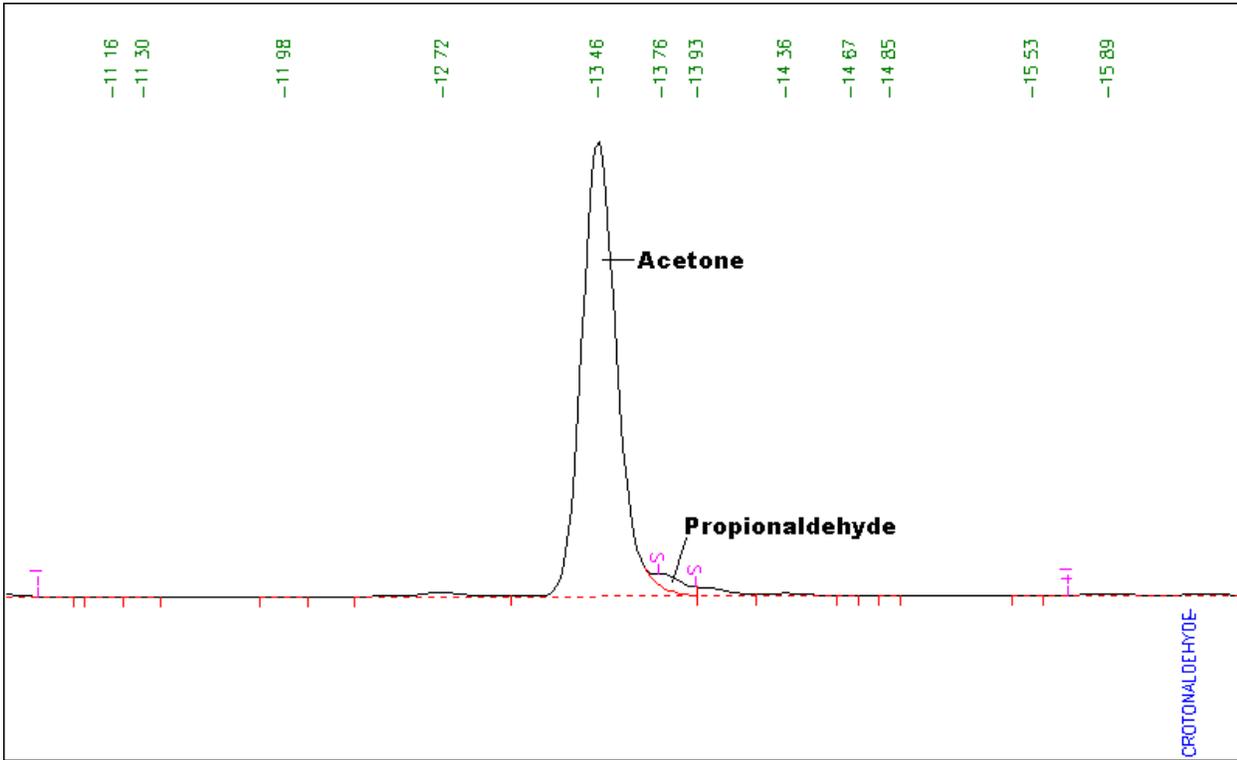


Figure 4.2-4. Same Chromatogram as Figure 4.2-3, with Acetone Peak on Scale

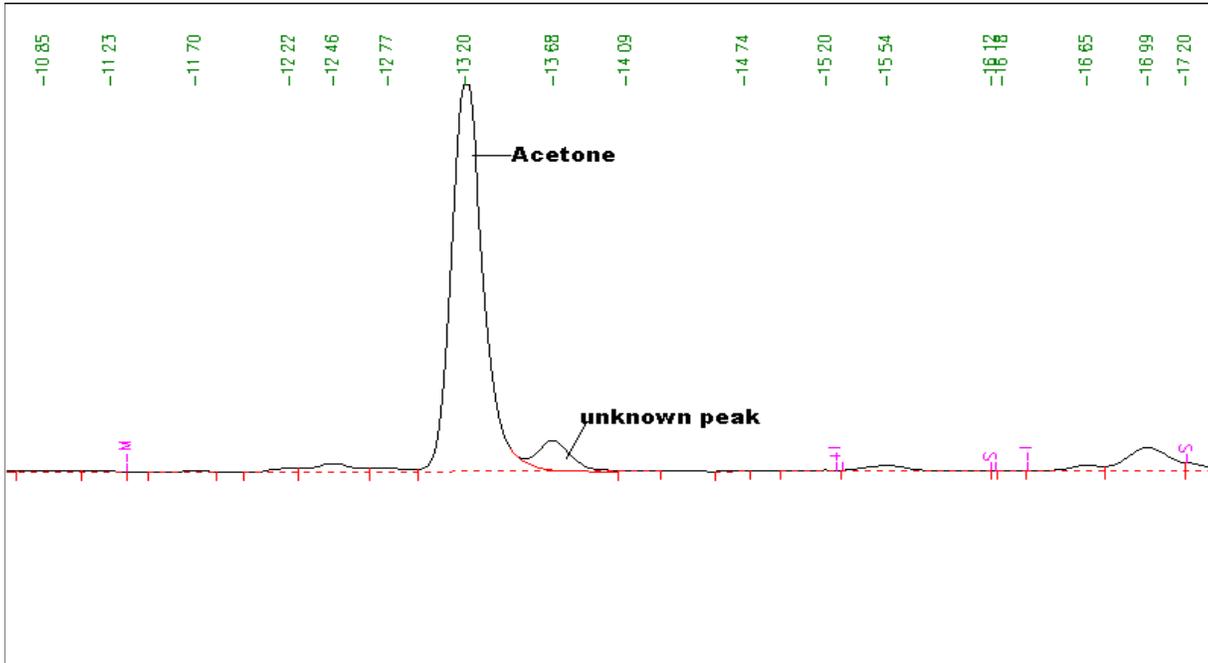


Figure 4.2-5. Chromatogram of a Field Sample for Which Propionaldehyde Appears Either Not to be Present or to be Completely Enveloped by the Acetone Peak

These chromatograms illustrate the difficulty of reporting accurate and reproducible values for propionaldehyde and acetone, as well as the difficulty of accurate identification of propionaldehyde in the presence of relatively large quantities of acetone. There is a very real concern that the acetone peak may be mistaken for propionaldehyde and, given the usual difference to be expected in the sizes of the two peaks in field samples, the reported value for propionaldehyde could be biased significantly higher than the actual concentration of propionaldehyde present in the sample.

The analytical conditions commonly used for EPA Compendium Method TO-11A clearly show that the acrolein hydrazone(s) are not to be reported using this methodology because quantitative analysis cannot be performed accurately:

- Because of the chemistry of the acrolein derivatization, two chromatographic “acrolein” peaks must be considered in the quantitative analysis; and
- The very likely presence of large quantities of acetone in the same chromatographic window is very likely to distort the chromatographic elution and will make confident identification of the two acrolein peaks very difficult under the common analytical conditions used for this analysis.

Acrolein is to be measured using EPA compendium TO-15 (see Section 4.1).

4.2.3.3 Sample Preparation

Once sampling has occurred, the field samples and field blanks are shipped back to the laboratory in individual, sealed foil pouches. Upon receipt of the samples, each sample and field blank is logged into the LIMS, given an ID number, placed in a sealable bag with a COC and stored in a refrigerator at 4°C until extraction. Extraction should occur within two weeks of the sampling episode. For remote sites involving great travel distances and long travel times, extraction must still occur within two weeks of sampling.

Sample Extraction

Field samples and a blank cartridge of the same lot are removed from the refrigerator and connected to a clean, solid phase extraction manifold. A glass syringe is attached to the cartridge, and 5 mL of ACN is back flushed from the syringe through the cartridge and into a 5-mL volumetric flask. A polypropylene syringe may be substituted for the glass syringe, but the polypropylene syringe MUST be considered disposable—i.e., discarded after a single use. The flask is then diluted with ACN to the 5-mL mark. This extract is transferred to vials for analysis and cold storage (4 °C). Samples must be analyzed within 30 days of extraction. An extraction log with the site code, sample date, identification number and comments section is kept for each sample. This log is permanently affixed in a logbook and kept in the laboratory.

4.2.3.4 Preparation of the Analytical System

Operating parameters for HPLC when formaldehyde is the compound of interest are described in Section 11.3.1 of EPA Compendium Method TO-11A.⁸ Samples are analyzed on the HPLC, Waters 2695 separations module, or equivalent, with a Zorbax C18 reversed phase column and guard column. The 2487 dual wavelength absorbance detector is set at 360 nm and must be allowed to warm up for 30 min before analysis is performed. Deionized distilled water, ACN and methanol used in the analyses should be HPLC grade, and each must be sonicated or degassed with helium prior to use. The HPLC grade water is filtered through a 0.2- μ m nylon membrane filter to eliminate microbial growth. Solvent should pump at the desired flow rate of 1 to 2-mL/min for 30 min. Prior to the first injection, system pressure should remain constant. A higher than normal pressure indicates a clogged in-line filter or guard column. Once the system has stabilized, calibration may begin. Other HPLC instruments, like the Hewlett-Packard LC-1050 with diode array detector, have also been used in aldehyde and ketone analysis under similar conditions.

Initial Calibration

HPLC calibration is performed using commercially prepared stock solutions ranging from 0.01 to 0.5 µg/mL of each target analyte purchased as a DNPH derivative of the carbonyl compound. These solutions are stable up to 6 months from the date opened. Each calibration standard (at least five levels) is analyzed three times, and area response is tabulated against mass concentration injected to prepare a calibration curve. The slope of the curve (instrument response per sample concentration) yields the response factor (RF). Linear response is indicated where a correlation coefficient of at least 0.999 for a linear least squares fit of the data is obtained. A commercially prepared standard from a second vendor is also analyzed three times to evaluate precision and to validate each new curve. Repeated analysis of this second source standard is used as the mid-level standard to evaluate precision, peak resolution and retention time drift throughout the life of the calibration curve. For calculations, refer to Section 12 of EPA Compendium Method TO-11A.⁸ The multipoint calibration is performed at least once every 6 months to verify the precision and calibration range. A new multipoint calibration curve is also required if the column is changed on the instrument, major maintenance is performed on the instrument or there is a change in the matrix or a reagent.

Acceptance Criteria for Initial Calibration Curve

The following criteria must be met for an acceptable initial calibration curve:

- Each analyte must have a correlation coefficient greater than or equal to 0.999; and
- The relative percent error for each set of triplicate injections of calibration standards should be within 20% of the theoretical concentration.

$$\text{Relative Percent Error} = \frac{\text{TLC} - \text{OLC}}{\text{TLC}} * 100 \quad (4.2-2)$$

where:

TLC = theoretical level of concentration

OLC = observed level of concentration

- The second source quality control (SSQC) sample must be within 15% of target concentrations.
- The intercept should be 10,000 area counts per compound, for the current analysis as performed on the Waters 2695 HPLC.

4.2.3.5 Process Blanks

To ensure data quality and obtain quantitative carbonyl compound concentrations, the collection of blanks is necessary. For national air toxics monitoring three types of blanks used to ensure data quality: certification blanks, field blanks and method blanks. The guidance here should be considered a minimum and users are encouraged to build upon this guidance.

- Certification blanks consist of three commercially prepared DNPH-coated, prepacked cartridges that are eluted with ACN and analyzed to verify the acceptability of a specific cartridge lot from the vendor. Certification blanks are analyzed for each specific lot used for sampling. Alternatively, a “Certificate of Analysis” accompanying each lot may be used for certification as long as it meets the blank acceptance criteria.
- Field blanks are blank cartridges which are sent to the field, connected to the sampling system and treated identically to the samples except that no air is drawn through the cartridge. Field blanks are used to assess the background carbonyl levels for cartridges used during the ambient sample collection process.
- Method blanks are blank cartridges that never leave the laboratory and are extracted with every batch of samples. Method blanks are used to assess possible laboratory contamination.
- If evaluation of the potential for contamination in the shipping process is desired, a trip blank may be used. A trip blank is shipped to and from the field but is not opened until it is extracted in the laboratory.

Acceptance Criteria for Blanks

A “Certificate of Analysis” accompanying each lot of DNPH-coated, prepacked cartridges may be used for certification as long as the analysis meets the blank acceptance criteria. If the values reported in the “Certificate of Analysis” do not meet acceptance criteria, three laboratory blanks from that lot must be analyzed and must meet blank acceptance criteria. If the mean mass ± 3 standard deviations ($\pm 3 s$) for the group of three laboratory blanks meets the criteria, no further certification of laboratory blanks is required for that particular cartridge lot. If large differences are observed for the three laboratory blank samples, additional laboratory blanks should be analyzed to obtain values for the mean and standard deviation. If the certification blanks or the “Certificate of Analysis” do not meet the specified blank acceptance criteria, the carbonyl tubes should be shipped back to the manufacturer and a new lot requested. For certification blanks or the “Certificate of Analysis” to be acceptable, the following criteria must be met:

- Formaldehyde: < 0.15 $\mu\text{g}/\text{cartridge}$
- Acetaldehyde: < 0.10 $\mu\text{g}/\text{cartridge}$
- Acetone: < 0.30 $\mu\text{g}/\text{cartridge}$
- Other: < 0.10 $\mu\text{g}/\text{cartridge}$.

For field blanks to be acceptable, the following criteria must be met:

- Formaldehyde: < 0.3 $\mu\text{g}/\text{cartridge}$
- Acetaldehyde: < 0.4 $\mu\text{g}/\text{cartridge}$
- Acetone: < 0.75 $\mu\text{g}/\text{cartridge}$
- Sum of others: < 7.0 $\mu\text{g}/\text{cartridge}$.

If a field blank does not meet the criteria and the corresponding sample has concentrations above the average mean from the previous year, the sample is blank subtracted and flagged on the report. If the corresponding sample concentration is not high, the sampling

site is notified so that another field blank can be scheduled. Field blank sampling should continue until the sample meets the acceptance criteria.

The following criteria must be met for method blanks:

- Formaldehyde: < 0.10 µg/cartridge
- Acetaldehyde: < 0.20 µg/cartridge
- Acetone: < 0.55 µg/cartridge
- Sum of others: < 3.00 µg/cartridge.

If the method blank fails to meet acceptance criteria, that method blank should be reanalyzed and the laboratory checked for signs of possible contamination. If the analysis still fails to meet acceptance criteria, the samples are blank subtracted and flagged on the report.

4.2.3.6 Precision and Accuracy

For 10% of field collections, samples must be collected in duplicate. A primary and a duplicate sample are collected from a common manifold and sample inlet line using the same sampling system but two independent flow control devices. Duplicate samples must be analyzed in replicate. Replicate analyses of the duplicate samples should agree to within 10% for concentrations > 0.5 µg/cartridge and the means of the replicate analyses for the duplicate samples should agree to within 20%. If the means of the duplicate samples do not agree to within 20% and the replicate analyses are within 10%, check the samples to ensure that they are truly duplicate, check the sample flow rates to ensure that the sampler is working correctly and check chromatography to make sure peaks are integrated correctly. If both sampler and chromatography are acceptable, repeat the sample analysis. Precision is determined as the RPD using the following calculation:

$$RPD = \frac{|X_1 - X_2|}{\bar{x}} \times 100 \quad (4.2-3)$$

where:

$X1$ = ambient air concentration of a given compound measured in one sample

$X2$ = concentration of the same compound measured during replicate analysis

x = arithmetic mean of $X1$ and $X2$.

Accuracy will be assessed by quarterly analysis of a PE sample supplied by EPA.

4.2.3.7 Method Detection Limits

Minimum MDLs that must be achieved for the NATTS Program are presented in Table 4.2-2. MDLs are determined at least annually using the procedures in 40 CFR Part 136 Appendix B. A low-level standard of the carbonyl derivatives is prepared at a concentration within two to five times the estimated method detection limit. Commercially prepared DNPH-coated, prepacked cartridges (7 to 10) are spiked with the standard. Spiked tubes are extracted as explained in Section 4.2.3.3. The measured concentration is calculated using the calibration curve. The concentration of derivatized aldehyde/ketone in the sample is calculated below:

$$C = \frac{(SR - I)}{S} \quad (4.2-4)$$

where:

C = concentration of derivatized compound ($\mu\text{g}/\text{mL}$)

SR = sample response area units

I = intercept of calibration curve

S = slope of calibration curve.

The standard deviation is calculated for the number of samples analyzed; the standard deviation and the appropriate Student's t value are used to calculate the MDL as described in 40 CFR Part 136 Appendix B. Table 4.2-2 presents Student's t values for different degrees of freedom. MDLs should be calculated in units of ppbv reflecting different collection volumes across the range of 800 L through 1300 L, as shown in Table 4.2-3.

Table 4.2-2. Student's t Values Used in Calculation of Method Detection Limits

Number of Replicates	Degrees of Freedom (n - 1)	t Values
7	6	3.143
8	7	2.996
9	8	2.896
10	9	2.821

Table 4.2-3. Target MDLs for Carbonyl Compounds for the NATTS Program

Compound (ppbv)	Sample Volume (L)					
	800	900	1000	1100	1200	1300
formaldehyde	0.007	0.006	0.006	0.0051	0.0047	0.0043
acetaldehyde	0.006	0.005	0.005	0.0045	0.0041	0.0038
acetone	0.010	0.009	0.008	0.0072	0.0066	0.0061
propionaldehyde	0.002	0.002	0.002	0.0016	0.0015	0.0014
crotonaldehyde	0.002	0.002	0.002	0.0014	0.0013	0.0012
butyr/isobutyraldehyde	0.002	0.002	0.002	0.0015	0.0014	0.0013
benzaldehyde	0.003	0.002	0.002	0.0020	0.0019	0.0017
isovaleraldehyde	0.002	0.002	0.001	0.0013	0.0011	0.0011
valeraldehyde	0.002	0.001	0.001	0.0012	0.0011	0.0010
tolualdehydes	0.004	0.003	0.006	0.0026	0.0024	0.0022
hexaldehyde	0.002	0.002	0.002	0.0016	0.0015	0.0014
2,5-dimethylbenzaldehyde	0.001	0.001	0.001	0.0009	0.0008	0.0007

4.2.3.8 Sample Analysis

When the calibration and MDLs meet acceptance criteria, the instrument is ready to analyze samples. The autosampler vials are placed in a carousel and loaded onto the instrument. An injection size of sample extract geared to the manufacturer's specifications for the analytical instrument is performed with an automatic sample injector. A mobile phase gradient of water, ACN and methanol is used to perform the analytical separation at a flow rate of 1.0 mL/min. Each sequence loaded onto the instrument must start with an ACN instrument blank followed by a QC standard, another ACN instrument blank, and the method blanks for each lot of samples to be analyzed followed by the samples. A QC standard must be analyzed every 12 hours to ensure that the instrument is within calibration and the retention times for the compounds have not shifted. The sequence is completed with a third ACN instrument blank, a final QC standard and a final ACN instrument blank. For the ACN to meet acceptance criteria, the compound concentrations must be less than or equal to five times the method detection limits. Carbonyl QC procedures are presented in Table 4.2-4.

4.2.3.9 Method Spikes

A method spike and method spike duplicate, consisting of coated sorbent spiked with derivatized aldehydes/ketones, must be analyzed once every quarter to verify calibration and extraction procedures. A 1-mL aliquot of the QC Standard is transferred to a 5-mL volumetric flask, diluted to volume with ACN and mixed. This solution is used to spike cartridges (1 mL per cartridge) for these tests. The spike and spike duplicate should be within $\pm 20\%$ of the target concentration. If the concentrations are outside these limits, the calibration and extraction procedures are checked. If the calibration and extraction procedures are acceptable, the analysis is repeated. Carbonyl QC procedures are presented in Table 4.2-4. An SSQC sample is a sample of known concentration prepared by an organization different from the analyzing laboratory or the supplier of the calibration standards. The SSQC must contain all of the analytes of interest at a known concentration.

Table 4.2-4. Summary of Carbonyl Quality Control Procedures

Parameter	QC Check	Frequency	Acceptance Criteria	Corrective Action
HPLC Column Efficiency	Analyze SSQC sample	At setup and 1 per sample batch	Resolution between acetone and propionaldehyde, 1.0 Column efficiency > 5000 plate counts	Eliminate dead volume, back flush or replace the column; repeat analysis
Linearity Check	Run a 5-point calibration curve and SSQC in triplicate per Method TO-11A	At setup or when calibration check is out of acceptance criteria	Correlation coefficient 0.999, relative error for each level against calibration curve $\pm 20\%$ or less relative error	Check integration, reintegrate or recalibrate
			Intercept acceptance should be 10,000 area counts per compound which correlates to ~ 0.06 mg/mL	Check integration, reintegrate or recalibrate
Retention Time	Analyze SSQC	Once per 12 hours or less	Acetaldehyde, benzaldehyde, hexaldehyde within retention time window established by determining 3σ or $\pm 2\%$ of the mean calibration and midpoint standards, whichever is greater	Check system for plug, regulate column temperature; check gradient and solvents
Calibration Check	Analyze SSQC	Once per 12 hours or less	85 to 115% recovery	Check integration, recalibrate or reprepare standard, reanalyze samples not bracketed by acceptable standard
Calibration Accuracy	Analyze SSQC	Once after calibration in triplicate	85 to 115% recovery	Check integration, recalibrate or reprepare standard, reanalyze samples not bracketed by acceptable standard
System Blank	Analyze ACN	Bracket sample batch, 1 at beginning and 1 at end of batch	Measured concentration, 5 times the MDL	Locate contamination and document levels of contamination in file
Lot Blank Check	Analyze blank cartridge for new lots	Every lot received	Compounds must be less than values listed: Formaldehyde <0.15 $\mu\text{g}/\text{cartridge}$ Acetaldehyde <0.10 $\mu\text{g}/\text{cartridge}$ Acetone <0.30 $\mu\text{g}/\text{cartridge}$ Others <0.10 $\mu\text{g}/\text{cartridge}$	Analyze another cartridge. Notify vendor if lot blank continues to fail. Failed lots are not used for sampling.

Table 4.2-4. Summary of Carbonyl Quality Control Procedures

Parameter	QC Check	Frequency	Acceptance Criteria	Corrective Action
Field Blank Check	Field blank samples collected in the field	10% of the sampling schedule	Compounds must be less than values listed: Formaldehyde <0.4 µg/mL derivatized <0.3 µg/cartridge underivatized Acetaldehyde <0.4 µg/mL derivatized <0.4 µg/cartridge underivatized Acetone <0.6 µg/mL derivatized <0.75 µg/cartridge underivatized Others <0.10 µg/mL derivatized <7.0 µg/cartridge underivatized	Data associated with an unacceptable Field Blank are flagged. Additional Field Blanks are collected until the problem is resolved.
Duplicate Analyses	Duplicate and replicate samples	10% of the sampling schedule	<20% difference as RPD	Check integration, check instrument function, reanalyze duplicate samples
Replicate Analyses	Replicate injections	Duplicate samples only	10% RPD for concentrations greater than 0.5 µg/cartridge.	Check integration, check instrument function, reanalyze duplicate samples
Method Spike/Method Spike Duplicate (MS/MSD)	Analyze MS/MSD, using calibration standard	One MS/MSD per quarter year	80 to 120% recovery for all compounds	Check calibration, check extraction procedures
PE Samples		Quarterly	No specific acceptance criteria; evaluation of performance is goal	To be determined by EPA

4.2.3.10 Data Reduction, Validation and Reporting

A sample analysis logbook is maintained to list pertinent sample information at the time of analysis. Entries include site code, sample date, analysis date and electronic file names. A data system, such as PE Turbochrome, HP Chemstation or equivalent, is needed to acquire, integrate, quantitate and store the analytical data. Preliminary peak identifications are determined based on elution times. A data reviewer compares the sample chromatogram and the QC chromatogram to determine proper peak identifications and determine whether reintegration is needed on any peak. If the concentration of an analyte exceeds the linear range of the instrument, the sample is diluted with ACN and reanalyzed. Only the diluted value is reported

for that compound and flagged on the data report. Quantitation is based on raw amounts of analyte in $\mu\text{g}/\text{mL}$ calculated by the data system from the curve. Results in ppbv are then calculated as described below.

$$\text{ppbv} = \frac{\text{raw amount } (\mu\text{g}/\text{mL}) * 122,000}{V * \text{MW}} \quad (4.2-5)$$

where:

$122,000 = (24.4 \mu\text{L}/\mu\text{Mole} * 5 \text{ mL (volume)} * 1000 \text{ (conversion factor from microliters to nanoliters)})$

$\text{MW} = \text{molecular weight of analyte } (\mu\text{g}/\mu\text{Mole})$

$V = \text{volume of air collected in liters (ambient conditions).}$

Once the chromatograms have been reviewed, the data are exported to LIMS for review. The analytical data reviewer examines all data for overall quality and completeness. When the final review is complete, a chromatogram and area count report are printed out and stored in a folder with the COC form. Sample files are stored by sample date in a specified data storage room. Electronic copies of the data are stored in LIMS and saved as an electronic data archive.

4.3 OVERVIEW OF EPA COMPENDIUM METHOD IO-3.5

EPA Compendium Method IO-3.5⁹ (<http://www.epa.gov/ttn/amtic/files/ambient/inorganic/mthd-3-5.pdf>) is the measurement method used for sampling and analytical procedures for the measurement of metals in ambient air. For the NATTS program, the method involves collection on total suspended particulate (TSP) or particulate material ≤ 10 micron (PM-10) filters and detection by inductively coupled plasma/mass spectrometry (ICP/MS). ICP/MS uses an argon plasma torch to generate elemental ions for separation and identification by mass spectrometry. This analysis technique allows many more than 60 elements to be quantitatively determined simultaneously, and the isotopes of an element can also be determined.

NATTS participants wishing to use alternate configurations and/or approaches other than those specified in this document may do so only with Regional EPA approval provided that the alternate configuration and/or approach meet the program MQOs. It is the responsibility of the NATTS participant to demonstrate equivalent performance to the methodology specified in this document, prior to the initiation of monitoring.

4.3.1 General Description of Sampling Method and Analytical Method Requirements/Capabilities (ICP/MS)

EPA Compendium Method IO-3.5⁹ describes the multielement determination of trace elements by ICP/MS. Ambient air is pulled through filter media using a high volume sampler. Particulate phase sample is collected on the filter, and the filter is digested yielding the sample material in solution. Sample material in solution is introduced by pneumatic nebulization into a radio frequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height. The ions transmitted through the quadrupole are registered by a continuous dynode electron multiplier, and the ion information is processed by a data handling system.

4.3.2 Sampling Procedures and Issues Associated with EPA Compendium Method IO-3.5

Sample collection for quantitative determination of metal species is accomplished by pulling ambient air at a known and constant flow rate through a filter over a 24-hour collection period.

4.3.2.1 Sample Collection Procedure

The metals sample collection is performed using a commercially available TSP high volume sampling system capable of maintaining a flow rate of approximately 1.1 to 1.7 scmm (39 to 60 ft³/min) through a filter to obtain a total sample volume greater than 1584 scm across a 24-hour duration. TSP in sizes up to 25 to 50 μm (aerodynamic diameter) is collected on the filter surface.

The glass fiber filter is 8 in. x 10 in. and is constructed of spectro-quality grade glass fiber material with a pH of approximately 7.5. The filters must have a collection efficiency of 99% for particles of 0.3 μm in diameter or larger. Each filter must have a unique ID number that is a permanent part of the filter.

The sampler should be located in an unobstructed area at least 2-m from any obstacle to airflow. The inlet of the high volume sampler must be positioned in the breathing zone, 4 to 10 feet above ground level.

Similar to monitoring for other pollutants, optimal placement of the sampler inlet for PM₁₀ monitoring should be at breathing height level. However, practical factors such as prevention of vandalism, security, and safety precautions must also be considered when siting a PM₁₀ monitor. Given these considerations, the sampler inlet for microscale PM₁₀ monitors must be 2 to 7 m above ground level. The lower limit was based on a compromise between ease of servicing the sampler and the desire to have measurements that are most representative of population exposures and the desire to avoid reentrainment from dusty surfaces. The upper limit

represents a compromise between the desire to have measurements which are most representative of population exposures and a consideration of the practical factors noted above. Although microscale or middle scale stations are not the preferred spatial scale for PM_{2.5} sites, there are situations in which such sites are representative of several locations within an area where large segments of the population may live or work (e.g., central business district of a metropolitan area). In these cases, the sampler inlet for such microscale PM_{2.5} stations must also be 2 to 7 m above ground level. For middle or larger spatial scales, increased diffusion results in vertical concentration gradients that are not as great as for the microscale. Thus, the required height of the air intake for middle or larger scales is 2 to 15 m.

If the sampler is located on a roof or other structure, there must be a minimum of a 2-m separation from walls, parapets, penthouses, etc. No furnace or incineration flues should be nearby. This separation distance from flues is dependent on the height of the flues, type of waste or fuel burned, and quality of fuel (ash content). In the case of emissions from a chimney resulting from natural gas combustion, the sampler should be placed at least 5 m from the chimney as a precautionary measure. On the other hand, if fuel oil, coal, or solid waste is burned and the stack is sufficiently short so that the plume could reasonably be expected to impact on the sampler intake a significant part of the time, other buildings/locations in the area that are free from these types of sources should be considered for sampling. Trees provide surfaces for particulate deposition and also restrict airflow. Therefore, the sampler should be placed at least 20 m from the drip line and must be 10 m from the drip line when the tree(s) acts as an obstruction. The sampler must also be located away from obstacles such as buildings, so that the distance between obstacles and the sampler is at least twice the height that the obstacle protrudes above the sampler except for street canyon sites. Sampling stations that are located closer to obstacles than this criterion allows should not be classified as neighborhood, urban, or regional scale, since the measurements from such a station would closely represent middle scale stations. Additional information for siting samplers is provided in 40 CFR Part 58 Appendix E.¹⁰

The high volume sampler is calibrated using a calibrated orifice transfer standard (i.e., high volume sampler calibrator) in accordance with the specifications of EPA Reference Method, *Reference Method for the Determination of Suspended Particulates in the Atmosphere*

(High Volume Method) (EPA-600/4-77-027a)¹¹. The individual orifice plates are placed in the sampling flow stream, and the differential pressure across the orifice plate is documented using a U-tube manometer. The differential pressure readings are used to create a curve that establishes the flow characteristics of the sampler.

The following generic steps are provided for operation of a typical high volume collection system:

1. Install a preweighed filter in the sampler according to the detailed instructions in Section 4.0 of the reference method¹¹, taking care to align the filter correctly. The individual identification number of the filter must not face into the gas flow so that particulate material will not obscure the sample identifier.
2. Close the shelter and run the sampler for at least 5 min to establish run temperature conditions.
3. Record the initial flow indicator reading, the barometric pressure, and the ambient temperature; then stop the sampler.
4. Determine the flow rate from the sampler's calibration relationship to verify that it is operating in the acceptable range. Record the sample identification information and the initial flow rate on the field data form.
5. Set the timer to run the sampler for 24 hours, from 12:00 a.m. to 11:59 p.m.
6. After the sample has been collected, close the shelter and run the sampler for at least 5 min to establish final run temperature conditions.
7. Record the final flow indicator reading, the barometric pressure, and the ambient temperature; then turn the sampler off.
8. Determine the flow rate from the sampler's calibration relationship to calculate the total volume of gas sampled.
9. Remove the filter and fold the filter in two onto itself (particulate-sampled sides facing) so that none of the particulate mass is lost.
10. Place the folded filter in an appropriately sized envelope for transport to the laboratory.

4.3.3 Analysis Procedures and Issues

A detailed SOP must be prepared to encompass all of the procedures involved in the analysis of field samples. Metals measured using EPA Compendium Method IO-3.5 for the NATTS Program are presented in Table 4.3-1.

Table 4.3-1. Metals Measured Using EPA Compendium Method IO-3.5

Metals	CAS No.
antimony and compounds	7440-36-0
arsenic and compounds	7440-38-2
beryllium and compounds	7440-41-7
cadmium and compounds	7440-43-9
<i>chromium and compounds</i>	7440-47-3
cobalt and compounds	7440-48-4
lead and compounds	7439-92-1
manganese and compounds	7439-96-5
<i>mercury and compounds</i>	7439-97-6
nickel and compounds	7440-02-0
<i>selenium and compounds</i>	7780-49-2

Compounds required for NATTS' first year are indicated in bold print. Shading indicates the other compounds that will ultimately be required for NATTS. Compounds listed in italics are being considered for removal from the list of measured metals.

4.3.3.1 Interferences and Contamination

Interferences relating to this technique must be recognized and corrected. Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, air, reagents, or sample matrix. Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix must be corrected by internal standardization.

Isobaric elemental interferences are caused by isotopes of different elements that form single- or double-charged ions of the same nominal mass-to-charge ratio and therefore cannot be resolved by the mass spectrometer. Any record of this correction process should be included with the report of the data. These corrections will be only as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios and instrument bias factors should be established prior to the application of any corrections.

Abundance sensitivity is the property defining the degree to which the wings of a mass peak contribute to adjacent masses. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

Isobaric polyatomic ion interferences are caused by ions consisting of more than one atom that has the same nominal mass-to-charge ratio as the isotope of interest and that cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gasses or sample components. Equations for the correction of data should be established at the time of analytical run sequence because the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions.

Physical interferences are associated with the physical processes that govern the transport of the sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma-mass-spectrometer interface. Internal standardization may be effectively used to compensate for many physical interference effects. ISs ideally should have analytical behavior similar to that of the elements being determined.

Memory interferences result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. These interferences can result from sample deposition on the sampler and skimmer cones and from the buildup of sample material in the plasma torch and spray chamber. The possibility of memory interferences should be recognized within an analytical run, and suitable rinse times between samples should be used to reduce them.

Arsenic Interference. A small number of elements are renowned for poor detection limits by ICP/MS. These elements suffer from a major spectral interference produced by ions generated from the argon gas, solvent, or sample matrix. Prominent examples of these interferences are $^{40}\text{Ar}^{16}\text{O}$ on the determination of ^{56}Fe ; ^{38}ArH on the determination of ^{39}K ; ^{40}Ar on the determination of ^{40}Ca ; $^{40}\text{Ar}^{2+}$ on the determination of ^{80}Se ; $^{40}\text{Ar}^{35}\text{Cl}$ on the determination of ^{75}As ; and $^{40}\text{Ar}^{12}\text{C}$ on the determination of ^{52}Cr . A cold/cool plasma approach, which uses a lower temperature to reduce the formation of the interferences, has been one way around some of these problems. However, this solution can be cumbersome to optimize, is time consuming, and is not effective on many of the interferences. Collision cells were developed for ICP/MS in the late 1990s to deal with these limitations. Designed originally for organic MS to generate daughter species to confirm identification of the structure of the parent molecule, collision cells found a use in ICP/MS to stop the formation of many argon-based spectral interferences. Ions enter the interface in the normal manner, where they are extracted into an off-axis, collision cell under vacuum. A gas such as H_2 or He is then bled into the collision cell, which consists of a multipole (usually a hexapole or octapole), operated in the RF-only mode. The RF-only field does not separate the masses like a traditional quadrupole but focuses the ions, which then collide and react with molecules of the collision/reaction gas. By a number of different mechanisms, which are predominantly ion-molecule collisions, polyatomic interfering ions like $^{40}\text{Ar}^{16}\text{O}$, and ^{38}ArH will be converted to harmless noninterfering species. The analyte ions, free of the interferences, then emerge from the collision cell, where they are directed towards the quadrupole analyzer for normal mass separation. This ICP/MS accessory is particularly useful for the determination of ng levels of arsenic in PM_{10} filter extract acid mixtures (Method IO-3.1) containing hydrochloric acid. One disadvantage of the collision cell is that the detection limits for most other elements suffer somewhat, possibly requiring the analyst to return the instrument to the “standard” (noncollision cell) mode for other elements, if maximum sensitivity is required.

An alternate approach for the determination of arsenic without the isobaric interferences is to avoid formation of the isobaric interferences by elimination of hydrochloric acid in the extraction solution to leave only dilute nitric acid, which imposes few mass interferences on the measurement. Certain elements such as antimony, however,

will not be stable in a solution containing only nitric acid. With this latter approach, the extract must be analyzed within minutes of completion of the extraction process.

4.3.3.2 Sample Preparation

This section describes both a microwave digestion procedure and a hot acid digestion procedure to extract inorganic elements from the particulate quartz glass fiber filter. Following digestion, target analytes are analyzed by ICP/MS.

Sample Receipt

Ambient air quartz fiber filters should be received folded in half lengthwise with the particulate material inward and with the entire filter enclosed in a protective envelope. These protective envelopes are stored at approximately 15 to 30 °C until analysis. The maximum sample holding time is usually 180 days.

Filter Cutting Procedure

A strip 1 in. × 8 in. is cut from the filter using a template and cutting tool as described in the Federal Reference Method (FRM) for lead. Filter material is sonicated in dilute nitric acid to extract the metals. After cooling, the extract is mixed and filtered through a syringe filter to remove any insoluble material.

Digestion Procedure: Microwave Digestion for Ambient Filters

Note: Nitric acid fumes are toxic. Samples must be prepared in a well-ventilated fume hood.

The filter material is retrieved and placed on its edge in a labeled test tube with vinyl gloves or plastic forceps. The filter is crushed with the plastic forceps into the lower portion of the centrifuge tube to ensure that the acid volume will cover the entire filter.

4.3.3.3 Standard and QC Sample Preparation

Standard stock solutions may be purchased from a commercial source or prepared from ultrahigh-purity grade chemicals or metals (99.99% or greater purity). The standards must include every metal of interest. Stock solutions should be stored in Teflon bottles.

When multielement standard solutions are prepared, care should be taken to ensure that the elements are compatible and stable. Originating element stocks should be checked for impurities that might influence the accuracy of the standard. The element concentrations in the standards should be sufficiently high to produce good measurement precision and to accurately define the slope of the response. Concentrations of 200 µg/L are suggested.

Internal Standards

ISs are prepared by diluting 10-mL stock standards of scandium, yttrium, indium, terbium, and/or bismuth stock standards to 100 mL with deionized water and storing these standards in a Teflon bottle. This solution concentrate is used to spike blanks, calibration standards, and samples or is diluted by an appropriate amount using 1% (v/v) nitric acid. These internal standards are normally added using a peristaltic pump.

Blanks

Three types of blanks are required for this method. A calibration blank establishes the analytical calibration curve and consists of 1% (v/v) nitric acid in deionized water. The laboratory reagent blank (LRB) assesses possible contamination from the sample preparation procedure and spectral background. The LRB must contain all of the reagents in the same volumes as used in processing the samples and must be carried through the entire sample digestion and preparation scheme. The rinse blank flushes the instrument between samples to reduce memory effects and consists of 2% (v/v) nitric acid in deionized water.

Tuning Solution

A tuning solution is used for instrument tuning and mass calibration prior to analysis. The solution is prepared by mixing beryllium, magnesium, cobalt, indium and lead stock solutions in 1% (v/v) nitric acid to produce a concentration of 100 µg/L of each element. ISs are not added to this solution.

QC Sample

A QC sample is obtained by diluting an appropriate aliquot of a second source standard in 1% (v/v) nitric acid.

Laboratory Fortified Blank

A laboratory fortified blank (LFB) is prepared by adding an aliquot from the multi-element stock standards to produce the LFB with a final concentration of 100 µg/L for each analyte. The LFB must be carried through the entire sample digestion and preparation scheme.

4.3.3.4 Calibration

Demonstration and documentation of acceptable initial calibration are required before samples are analyzed and then periodically throughout sample analysis as dictated by results of continuing calibration checks. After the initial calibration is successful, a calibration check is required at the beginning and end of each period during which the analyses are performed and at requisite intervals.

After the instrument has warmed up for at least 30 min, mass calibration and resolution checks using the tuning solution must be conducted. Resolution at low mass is indicated by magnesium isotopes 24, 25, and 26. Resolution at high mass is indicated by lead isotopes 206, 207, and 208. For good performance, spectrometer resolution should be adjusted to produce a

peak width of approximately 0.75 amu at a 5% peak height. Mass calibration should be adjusted if it has shifted by more than 0.1 amu from unit mass.

Instrument stability must be demonstrated by analyzing the tuning solution a minimum of five times with resulting relative standard deviations of absolute signals for all analytes of less than 5%.

The instrument must be calibrated for the analytes to be determined using the calibration blank and calibration standards prepared at multiple concentration levels. A minimum of three replicate integrations at each concentration level is required.

A rinse blank should be used to flush the system between solution changes for blanks, standards, and samples. Sufficient rinse time should be allowed to remove traces of the previous sample. To establish equilibrium, solutions should be aspirated for at least 30 sec prior to the acquisition of data.

4.3.3.5 Internal Standards

Internal standardization must be used to correct operational anomalies, including instrument drift and physical interferences. Metals commonly used as ISs include scandium, yttrium, indium, terbium, and/or bismuth. For a full mass range scan, a minimum of three ISs must be used. ISs must be present in all samples, standards, and blanks at identical levels and may be included either by directly adding an aliquot of the IS to the calibration standards, blank and sample solution or by mixing the IS with the solution prior to nebulization using a second channel of the peristaltic pump and a mixing coil. The concentration of the IS should be sufficiently high to obtain a precise measurement of the isotope used for data correction and to minimize the possibility of correction errors if the internal standard is naturally present in the sample. A concentration of 200 µg/L of each IS is recommended.

4.3.3.6 Instrument Procedure

After establishing calibration, a QC sample must be verified before analysis may be conducted. If replicate measurements of the QC sample exceed $\pm 10\%$ of the theoretical value, the analyst should identify and correct the problem, recalibrate if necessary and verify again with another QC sample.

Calibration blanks and standards should be run after every 10 samples to verify calibration on a continual basis. If the indicated concentration of any analyte deviates from the true concentration by more than 10%, analysis of the standard is repeated. If the analyte is again outside the 10% limit, the instrument must be recalibrated and the previous ten samples reanalyzed. If the sample matrix is responsible for the calibration drift, the previous 10 samples should be reanalyzed in groups of five between calibration checks to prevent a similar drift situation from occurring.

4.3.4 QC

Each laboratory analyzing filters following EPA Compendium Method IO-3.5 is required to operate a formal QC program. The minimal requirement of such a program is an initial demonstration of laboratory capability and the analysis of laboratory reagent blanks, fortified blanks and samples as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data generated.

4.3.4.1 Precision

For 10% of field collection episodes, collocated samples must be obtained. A primary and a collocated sample are collected using two independent sampling systems. Collocated sample pairs must be analyzed in replicate. Replicate analyses of the collocated sample pairs should agree to within $\pm 10\%$, and the means of the replicate analyses for the collocated sample pairs should agree to within $\pm 20\%$. If the collocated sample pairs do not agree to within $\pm 20\%$ and the replicate analyses are within $\pm 10\%$, the sample COC information should be checked to

ensure that they are truly collocated and collected over the same time period, the sample flow rates should be checked to ensure that the samplers are working correctly and the raw data should be checked to make sure values are integrated and calculated correctly. Precision is determined as the RPD using the following calculation:

$$RPD = \frac{|X1 - X2|}{\bar{x}} \times 100 \quad (4.3-1)$$

where:

X1 = ambient air concentration of a given metal measured in one sample

X2 = concentration of the same metal measured during replicate analysis

x = arithmetic mean of X1 and X2.

4.3.4.2 MDLs

MDLs are determined according to the procedures of 40 CFR Part 136 Appendix B using spiked and digested filters fortified at a concentration of two to five times the estimated MDL.

The minimum MDLs that must be achieved are shown in Table 4.3-2.

Table 4.3-2. Target MDLs for EPA Compendium Method IO-3.5

Compound	47 mm Teflon		8x10" Quartz	
	(ng/filter)	ng/m3 (assuming 20m3)	ng/filter	ng/m3 (assuming 20m3)
Antimony	8.3	0.4150	58.7	0.0293
Arsenic	7.9	0.3950	44.2	0.0221
Beryllium	5.7	0.2850	49.7	0.0248
Cadmium	5.8	.02900	37.9	0.0190
Chromium	43.0	.2.1500	1019	0.5093
Cobalt	6.7	0.3350	44.3	0.0221
Lead	10.5	0.5250	136.7	0.0683

Table 4.3-2. Target MDLs for EPA Compendium Method IO-3.5

Compound	47 mm Teflon		8x10" Quartz	
	(ng/filter)	ng/m3 (assuming 20m3)	ng/filter	ng/m3 (assuming 20m3)
Manganese	9.5	0.4750	250.7	0.1253
Mercury	51.4	2.5700	424.6	0.2123
Nickel	23.1	1.1550	367.0	0.1835
Selenium	9.3	0.4650	54.6	0.0273

MDLs are established for all analytes by preparing a filter strip fortified at a concentration of two to five times the estimated detection limit. To determine MDL values, at least seven replicates of a spiked filter strip are used, and each is processed through the entire analytical method. The MDL is calculated as follows:

$$MDL = (t) \times (S) \tag{4.3-2}$$

where:

t = Student's t value for a 99% confidence level and a standard deviation estimate with $n - 1$ degrees of freedom [$t = 3.14$ for seven replicates]

S = standard deviation of the replicate analysis.

MDLs must be determined prior to initiation of sample analysis and whenever a significant change in background or instrument response is expected (e.g., detector change). Linear calibration ranges are a function of the linear range of the detector. The upper limit of the linear calibration range should be established for each analyte by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. Damage to the detector should be avoided during this process. The linear calibration range that may be used for the analysis of samples should be judged by the analyst from the resulting data. Linear calibration ranges should be determined every year or whenever a significant change in instrument response is expected (e.g., detector change).

4.3.4.3 QC Specifications

QC specifications (QCS) for ICP/MS analysis are summarized in Table 4.3-3.

Table 4.3-3. QCS for ICP/MS Analysis

QC Procedure	Typical Frequency	Criteria
Initial calibration (IC)	At the beginning of the analysis	None
Initial calibration verification (ICV) using the QCS	Immediately after initial calibration	90 to 110% of the actual concentration
Initial calibration blank (ICB)	Immediately after initial calibration verification	Must be less than MDLs
High standard verification (HSV)	Following the initial calibration blank analysis	95 to 105% of the actual concentration
Interference check standard (ICS)	Following the high standard verification every 8 hours and at the end of a run	80 to 120% of the actual concentration
Continuing calibration verification (CCV)	Analyzed before the first sample, after every 10 samples and at the end of the run	90 to 110% of the actual concentration
Continuing calibration blanks (CCBs)	Analyzed following each continuing calibration verification	Must be less than MDLs
Reagent blank (RB) or Method blank (MB)	1 per 20 samples, a minimum of 1 per batch	Must be less than MDLs
Laboratory control spike (LCS) or LFB	1 per 20 samples, a minimum of 1 per batch	80 to 120% recovery, with the exception of Ag and Sb
Matrix spike (MS)	1 per 20 samples per sample batch	Percent recovery of 75 to 125%
Serial dilution	1 per sample batch	90 to 110% of undiluted sample
Sample dilution	Dilute sample beneath the upper calibration limit but no lower than at least 5 times the MDL	As needed

4.3.5 Instrument Operating Conditions

Example instrument operating conditions for the ICP/MS analysis are presented below. Exact procedures/conditions will be established by individual laboratories for specific instruments.

<u>Instrument</u>	<u>VG PlasmaQuad Type I</u>
Plasma forward power	1.35 kW
Coolant flow rate	13.5 Lpm
Auxiliary flow rate	0.6 Lpm
Nebulizer flow rate	0.78 Lpm
Solution uptake rate	0.6 mL/min
Spray chamber temperature	15 °C

<u>Data Acquisition</u>	
Detector mode	Pulse counting
Replicate integrations	3
Mass range	8 to 240 amu
Dwell time	320 microsecond
Number of MCA channels	2048
Number of scan sweeps	85
Total acquisition time	3 min/sample

4.3.6 Analysis Procedure

Samples are received from the preparation laboratory in centrifuge tubes. The metals may be contained in a mixture of nitric and hydrochloric acids or in nitric acid alone. For every new or unusual matrix, a semi-quantitative analysis should be performed to screen for high element concentrations. Information gained from this procedure may be used to prevent potential damage to the detector during sample analysis and to identify elements that may be higher than the linear range. Matrix screening may be carried out by diluting the sample by a factor of 500 and analyzing in a semiquantitative mode. The sample should also be screened for background levels of all elements chosen for use as internal standards to prevent bias. The analyst should also follow the steps listed below:

1. The instrument operating configuration is initiated by tuning and calibrating the instrument for the analytes of interest.
2. Instrument software procedures are established for quantitative analysis. For all sample analyses, a minimum of three replicate integrations are required for data acquisition. Any integrations considered to be statistical outliers are discarded, and the average of the integrations is used for data reporting.
3. All masses that might affect data quality are monitored during the analysis. At a minimum, IS masses must be monitored in the same scan used for the collection

of the data. This information should be used to correct the data for identified interferences.

4. The rinse blank is used to flush the system between samples. Sufficient time must be allowed to remove traces of the previous sample (a minimum of one min).
5. Samples are aspirated for 30 sec prior to the collection of data.
6. Samples having concentrations higher than the established linear dynamic range must be diluted into range and reanalyzed. First, the sample is analyzed for trace elements; the detector is protected from the high concentration elements, if necessary, by selecting appropriate scanning windows. Then the sample is diluted to determine the remaining elements. Alternatively, the dynamic range may be adjusted by selecting an alternative isotope of lower natural abundance, provided QC data for that isotope have been established. The dynamic range must not be adjusted by altering instrument conditions to an uncharacterized state.

Sample data must be reported in units of ng/m^3 . All calculated values are reported, with metal concentrations below the determined MDL appropriately flagged. For data values less than 10, two significant figures are used to report element concentrations. For data values greater than or equal to 10, three significant figures are used. Reported values should be calibration blank subtracted.

Data values for instrument drift or sample-matrix-induced interferences are corrected by applying internal standardization. Corrections for characterized spectral interferences should be applied to the data. The chloride ion is a common constituent of environmental samples, and i hydrochloric acid is added during filter extraction, chloride interference corrections should be made on all samples.

If a metal has more than one monitored isotope, the calculated concentration is examined for each isotope, or the isotope ratios, to detect a possible spectral interference. Both primary and secondary isotopes should be considered when evaluating the element concentration. In some cases, secondary isotopes may be less sensitive or more prone to interferences than the primary recommended isotopes. Differences between the results do not, therefore, necessarily indicate a problem with data calculated for the primary isotopes.

The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

4.4 HEXAVALENT CHROMIUM SAMPLING AND ANALYSIS

Chromium is a natural constituent of the earth's crust and is present in several oxidation states. Trivalent chromium is naturally occurring and environmentally pervasive as a trace element in man and animals. Hexavalent chromium is anthropogenic and arises from a number of commercial and industrial sources, primarily those associated with the chrome plating and anodizing process and with emissions from chromate-treated cooling towers. Hexavalent chromium readily penetrates biological membranes and is identified as a toxic and cancer-causing substance associated with respiratory cancer. This element is a known inhalation irritant and is associated with respiratory cancer.

Because of the high level of toxicity of hexavalent chromium, speciation of chromium must be performed to identify the presence of the hexavalent state. The analysis of hexavalent chromium is essential when there is a public concern and high probability for the detection of this element in an urban area, especially if the total chromium value is over the limits that the individual states set. Hexavalent chromium cannot be detected by EPA Compendium Method IO-3.5.⁹ A procedure for sample preparation and analysis, written by California Air Resources Board (CARB-039)¹², has been modified and adapted by ERG in a Standard Operating Procedure for the Determination of Hexavalent Chromium In Ambient Air Analyzed By Ion Chromatography (IC)¹³.

The method determines hexavalent chromium from bicarbonate impregnated ashless cellulose filters exposed to ambient air. The filters are extracted with a sodium bicarbonate solution via sonication for one hour. The extract is analyzed by ion chromatography using a system comprised of a guard column, an analytical column, a post-column derivatization module, and a UV-VIS detector. In the analysis determination, hexavalent chromium exists as chromate due to the near neutral pH of the eluent. After separation through the column, hexavalent chromium forms a complex with the 1,5-Diphenylcarbohydrazide (DPC) which is detected at 530 nm.

NATTS participants wishing to use alternate configurations and/or approaches other than those specified in this document may do so only with Regional EPA approval provided that the alternate configuration and/or approach meet the program MQOs. It is the responsibility of the NATTS participant to demonstrate equivalent performance to the methodology specified in this document, prior to the initiation of monitoring.

4.4.1 Hexavalent Chromium Sample Collection

A hexavalent chromium sample is collected by pulling ambient air through a prepared filter at a known flow rate for a period of 24 hours. A detailed SOP must be prepared to encompass all the procedures involved in the collection of field samples.

4.4.1.1 Preparation for Sample Collection

The sampling methodology uses a glass inlet funnel attached to a Teflon filter holder assembly. In the laboratory, all components are cleaned with distilled deionized water and dried prior to assembly of the filter apparatus. Unassembled components are placed in the nitrogen-purged glove box, the components are assembled, and a prepared filter (see Section 4.3.7.1.3) is loaded. The inlet and outlet of the filter holder are plugged with a section of 1/4-in. o.d. Teflon rod stock. The prepared filter assembly, its funnel, and its field data sheet are placed in a plastic shipping container. The shipping container is placed in a cooler with Blue Ice and shipped to the field using overnight service. Upon receipt in the field, the plastic shipping container is placed in a freezer until it is ready for deployment.

4.4.1.2 Sample Collection Procedures

Samples are collected using an individual filter apparatus and flow control device. An oil-free vacuum pump draws ambient air from the filter apparatus and manifold assembly through the rotameter at a relatively constant flow rate during each specific sampling event. A flow control device(s) is used to maintain a relatively constant sample flow rate through each sample filter over a specific sampling period. The flow device can be a mass flow controller or a

rotameter. A nominal flow rate of 15 L/min is applied for sample collection. During operation, the control device is programmed to activate and deactivate the components of the sample collection system, consistent with the beginning and end of the sample collection period. The connecting lines between the filter assembly and the sampling system should be kept as short as possible to minimize the system residence time. If a rotameter is used, it should be calibrated in the field to determine true readings. Figure 4.4-1 presents the hexavalent chromium sampling system configuration using a flow rotameter.

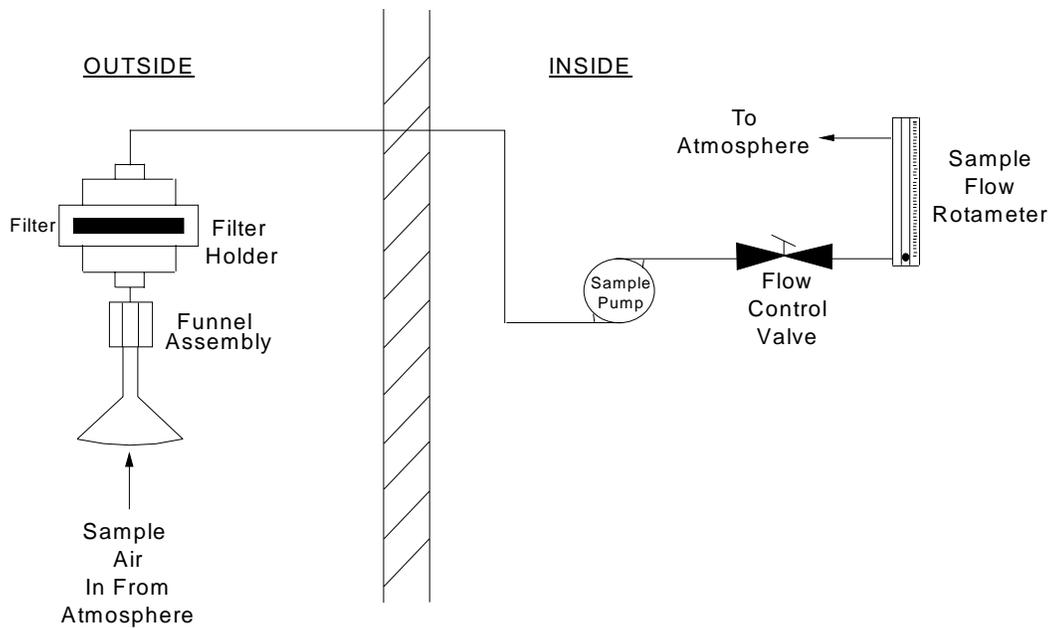


Figure 4.4-1. A Typical Hexavalent Chromium Sampling System

The following generic steps are provided for operation of a typical collection system while collecting a sample:

1. Set the sampling system to the desired sample collection flow rate(s) (i.e., referencing the corresponding ambient calibration curve(s) and considering the desired total volume of ambient air to be sampled and the sampling period for each sampling event).

2. Attach the prepared filter assembly to the inlet of the probe, and the funnel to the inlet of the filter assembly: one filter to collect a single sample, two filters for collocated samples.
3. Record the start and end time of the collection event and the corresponding flow rate onto the sampling field data sheet and calculate an average flow rate.
4. Using vinyl gloves, remove each sample filter (i.e., one at a time), and cap both ends. Sample event number, sample type, location, and collection date should be recorded on the field data sheet.
5. The entire filter assembly, its funnel, and the completed data sheet are returned to the plastic shipping vessel, placed in a cooler with Blue Ice, and returned to the laboratory for analysis using overnight service.
6. Upon receipt at the laboratory, the sample is logged into the LIMS, and the plastic shipping container is placed in a freezer until it is ready for sample preparation and analysis.

It is imperative that the recovery is performed the day after an event, regardless of weekends or holidays. To avoid recovery date issues, alternate sampling days could be approved in advance.

4.4.1.3 Filter Preparation

Whenever filters are handled, clean Teflon[®] coated or plastic tweezers and disposable Nitrile gloves are used. Because the filters must be handled in the cleanest possible laboratory environment, the filter preparation is performed in a nitrogen-purged glove box dedicated to this purpose to minimize the potential for contamination. Whatman No. 41 47-mm ashless cellulose filters are soaked in a 10% Nitric acid bath for a minimum of 2 hours and a maximum of 18 hours. The filters are rinsed thoroughly with DI water on a Teflon[®] coated or plastic rack. The pH is checked on top of a wet filter. The pH should match the DI water. This test filter should be discarded. The filters are then removed to Teflon[®] coated or a plastic net in the glove box and nitrogen-purged until dried. The filters are then soaked in the Sodium Bicarbonate impregnating solution (0.12 M Sodium Bicarbonate) overnight. If the filters are not completely dry before placing them in the impregnating solution, the solution will become dilute and will not collect samples as efficiently.

The filters are removed from the impregnating solution and allowed to dry on the Teflon[®] coated or a plastic net in the glove box and nitrogen-purged until dried. Prepared filters are placed in separate petri dishes labeled with preparation date, initials of the preparer, and a unique lot number. The filters, in individual petri dishes, can be stored in the freezer until ready for field deployment for up to 3 weeks.

4.4.2 Analysis Procedures and Issues

A detailed SOP must be prepared to encompass all the procedures involved in the analysis of field samples.

4.4.2.1 Analytical Interferences and Contamination

Contamination and interference can occur throughout the process from sampling to analysis and must be examined closely. Pure solvents and clean laboratories environments can prevent interference and contamination. Solutions used in extractions and analysis must be high purity or reagent grade.

Sodium carbonate should not be used as the stabilizing medium with the filters as it has been observed to cause interferences with the analysis. The use of an impregnated filter of smaller pore size or by using higher concentrations of the sodium bicarbonate impregnating solution on the filters can cause flow restrictions during ambient air sampling.

4.4.2.2 Equipment and Materials for Hexavalent Chromium Analysis

The following equipment and materials are required for performing successful analysis of hexavalent chromium.

- Automated IC and autosampler. This instrument is an analytical system complete with a chromatography compartment, a 1.0 mL autosampler syringe, an advanced

gradient pump (AGP) with vacuum degas option, an eluent container set with rack, an eluent degas module, a Rheodyne injection valve, an UV/VIS absorbance detector, and a post-column pneumatic delivery package.

- Data acquisition and processing software. The instrument is controlled and data is collected and processed using the software.
- Instrument accessories. A waste container and a Helium regulator is needed to regulate the pressure source for the carrier gas and degassing of the eluents.
- Guard Column. Dionex IonPac NG1, or equivalent.
- Analytical Column. Dionex IonPac AS7, or equivalent.
- Nanopure ASTM Type I DI water. The water (> 16 MW-cm) should be used for preparing eluent, post-column derivatizing reagent, Sodium Bicarbonate solutions, and standards.
- Volumetric flasks. 100 mL, 1 L, and 2 L
- Wide-mouth high-density polyethylene storage bottles. 125 mL
- Analytical balance.
- Digestion vessels. Polystyrene tubes with caps and tube rack, 14 mL
- Ultrasonicator.
- Glove box. The glove box should be supplied with a screen rack and ultra-pure nitrogen to purge while handling and drying filters.
- Graduated cylinders. 50 mL, 100 mL, and 500 mL.
- Large plastic containers for rinsing filters and filter baths. Three baths are needed.
- Freezer. The freezer needs to measure less than -15°C.
- Tweezers. Teflon® coated or plastic tweezers for handling filters.
- Pipettes. 100 µL, 5000 µL, and 10 mL.
- Disposable Nitrile gloves.

4.4.2.3 Chemicals, Reagents, and Standards for Hexavalent Chromium Analysis

The following chemicals are required for performing successful analysis of hexavalent chromium.

- Eluent Stock. A standard eluent solution of the following reagents is prepared in deionized water:

— 100 mM Ammonium hydroxide

In a 2 L volumetric flask, dissolve 33 g of Ammonium sulfate in ~1 L DI water and add 7 mL of Ammonium hydroxide and dilute to 2 L with DI water.

- Post-column Derivatizing Reagent (PCR). In a 1 L volumetric flask, dissolve 0.5 g of 1,5-Diphenylcarbazide in 100 mL of HPLC-grade Methanol. While stirring, add 500 mL of DI water containing 28 mL of 98% Sulfuric acid and dilute to 1 L with DI water. This reagent is stable for four or five days. To minimize waste it should be prepared in 1 L quantities as needed.
- Sodium Bicarbonate Impregnating Solution. In a 500 mL volumetric flask, dissolve 5.0 g of Sodium Bicarbonate in ~250 mL DI water. Dilute to 500 mL with DI water.
- 20 mM Sodium Bicarbonate Solution. In a 1 L volumetric flask, dissolve 1.68 g of Sodium Bicarbonate in ~500 mL DI water. Dilute to 1 L with DI water.
- Primary Stock Solutions. A primary stock solution 1000 $\mu\text{g/mL Cr}^{6+}$ is available commercially or can be prepared by diluting 0.283 g of Potassium dichromate (K_2CrO_7), dried at 100°C for one hour, to 100 mL using DI water. Two primary stock solutions should be prepared and/or obtained from separate sources. One is to be used exclusively for the calibration standards and the other for laboratory control samples (LCS) and calibration verification.
- Working Stock Solutions. Working stock solutions are at 1000 ng/mL Cr^{6+} . Working stock solutions should be prepared for both calibration standards and laboratory control samples/calibration verification. It is important not to use the same primary stock solution for both working stock solutions.
 - Calibration Working Stock Solution. Dilute 100 μL of the calibration primary stock solution to 100 mL using the 20 mM Sodium Bicarbonate in DI water solution.
 - LCS Spike Solution. Dilute 100 μL of the laboratory control primary stock solution to 100 mL using the 20 mM Sodium Bicarbonate in DI water solution.

The LCS Spike solution is used to spike laboratory control samples and to make the calibration verification solution.

- Calibration Standards. The five calibration standards are prepared by diluting the calibration working stock solution to the concentrations specified below.
 - Dilute 200 μL of the working stock solution to 100 mL using the 20 mM Sodium Bicarbonate in DI water solution.
- Calibration Verification Solution. As part of the quality assurance program in the evaluation of the data, a calibration verification from a secondary source at an intermediate concentration (0.5 ng/mL) is run as a check of the precision of the instrument and calibration. An Initial Calibration Verification (ICV) is run immediately following the calibration standards and Continuing Calibration Verifications (CCV) is run after every 10 samples.
 - Calibration Verification Solution Preparation. Dilute 50 μL of the LCS Spike Solution to 100 mL using the 20 mM Sodium Bicarbonate in DI water solution.

4.4.2.4 Hexavalent Chromium Sample Preparation and Analytical Method

Due to the oxidation/reduction and conversion problems associated with trivalent and hexavalent chromium, extraction of the exposed filters should be performed immediately prior to analysis. The exposed filters are extracted in 20 mM Sodium Bicarbonate via sonication for one hour. It is essential that the ion chromatograph be equilibrated, calibrated and ready to perform the analysis when extraction of the filters is finished.

Sample Preparation

All glassware used in the extraction process is soaked in a 10% nitric acid solution for at least 24 hours. The glassware is rinsed with deionized distilled water to remove all traces of acid before it is used for standard preparation. The exposed filter is removed from the collection assembly inside the nitrogen-purged glove box wearing disposable nitrile gloves using plastic or Teflon[®] tweezers. The filter is folded and placed in a 14-mL polystyrene test tube and 10-mL of 20 mM Sodium Bicarbonate is added. The test tube is capped tightly with a Teflon-lined screw cap.

The sealed test tubes are placed in a test tube rack and removed from the glove box to be placed in a sonicator for one hour. After sonication, the tubes are removed and a sample of the extract is removed for analysis. Samples, filter blanks, method blanks, and filter spikes are prepared in the same manner. For replicate samples, sample aliquots are transferred into two separate vials. Extracts are refrigerated until all analyses are completed, nominally within 12 hours of extraction. The samples should be analyzed immediately after preparation; however, extracts are stable for up to 24 hours in the freezer.

Typical Analytical System Operating Conditions

To perform analysis of exposed filters for hexavalent chromium, an ion chromatograph consisting of the following modular units is required:

Instrument Information

- Gradient pump
- Reagent delivery module
- Variable wavelength detector
- Automated sampler

Operating Conditions

- Guard Column – Dionex IonPac NG1 or equivalent.
- Analytical Column – Dionex IonPac AS7 or equivalent.
- Eluent flow rate – 1.5mL/minute (250 mM Ammonium sulfate and 100 mM Ammonium hydroxide).
- Postcolumn Reagent flow rate – 0.5 mL/min (2-mM DPC in 10% methanol and 1 N Sulfuric acid).
- Detection Wavelength – 530 nm.
- Sample Volume – 830 μ L.

The analysis is performed by IC with postcolumn derivatization using 1,5-diphenylcarbohydrazide. In the analysis, hexavalent chromium exists as chromate due to the near-neutral pH of the eluent. After separation through the column, hexavalent chromium forms a specific derivative complex with the diphenylcarbohydrazide, which is detected at 530 nm. Due to the oxidation/reduction and the interconversion of trivalent chromium and hexavalent chromium, filter extraction should be performed immediately prior to analysis. The IC must be equilibrated and ready for analysis before the samples are prepared. After calibration is

performed, a control check standard, filter blank and filter spike should be analyzed. The ambient samples are analyzed along with a check standard and blank after every tenth sample, and at the end of the sampling sequence. Hexavalent chromium stock standards are NIST certified.

4.4.2.5 Preparation of the IC Analytical System

The analytical system must be characterized and optimized prior to operation. Parameters as retention times, identification of coeluting peaks, and method detection limits should be established prior to sample analysis. The following procedures need to be accomplished to prepare the instrument for analysis.

- Make sure all tubing and columns are in the correct sequence for the analysis (see operator's manual).
- Check the volume of the eluent in the reservoirs and check for undissolved particulate matter. Make sure the end of the eluent tube reaches the bottom of the reservoir to prevent air from being drawn up into the system. Tighten the caps on the reservoirs securely.
- Degas the eluent by turning on the helium tank (pressure at the regulator should be between 80 - 120 psig). Turn on the pressure switch for the reservoirs and adjust the pressure to 5 psig for approximately 5 minutes.
- After the eluent and regeneration reservoirs have been connected and pressurized, the pumps must be primed. See IC Operators Manual for specific directions.
- Turn on the UV Cell on the IC. See Operator's Manual for specific directions.

4.4.2.6 Initial Calibration

An initial multipoint calibration curve must be performed during setup of the analytical system. The calibration standards should be prepared at a minimum of five levels as described in Section 4.4.2.3. The initial calibration ranges from 0.1 to 2.0 ng/mL Cr⁶⁺. An acceptable coefficient of correlation is ≥ 0.995 . Analyze each calibration standard and tabulate the area response against mass injected. Use these results to prepare a calibration curve. Use a least squares linear regression routine (using Chromeleon® Client chromatography software) to

calculate a correlation coefficient, slope, and intercept. Use concentration as the X-term (independent variable) and response as the Y-term (dependent variable). A coefficient of correlation of at least 0.995 is required.

The Coefficient of Correlation, R, is the square root of R^2 where:

$$R^2 = \frac{\left[\sum (XY) - \frac{\sum (X)\sum (Y)}{n} \right]^2}{\left[\sum (X^2) - \frac{(\sum X)^2}{n} \right] \left[\sum (Y^2) - \frac{(\sum Y)^2}{n} \right]}$$

The retention time must be within ± 5 of the expected retention time in order to be identified as a positive hit. If they vary by more than $\pm 10\%$ from check sample to check sample, stop the analysis, and check for an instrument problem. If the retention times change from the beginning to the end of the sequence, the system may be changing over the course of the day.

4.4.2.7 Analytical Sequence

Sample analysis can begin after the initial calibration, initial calibration verification (ICV) and initial blank verification (ICB) samples have met acceptance criteria. Continuing calibration verifications (CCV) and continuing blank verifications (CBV) are analyzed after every 10 samples and at the end of the sample sequence. Daily QC criteria are presented in Section 4.3.7.11.

- Initial Calibration Verification/Continuing Calibration Verification. Analyze initial calibration verification (ICV) after the calibration. Analyze a Continuing calibration verification (CCV) after every 10 samples and at the end of the sequence to verify instrument calibration. If the calibration check response is not within $\pm 15\%$ of expected response, determine the cause (85-115% recovery). The instrument may be malfunctioning, the check standard may not be valid, or the instrument may need to be recalibrated. The ICV and CCV percent recovery is calculated below:

$$\text{Cr}^{6+} \text{ Percent Recovery} = \frac{\text{Concentration in CCV (ng/mL)}}{\text{Expected Concentration (ng/mL)}} \times 100$$

- Initial Calibration Blank/Continuing Calibration Blank. Analyze an initial calibration blank (ICB) after the ICV. Analyze a continuing calibration blank (CCB) after every CCV and at the end of the sequence to verify that no contamination is occurring during the analysis. The acceptance criterion is less than the MDL.
- Laboratory Control Sample (LCS). Prepare a LCS for every 10 samples prepared to ensure there are no matrix effects from the filters. Spike 10 μL of the LCS spike solution onto an unused filter, dry in the Nitrogen purged glove box, and prepare and analyze with the rest of the samples. The acceptance criterion is 80-120% recovery. If the spikes are outside of these limits, check the calibration and extraction procedures. The corrected weight of Cr^{6+} is divided by the amount of Cr^{6+} spiked and multiplied by 100 as shown below:

$$\text{LCS Cr}^{6+} \text{ Percent Recovery} = \frac{\text{Concentration in LCS (ng/mL)}}{\text{Spiked Concentration (ng/mL)}} \times 100$$

4.4.2.8 Sample Tracking

Each sample received into the laboratory should be assigned a unique laboratory identification number from LIMS. The quality control criteria for the filters are given below. If a sample that is being logged in from the field meets these criteria, it is considered invalid.

- Filters dropped or contaminated with any foreign matter (i.e., dirt, finger marks, ink, liquids, etc.).
- Filters with tears or pinholes that occurred before or during sampling.
- Sample flowrate:
 - If the average flowrate is less than 9.0 LPM or exceeds 16 LPM.
 - If the start and stop flowrates differ more than $\pm 10\%$.
- Filter samples collected by samplers that operate less than 23 hours or more than 25 hours.

- If a power failure occurs during a sample run which causes the stop time or sample duration requirements to be violated

4.4.2.9 Sample Analysis

The analysis time is approximately 9 minutes. The following conditions are used for analysis.

- Guard Column – Dionex IonPac NG1 or equivalent.
- Analytical Column – IonPac AS7.
- Eluent flow rate – 1.5mL/minute (250 mM Ammonium sulfate and 100 mM Ammonium hydroxide).
- Postcolumn Reagent flow rate – 0.5 mL/min (2-mM DPC in 10% methanol and 1 N Sulfuric acid).
- Detection Wavelength – 530 nm.
- Sample Volume – 830 μ L.

The Cr⁶⁺ ID in the sample must be verified by retention time. The compound chromatogram is compared against a chromatogram from the initial calibration or calibration verification. Cr⁶⁺ concentration in units of ng/mL are calculated below:

$$\text{Cr}^{6+} \text{ in Sample (ng/mL)} = \frac{\text{Sample Response} - \text{Intercept}}{\text{Slope}}$$

To calculate the concentration of Cr⁶⁺ in the air sampled, the volume of air sampled must be known.

$$\text{Cr}^{6+} \text{ Concentration (ng/m}^3\text{)} = \frac{C \text{ (ng/mL)} \times V_2 \text{ (mL)}}{V_1 \text{ (m}^3\text{)}}$$

Where:

C	=	Concentration of Cr ⁶⁺ in analyzed sample
V ₁	=	Volume of air sampled
V ₂	=	Total volume of sample extract

Samples with concentrations greater than the calibration range should be diluted, if there is enough sample volume. The dilution factor must be applied to the sample data. All results obtained from dilutions or concentrations over the calibration range should be flagged.

4.4.2.10 Requirements for Demonstrating Method Acceptability for Hexavalent Chromium Analysis

Two measurements of method acceptability are presented below.

Method Detection Limits

MDLs are based on procedures from 40 CFR Part 136 Appendix B, with 99% confidence level and a standard deviation estimate having n-1 degrees of freedom. **The maximum method detection limits from hexavalent chromium is 0.19 ng/mL.** Comparability of data reported is essential at the low levels of hexavalent chromium detected in the ambient air.

At least seven (usually 7 to 10) filters are spiked and prepared at the same concentration. A concentration that is one to five times the expected detection limit should be chosen. Filters are spiked at a level of two to five times the estimated MDL. Because the detection limits using this method are normally lower than 0.05 ng/mL, the MDL spike filters should be prepared at a concentration of 0.15ng/mL or lower. The standard deviation should be calculated and should be multiplied by the applicable Student's t value. See Table 4.4-1 for applicable Student's t values.

Table 4.4-1. Student's t Values at the 99% Confidence Level

Number of Replicates	Degrees of Freedom	Student's t Value
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821

Table 4.4-1. Student’s t Values at the 99% Confidence Level

Number of Replicates	Degrees of Freedom	Student’s t Value
11	10	2.764

Any analyzed concentrations below the MDL value should be flagged when the data are reported. All calculated values should be reported.

4.4.2.11 Analytical and Sampling Precision

Precision refers to the agreement between independent measurements performed according to identical protocols and procedures. Sampling and analytical precision quantifies random errors associated not only with analyzing ambient air samples in the laboratory but also with collecting the samples. This type of precision is most easily evaluated by comparing concentrations measured in collocated samples collected from the same air parcel. Collocated samples were collected at least 10 percent of the scheduled sampling days.

To normally quantify analytical precision (i.e., how precisely the analytical methods measure ambient air concentrations), concentrations measured during analysis of collocated samples are replicated. Analytical precision is a measurement of random errors associated with the process of analyzing environmental samples. Replicate analysis is performed on all collocated samples taken in the field, (i.e., 10% of the total sample number per year).

The RPD between the collocated samples and the replicate analyses must be within 20%, except with concentrations less than five times the method detection limit. The equation for percent difference is:

$$RPD = \frac{(|X_1 - X_2|)}{\bar{X}} \times 100$$

Where:

- X_1 is the ambient air concentration in one sample;
- X_2 is the concentration for the collocated sample analysis; and
- \bar{X} is the arithmetic mean of X_1 and X_2 .

4.4.2.12 Quality Control Specifications

QC specifications for the NATTS hexavalent chromium are presented in Table 4.4-2.

Table 4.4-2. Summary of Hexavalent Chromium Quality Control Procedures

Parameter	Frequency	Acceptance Criteria	Corrective Action
Initial 5-point calibration standards	Before every sequence	Correlation coefficient 0.995	1) Repeat analysis of calibration standards. 2) Reprepare calibration standards and reanalyze.
Initial Calibration Verification (ICV)	Before every sequence, following the initial calibration	Recovery 85-115%	1) Repeat analysis of initial calibration verification standard. 2) Repeat analysis of calibration standards. 3) Reprepare calibration standards and reanalyze.
Initial Calibration Blank (ICB)	One per Batch, following the ICV	Below MDL	1) Reanalyze. 2) Reprepare blank and reanalyze. 3) Correct contamination and reanalyze blank. 4) Flag data of all samples in the batch.
Continuing Calibration Verification (CCV)	Every 10 samples	Recovery 85-115%	1) Repeat analysis of CCV. 2) Reprepare CCV. 3) Flag data bracketed by unacceptable CCV.
Laboratory Control Sample	One per 10 samples	Recovery 80-120%	1) Reanalyze. 2) Reprepare spike and reanalyze. 3) Flag data of all samples since the last acceptable spike.
Replicate Analysis	Duplicate and/or Replicate samples only	RPD < 20% for concentrations greater than 5 x the MDL.	1) Check integration 2) Check instrument function 3) Flag samples
Continuing Calibration Blank (CCB)	After every CCV and at the end of the sequence	Below MDL	1) Reanalyze. 2) Reprepare blank and reanalyze. 3) Correct contamination and reanalyze blank. 4) Flag data of all samples in the batch.

4.5 OVERVIEW OF SEMIVOLATILE ORGANIC COMPOUNDS MEASUREMENT

EPA Compendium Method TO-13A¹⁴ (<http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-13ar.pdf>) sample collection procedures will be used to collect samples and EPA SW-846 Method 8270C¹⁵ (<http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8270c.pdf>) will be used to analyze samples for SVOCs in ambient air as required for the NATTS Program. Method 8270C analytical procedures paired with Method 3540C¹⁶ (Soxhlet extraction) (<http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3540c.pdf>) are used to prepare and analyze ambient air field samples collected on a filter and XAD-2[®] sorbent. In Method 8270C analysis, the filter and the sorbent are extracted together because of the problem of postcollection volatilization that prohibits accurate determination of the distribution of SVOCs between the gaseous and particulate phase.

4.5.1 *Sampling Procedures and Issues Associated with EPA Compendium Method TO-13A*

Sample collection for quantitative determination of SVOCs is accomplished by pulling ambient air at a known and constant flow rate through a quartz fiber filter followed by a sampling cartridge containing 40 grams (g) of XAD-2[®] across a 24-hour collection period.

4.5.1.1 **Sampling Equipment and Materials**

Materials and equipment used to conduct SVOC sampling for EPA Compendium Method TO-13A are presented below.

- High volume sampler. The sample collection is performed using a commercially available PS-1 high volume sampling system capable of maintaining a flow rate through the filter/XAD-2[®] sampling cartridge that will yield a total sample volume greater than 180 standard cubic meters (scm) across a 24-hour duration.
- High volume sampler calibrator. The high volume sampler is calibrated using a compatible calibrator to apply multiple levels of simulated resistance to the

sampler flow path and characterizing the sampler's performance. The multiple levels of simulated resistance are typically accomplished using individual orifice plates, or a variable orifice device.

- Quartz fiber filter. The filter is a 102-mm bindless quartz microfiber filter.
- XAD-2[®] Resin. XAD-2[®] resin is a styrene-divinylbenzene polymer. Cleaning and preparation of XAD-2[®] is discussed in detail in Sections 4.5.2.3 and 4.5.2.4, respectively. The amount of XAD-2[®] used for each sampling episode is 40 g.
- Glass sample cartridge. The cartridge used to contain/secure the XAD-2[®] resin during sample collection is comprised of a thick-walled glass tube outfitted with a coarse quartz frit at the outlet end. The frit is used to ensure that the resin is not pulled out of the sampling module by the sampling system during sample collection.

4.5.1.2 Sample Collection Procedures

The sampler should be located in an unobstructed area at least 2-m from any obstacle to airflow. The inlet of the high volume sampler must be positioned in the breathing zone, 4 to 10 feet above ground level. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air into the sampling head.

Calibration

The high volume sampler is calibrated using a calibrated orifice transfer standard (i.e., high volume sampler calibrator) in accordance with the specifications of EPA Compendium Method TO-13A.¹⁴ The individual orifice plates are placed in the sampling flow stream, and the differential pressure across the orifice plate is documented. Simultaneously, a corresponding Magnehelic pressure reading is recorded. The differential pressure and the Magnehelic readings are used to create a curve that establishes the flow characteristics of each individual sampler. Note that the Magnehelic readings associated with use of a glass frit XAD-2[®] cartridge will be significantly lower than the readings typically achieved using polyurethane foam (PUF) cartridges because the glass frit material is more restrictive of flow. Readings in the range of

8 to 30 in. H₂O for glass frit XAD-2[®] cartridges are not unusual.

Sample Collection

The prepared XAD-2[®] cartridge is placed and secured into the sampling head of the high volume sampler. The quartz fiber filter is placed and secured onto the inlet of the high volume sampler. The system is activated manually and the desired Magnehelic reading is achieved by adjusting the ball valve located at the exit of the sampling head. The sampler is then programmed to turn on at 12:00 a.m. and turn off at 11:59 p.m. automatically for the 24-hour sampling period. At the end of the sampling period, the sampler is once again activated manually, and a final Magnehelic reading is made without any adjustment to the ball valve. The filter is removed, folded in quarters and placed inside the glass cartridge with the XAD-2[®]. The XAD-2[®] cartridge is then removed from the high volume sampler and transported to the laboratory.

4.5.2 Analysis Procedures and Issues

Table 4.5-1 presents the SVOCs that can be measured using EPA Compendium Method TO-13A¹⁴ (with XAD-2[®] as the collection medium) and GC/MS as the analytical technique for the NATTS Program.

Table 4.5-1. SVOCs Measured for the NATTS Program Using the Procedures of EPA Compendium Method TO-13A

Compound	CAS Number	Compound	CAS Number
N-nitrosodimethylamine	62-75-9	3-nitroaniline	99-09-2
ethyl methane sulfonate	62-50-0	acenaphthylene	208-96-8
2-picoline (2-methylpyridine)	109-06-8	2,4-dinitrophenol	51-28-5
2-fluorophenol (surr)	367-12-4	4-nitrophenol	100-02-7
methyl methane sulfonate	66-27-3	acenaphthene-d ₁₀ (IS)	--
phenol-d ₅ (surr)	--	acenaphthene	83-32-9
phenol	108-95-2	2,4-dinitrotoluene	121-14-2
bis(2-chloroethyl) ether	111-44-4	2-naphthylamine	91-59-8

Table 4.5-1. SVOCs Measured for the NATTS Program Using the Procedures of EPA Compendium Method TO-13A

Compound	CAS Number	Compound	CAS Number
aniline	62-53-3	dibenzofuran	132-64-9
2-chlorophenol	95-57-8	pentachlorobenzene	608-93-5
1,3-dichlorobenzene	541-73-1	1-naphthylamine	134-32-7
1,4-dichlorobenzene-d ₄ (IS)	--	diethyl phthalate	84-66-2
1,4-dichlorobenzene	106-46-7	2,3,4,6-tetrachlorophenol	58-90-2
benzyl alcohol	100-51-6	4-nitroaniline	100-01-6
<i>o</i> -cresol (2-methylphenol)	95-48-7	4-chlorophenyl phenyl ether	7005-72-3
1,2-dichlorobenzene	95-50-1	fluorene	86-73-2
<i>bis</i> (2-chloroisopropyl) ether	108-60-1	4,6-dinitro-2-methylphenol	534-52-1
<i>p</i> -cresol (4-methylphenol)	106-44-5	diphenylamine	122-39-4
N-nitrosodi- <i>n</i> -propylamine	621-64-7	azobenzene	103-33-3
hexachloroethane	67-72-1	phenacetin	62-44-2
acetophenone	98-86-2	4-bromophenyl phenyl ether	101-55-3
nitrobenzene-d ₅ (surr)	--	4-aminobiphenyl	92-67-1
nitrobenzene	98-95-3	hexachlorobenzene	118-74-1
N-nitrosopiperidine	100-75-4	pronamide	23950-58-5
isophorone	78-59-1	pentachlorophenol	87-86-5
2-nitrophenol	88-75-5	phenanthrene-d ₁₀ (IS)	
2,4-dimethylphenol	105-67-9	phenanthrene	85-01-8
<i>bis</i> (2-chloroethoxy) methane	111-91-1	anthracene	120-12-7
2,4-dichlorophenol	120-83-2	carbazole	86-74-8
α , α -dimethylphenethylamine	122-09-8	di- <i>n</i> -butyl phthalate	84-74-2
4-chloroaniline	106-47-8	benzidine	92-87-5
1,2,4-trichlorobenzene	120-82-1	fluoranthene	206-44-0
naphthalene-d ₈ (IS)	--	pyrene	129-00-0
naphthalene	91-20-3	2,4,6-tribromophenol (surr)	118-79-6
2,6-dichlorophenol	87-65-0	4-dimethylaminoazobenzene	60-11-7
hexachlorobutadiene	87-68-3	butyl benzyl phthalate	85-68-7
1,4-phenylenediamine	106-50-3	3,3'-dichlorobenzidine	91-94-1
N-nitrosodi- <i>n</i> -butylamine	924-16-3	<i>bis</i> (2-ethylhexyl) phthalate	117-81-7
4-chloro-3-methylphenol	59-50-7	benzo(a)anthracene	56-55-3
2-methylnaphthalene	91-57-6	chrysene-d ₁₂ (IS)	--
1,2,4,5-tetrachlorobenzene	95-94-3	chrysene	218-01-9
2,4,6-trichlorophenol	88-06-2	di- <i>n</i> -octyl phthalate	117-84-0

Table 4.5-1. SVOCs Measured for the NATTS Program Using the Procedures of EPA Compendium Method TO-13A

Compound	CAS Number	Compound	CAS Number
2-fluorobiphenyl (surr)	321-60-8	7,12-dimethylbenz(a)anthracene	57-97-6
hexachlorocyclopentadiene	77-47-4	benzo(b)fluoranthene	205-99-2
2,4,5-trichlorophenol	95-95-4	benzo(k)fluoranthene	207-08-9
2-nitroaniline	88-74-4	terphenyl-d ₁₄ (surr)	--
2-chloronaphthalene	91-58-7	benzo(a)pyrene	50-32-8
1-chloronaphthalene	90-13-1	indeno(1,2,3-cd)pyrene	193-39-5
dimethyl phthalate	131-11-3	dibenz(a,h)anthracene	53-70-3
2,6-dinitrotoluene	606-20-2	benzo(g,h,i)perylene	191-24-2

surr = surrogate compound

4.5.2.1 Interferences

Method interferences may arise from contaminants in solvents, reagents, glassware, sorbent and other materials used in sample preparation that produce distinct peaks in the chromatogram or from mixtures of compounds that produce an elevated baseline in the chromatogram. All materials used in sampling and in preparation of samples must be free from contamination. Proper cleaning of XAD-2[®] is especially critical.

Contamination by carryover occurs when a high concentration sample is followed by a low concentration sample. Whenever an unusually concentrated sample is encountered, analysis of solvent or of a blank should follow to demonstrate that cross-contamination is not occurring.

4.5.2.2 Preparation of Reagents and Materials

- Glassware. Glassware must be carefully cleaned before use. Glassware should be cleaned as soon as possible after use by rinsing with the last solvent that was used and then rinsing in high-purity methylene chloride. After these rinses, glassware should be washed carefully using laboratory detergent and hot water, rinsed with tap water, then rinsed with reagent water. The glassware should then be drained dry and heated in a muffle furnace at 400°C for four hours. After drying and rinsing, glassware should be sealed and stored in a clean environment

to prevent contamination. Glassware should be stored inverted or capped with solvent-rinsed aluminum foil. **Note: Volumetric glassware must not be heated in a muffle furnace.** Volumetric glassware should be rinsed with chromatographic-grade methylene chloride.

- Solvents and materials. Solvents used in the preparation or extraction of the sorbent (methanol, methylene chloride) should be high purity and glass distilled. Boiling chips should be solvent extracted and/or heated in a muffle furnace at 450°C for two hours. Sodium sulfate (anhydrous, granular, ACS grade) should be heated at 400°C in a shallow tray in a muffle furnace for two hours. Chromatographic-grade stainless steel tubing and stainless steel fittings should be used for all connections in the gas chromatograph. Quartz filters (110 mm) should be extracted with methylene chloride, baked at 400°C for five hours prior to use, then stored in a clean container for shipment to and from the field.

4.5.2.3 Cleaning of XAD-2[®]

The procedure below for cleaning XAD-2[®] is designed to meet EPA-recommended criteria for cleanliness. Although some forms of “clean” resin are commercially available, laboratory cleaning has proven to be a cost-effective, high quality procedure for obtaining very clean resin usable for ambient air sampling applications. The procedure for cleaning XAD-2[®] is derived from the EPA Level 1 Procedures Manual¹⁷. The original methodology has been improved to provide a reproducible procedure for preparing sorbent material that will yield sorbent that is clean enough for low level organic compound collection and analysis. The complete cleaning cycle requires approximately five working days to complete (exclusive of quality control analyses). The typical background or blank total organic concentrations from XAD-2[®] prepared by this procedure are on the order of 1 µg per gram of sorbent medium. Individual analytes are typically below MDLs. The following steps are utilized to clean and prepare the sorbent for sampling:

- XAD-2[®] resin is obtained from the supplier or recycled from prior use (recycled material is preferred). Recycled and recleaned resin usually contains less organic contamination and is preferred over raw material directly from the manufacturer.
- The resin is washed with water if new from the supplier. The resin is soaked in tap water at room temperature for three days (or longer) in a clean plastic, glass, or metal vessel large enough to contain the amount of resin to be cleaned. The

water and fine particles are decanted by carefully pouring, and fresh water is added. The resin is soaked with fresh tap water for another three days. The water and fine particles are again decanted, after which the new XAD-2[®] is cleaned in the same manner as the used XAD-2[®].

- Recycled or used resin is loaded directly into a large extractor for solvent cleaning. The entire cleaning process is done “wet”; final drying takes place only at the end of the process. An extractor capable of holding 900 g of resin is used to extract the resin using sequential 18-hour extractions with methanol, methylene chloride, and a final extraction with fresh methylene chloride. The solvent is drained between steps, and the extractor is prerinsed with the solvent to be used in the next step. The extractor operates like a Soxhlet extractor with distilled solvent constantly passing over the XAD-2[®].
- After the final extraction, the methylene chloride is drained and the extractor body is removed to a hood where the resin is dried. Drying is accomplished using a gentle stream of nitrogen passed through the bottom of the extractor body. Very clean nitrogen is delivered through a heat exchanger attached to the liquid output of a liquid nitrogen tank.
- A methylene chloride extract of approximately 40 g of the resin (approximately 300 mL) is concentrated to 1 mL and analyzed by Method 8270C as a QC check of the cleaned material.
- The jar of dry XAD-2[®] that has met QC criteria (no Method 8270C analytes observed at levels above the MDL) is labeled with a laboratory identification and stored in a clean, solvent-free cabinet for use in sampling activities. The cleaned dried resin will remain usable for 2 to 3 weeks stored at room temperature. Longer storage times are possible if the material is refrigerated, but a blank sample must be checked before resin stored for longer than three weeks may be considered usable for field sampling.
- A 2-L glass bottle is filled nearly full with XAD-2[®], wet or as a slurry or dry. Sufficient clean methanol is transferred to the bottle to just cover the XAD-2[®], and the resin is allowed to soak for three days. The methanol and fine particles are decanted. The bottle is again filled with methanol and sealed (screw cap and Teflon tape). The XAD-2[®] is allowed to soak indefinitely in the methanol until the resin is needed for sampling; the resin can be dried immediately before it is needed.

Contaminants may appear in the resin and will cause the cleaned resin to fail the QC test performed at the end of the cleaning procedure. Common resin contaminants include inorganic salts and preservatives often present in new resin as received from the supplier (careful rinsing with water at the first step will rinse these materials from the resin) and hydrocarbon

contaminants. Dirty resin often contains hydrocarbon contamination that appears in the C₈ to C₁₂ range in the GC/MS analysis. This interference is eliminated by sufficiently cleaning the resin with the recommended solvent extractions. Some analytical interferences of contaminants appear in the resin after storage. These contaminants may cause the cleaned resin to fail the QC requirements for the analytical method. Contaminants may originate from both external contamination or oxidation and from internal “bleeding” of entrained chemicals from very small or inaccessible pores in the resin. Subsequent recleaning and reuse reduce the internal contributions to the blank level during storage. Contaminant levels may also increase if XAD-2[®] is exposed to high concentrations of oxidizing agents such as ozone or oxides of nitrogen. In an oxidizing matrix, oxidation or decomposition products of XAD-2[®], such as naphthalene, benzoic acid, benzaldehyde, carboxylic acids and aldehydes, will be observed. Sufficiently high levels of oxides of nitrogen (NO_x) (percentage levels) can cause destruction of the resin itself.

4.5.2.4 Preparation of a Sampling Cartridge

Cleaned XAD-2[®] (approximately 40 g) that has passed Method 8270C acceptance criteria for cleanliness is loaded into a glass thimble with an extra coarse glass frit. The glass thimble is 55 mm in diameter and measures 100 mm from the frit to the top of the thimble. Clean thimbles are rinsed with methylene chloride, tared and dried for use. The thimble filled with XAD-2[®] is wrapped tightly with aluminum foil that has been rinsed with methylene chloride and oven dried, wrapped securely in bubble wrap and placed in a plastic jar for shipment to the field. Multiple filled thimbles are shipped to the field as a batch, together with 110-mm quartz filters that have been precleaned with methylene chloride and placed in individual sealable plastic bags with chain of custody documentation. The XAD-2[®] modules and filters are shipped in coolers over Blue Ice to keep them cool in shipment.

4.5.2.5 Reagents

Any water used must be organic-free reagent water. Standard solutions may be prepared from pure standard materials or purchased as certified solutions. Stock standard solutions are

considered stable for one year but must be replaced whenever comparison with QC check samples indicates a problem.

The ISs used for Method 8270C are 1,4-dichlorobenzene-d₄, naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, and perylene-d₁₂. These compounds may be purchased as pure standard materials or purchased as a certified solution. Stock standard solutions are considered stable for one year but must be replaced whenever comparison with QC check samples indicates a problem.

A tuning/column performance solution containing 50 ng/μL each of decafluorotriphenylphosphine (DFTPP), 4,4'-*p,p'*-dichlorodiphenyltrichloroethane (DDT), pentachlorophenol, and benzidine may be prepared from pure standards or purchased as a certified solution. This solution is used to establish/verify the instrument tune, the inertness of the injector port and column performance. The tuning/column performance solution should be stored at -10 °C when not in use. Degradation of DDT to *p,p'*-dichlorodiphenyldichloroethylene (DDE) and *p,p'*-dichlorodiphenyldichloroethane (DDD) should not exceed 20%, benzidine and pentachlorophenol should be present at their normal responses and no peak tailing should be visible. If degradation is excessive and/or poor chromatography is noted, the injector liner may need to be replaced and/or column maintenance may need to be performed.

A minimum of five calibration standards should be prepared at five different concentrations, with at least one of the concentrations corresponding to a sample concentration near the MDL. The highest concentration calibration standard must not exceed the linear range of the instrument. All of the compounds of interest should be included in the calibration standards; the laboratory may not report a quantitative result for a compound not included in the calibration standards. The calibration standards should be stored at a temperature ≤ -10 °C and should be freshly prepared at least once a year (sooner if check standards indicate a problem).

The surrogate compounds for Method 8270C are phenol-d₆, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d₅, 2-fluorobiphenyl, and *p*-terphenyl-d₁₄. Surrogate compounds

are spiked into the sample immediately before extraction. The surrogate compound solution may be prepared from pure standards or purchased as a certified solution.

A matrix spike is typically not performed for Method 8270C analysis of ambient air samples. However, a method spike (or LCS) and method spike duplicate can be prepared by spiking clean XAD-2[®] with a solution containing all of the compounds of interest at levels comparable to those expected in the field samples. Surrogate compounds are also added to the method spike.

4.5.2.6 Analytical Equipment

A GC/MS with a data system and autosampler is used in the analysis of calibration samples, field samples and QC samples. The GC must be equipped for temperature programming, splitless/split injection and a capillary column. A fused silica DB-5 column (30-m × 0.32-mm i.d.) cross-linked 5% phenyl methyl silicone, 1.0-µm film thickness (or equivalent) may be used. The GC is coupled directly to the ion source of the mass spectrometer. The mass spectrometer must be capable of scanning from 35 to 500 amu every second or less, using an electron energy of 70 electron volts (eV) (nominal) to produce electron ionization mass spectra. The mass spectrometer must be capable of producing a mass spectrum for DFTPP that meets the criteria in Table 4.5-2 when 1 microliter (µL) of the GC/MS tuning standard (50 ng DFTPP on-column) is injected through the GC.

Table 4.5-2. DFTPP: Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30 - 60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40 - 60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5 - 9% of mass 198

Table 4.5-2. DFTPP: Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
275	10 - 30% of mass 198
365	>1% of mass 198
441	Present but <mass 443
442	>40% of mass 198
443	17 - 23% of mass 442

4.5.2.7 Sample Extraction, Concentration and Cleanup

The XAD-2[®] sampling module and filter are carefully packed with padding, placed in a cooler with Blue Ice and returned to the laboratory from the field. Field samples should be stored and shipped chilled (<4 °C) using Blue Ice until the samples are received at the analytical laboratory. After receipt at the analytical laboratory, the samples should be refrigerated at ≤4 °C. Samples should be extracted within 14 days after sampling; extracts should be analyzed within 45 days after extraction. The sorbent and filter are extracted together. Extraction procedures follow Method 3540C (Soxhlet extraction). Sample extracts are concentrated to a final volume of 1 mL and stored at -10 °C protected from light in sealed vials equipped with an unpierced PTFE-lined septum.

A Soxhlet extraction is performed using approximately 700 mL of methylene chloride, with the sorbent and filter extracted together in the Soxhlet extractor; the extractor should reflux for 18 hours at a rate of at least three cycles per hour. Prior to extraction, the laboratory surrogate standards are spiked into each sample and blank at a level of 1 µg/mL. The recovery of the laboratory surrogates is used to monitor for matrix effects or errors in sample preparation and should be in the range of 60 to 120%. The extractor is allowed to cool then disassembled. The extract is dried by passing it through a drying column containing ~10 g of cleaned anhydrous sodium sulfate, then concentrated using a Kuderna-Danish concentration apparatus with nitrogen blow-down to a final volume of 1.0 mL. The extract is transferred to a Teflon-sealed, screw cap amber vial and stored at 4 ± 2 °C until analysis.

To perform a matrix spike analysis, a specific field sample must be taken and designated for this purpose. Matrix spikes are generally not performed for ambient air samples. An LCS in which all of the analytes are spiked onto a clean sorbent matrix and recovered in the laboratory is performed to monitor matrix effects.

If the extract is cloudy, the extract may be purified by solid phase extraction using activated silica gel. If the sample matrix is clean, sample cleanup is not needed. The extract is cleaned up using a succession of solvents with approximately 10 g of cleaned activated silica gel, according to the procedures of EPA Compendium Method TO-13A.¹⁴ The extract eluted from the silica gel cleanup column is concentrated to < 5 mL using a Kuderna-Danish concentrator, then to a final volume of 1 mL using nitrogen blow-down.

4.5.2.8 Initial Calibration

The GC/MS system must be hardware tuned to meet tuning criteria (Table 4.5.2) according to the procedures recommended in Method 8270C using a 50-ng injection of DFTPP; no analyses may begin until tuning criteria are met. All subsequent standards, samples, LCS, method spikes, and blanks associated with a specific DFTPP analysis must use the identical mass spectrometer instrument conditions.

The ISs selected above have been chosen to cover the chromatographic elution times of the compounds to be measured for the NATTS Program and should permit the compounds of interest in the chromatogram to have retention times of 0.80 to 1.20 relative to one of the ISs. The typical quantitation scheme for Method 8270C analytes is shown in Table 4.5-3. The primary ion of both the IS and the compound of interest should be used to perform quantitative calculations, unless analytical interferences are noted. If interferences are observed, the next most intense ion of the mass spectrum should be used as the quantitation ion. Note that secondary ion quantitation is permissible ONLY if analytical interferences are encountered; secondary ion quantitation may not be used if the primary ion is saturated because the quantitative calculations performed for a compound that is saturated will be biased significantly low.

Table 4.5-3. Quantitation Scheme for Semivolatile Organic Compounds According to Method 8270

1,4-dichlorobenzene-d4 (IS)	naphthalene-d8 (IS)	acenaphthene-d10 (IS)
Compounds to be quantitated against each IS above		
aniline	acetophenone	acenaphthene
benzyl alcohol	benzoic acid	acenaphthylene
<i>bis</i> (2-chloroethyl) ether	<i>bis</i> (2-chloroethoxy) methane	1-chloronaphthalene
<i>bis</i> (2-chloroisopropyl) ether	4-chloroaniline	2-chloronaphthalene
2-chlorophenol	4-chloro-3-methylphenol	4-chlorophenyl phenyl ether
1,3-dichlorobenzene	2,4-dichlorophenol	dibenzofuran
1,4-dichlorobenzene	2,6-dichlorophenol	diethyl phthalate
1,2-dichlorobenzene	α,α -dimethylphenethylamine	dimethyl phthalate
ethyl methanesulfonate	2,4-dimethylphenol	2,4-dinitrophenol
2-fluorophenol (surrogate)	hexachlorobutadiene	2,4-dinitrotoluene
hexachloroethane	isophorone	2,6-dinitrotoluene
methyl methanesulfonate	2-methylnaphthalene	fluorene
2-methylphenol (<i>o</i> -cresol)	naphthalene	2-fluorobiphenyl (surrogate)
4-methylphenol (<i>p</i> -cresol)	nitrobenzene	hexachlorocyclopentadiene
N-nitrosodimethylamine	nitrobenzene-d8 (surrogate)	1-naphthylamine
N-nitrosodi- <i>n</i> -propylamine	2-nitrophenol	2-naphthylamine
phenol	N-nitrosodi- <i>n</i> -butylamine	2-nitroaniline
phenol-d6 (surrogate)	N-nitrosopiperidine	3-nitroaniline
2-picoline	1,2,4-trichlorobenzene	4-nitroaniline
		4-nitrophenol
		pentachlorobenzene
		1,2,4,5-tetrachlorobenzene
		2,3,4,6-tetrachlorophenol
		2,4,6-tribromophenol (surrogate)
		2,4,6-trichlorophenol
		2,4,5-trichlorophenol

Table 4.5-3. Quantitation Scheme for Semivolatile Organic Compounds According to Method 8270

1,4-dichlorobenzene-d4 (IS)	naphthalene-d8 (IS)	acenaphthene-d10 (IS)
Compounds to be quantitated against each IS above		
4-aminobiphenyl	benzidine	benzo(b)fluoranthene
anthracene	benzo(a)anthracene	benzo(k)fluoranthene
4-bromophenyl phenyl ether	<i>bis</i> (2-ethylhexyl) phthalate	benzo(g,h,i)perylene
di- <i>n</i> -butyl phthalate	butyl benzyl phthalate	benzo(a)pyrene
4,6-dinitro-2-methylphenol	chrysene	dibenz(a,j)acridine
diphenylamine	3,3'-dichlorobenzidine	dibenz(a,h)anthracene
fluoranthene	<i>p</i> -dimethylaminoazobenzene	
hexachlorobenzene	pyrene	
N-nitrosodiphenylamine	terphenyl-d14 (surrogate)	
pentachlorophenol	7,12-dimethylbenz(a)anthracene	
pentachloronitrobenzene	di- <i>n</i> -octyl phthalate	
phenacetin	indeno(1,2,3-cd)pyrene	
phenanthrene	3-methylcholanthrene	
pronamide		

An injection of 1 µL of each calibration standard (calibration range 20, 50, 80, 120, 160 µg/mL) containing ISs is analyzed and response factors for each compound of interest relative to the nearest eluting ISs are calculated according to Eq. 4.5-1.

$$RF = (A_s \times C_{is}) / (A_{is} \times C_s) \quad (4.5-1)$$

where:

A_s = area of the quantitation ion of the compound of interest

A_{is} = area of the quantitation ion of the IS

C_s = concentration of the compound of interest, µg/mL

C_{is} = concentration of the IS, µg/mL.

A system performance check must be performed to ensure that minimum average response factors for a specific set of compounds are obtained before the calibration curve may be used. For SVOCs, the system performance check compounds are:

- N-nitrosodi-*n*-propylamine;
- hexachlorocyclopentadiene;
- 2,4-dinitrophenol; and
- 4-nitrophenol.

The minimum acceptable average response factor for these compounds is 0.050. These compounds typically have low response factors (0.1 to 0.2), and the compound responses tend to decrease as the chromatographic system deteriorates or the standards degrade. These compounds are usually the first to show poor system performance. If the minimum average RF requirement is not met, the GC/MS system must be evaluated, and corrective action must be taken before samples are analyzed. Possible problems include degradation of standards, injector or column contamination or active sites in the column or in the chromatographic system. The problem must be corrected and the IC must be repeated.

The calibration check compounds are used to evaluate the calibration and the analytical system: high variability in the response factors for these compounds may be indicative of analytical system leaks or reactive sites on the chromatographic column. The calibration check compounds are shown in Table 4.5-4.

Table 4.5-4. Calibration Check Compounds for Analysis of SVOCs for the NATTS Program

Base/Neutral Compounds	Acid Compounds
acenaphthene	4-chloro-3-methylphenol
1,4-dichlorobenzene	2,4-dichlorophenol
hexachlorobutadiene	2-nitrophenol
diphenylamine	phenol
di- <i>n</i> -octyl phthalate	pentachlorophenol
fluoranthene	2,4,6-trichlorophenol

Table 4.5-4. Calibration Check Compounds for Analysis of SVOCs for the NATTS Program

Base/Neutral Compounds	Acid Compounds
benzo(a)pyrene	

After the IC samples have been analyzed, the mean response factor and standard deviation are calculated, and the RSD is calculated according to Equation 4.5-2.

$$RSD = \left(\frac{SD}{\overline{RF}} \right) \times 100 \quad (4.5-2)$$

where:

SD = standard deviation

RF = mean response factor.

If the RSD of any calibration check compound is > 30%, the chromatographic system is too reactive for analysis to begin and the injector liner and/or chromatographic column must be cleaned or replaced and the IC must be repeated.

If the RSD of any compound of interest is 15% or less, the RRF is assumed to be constant over the calibration range and the average RRF may be used for quantitation. If the RSD exceeds 15%, plotting and visual inspection of a calibration curve may indicate the source of the analytical problems such as errors in standard preparation, presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

The RRTs for each compound of interest in each calibration standard should agree within 0.06 RRT units.

Calibration Verification

The calibration of the analytical system must be verified every 12 hours. The analysis of DFTPP must be repeated and tuning criteria must be met. If tuning criteria are not met, the analytical system must be retuned and the IC must be repeated. To verify the calibration, a

calibration standard at a concentration near the midpoint of the calibration range of the GC/MS must be analyzed. Each system performance check compound must exhibit a minimum response factor of 0.050; if acceptance criteria are not met, the analytical system must be evaluated and corrective action must be taken before analysis is performed. Depending upon the nature of the corrective action, it may be necessary to repeat the IC.

After the system performance check has been performed, the calibration check compounds listed in Table 4.5-4 are used to verify the validity of the IC. Percent difference between the average response factor from the IC and the response factor calculated from the calibration verification sample must be $\leq 20\%$ in order for the IC to be considered valid. If the percent difference is $>20\%$, corrective action must be taken before samples can be analyzed. Depending upon the nature of the corrective action, it may be necessary to repeat the IC.

The retention times for each of the ISs in the calibration verification sample must be within ± 30 seconds of the retention time of that IS in the mid-level standard of the most recent IC. If the retention time for any IS changes by more than 30 seconds, analytical system corrections must be made, as required, and reanalysis of samples analyzed while the analytical system was malfunctioning is required.

If the extracted ion current plot area for any IS in the calibration verification standard changes by a factor of two (-50 to $+100\%$) from the comparable value of that IS in the mid-level standard of the most recent IC, analytical system corrections must be made, as required, and reanalysis of samples is required.

4.5.2.9 Analysis of Samples

The sample extracts must warm to room temperature before analysis. Just prior to analysis, the IS is added to the concentrated sample extract in an autosampler vial. A 1- μL sample aliquot of the sample extract is injected into the GC/MS system; this volume should contain 100 ng of base/neutral surrogate compounds and 200 ng of acid surrogate compounds (assuming 100% recovery).

If the response for any primary quantitation ion exceeds the IC range of the analytical system, the sample extract must be diluted and reanalyzed, maintaining the IS level at 40 ng/ μ L.

Qualitative Analysis

The ID of compounds of interest using Method 8270C is based on comparison of retention times with standards and comparison of the mass spectrum (after background subtraction) with the characteristic ions of a reference mass spectrum generated by the laboratory using the same analytical conditions. The following criteria must be met:

- The characteristic ions of a compound of interest must maximize in the same scan or within one scan of each other;
- The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component;
- The relative intensities of the characteristic ions agree within 30% with the relative intensities of these ions in the reference spectrum;
- Structural isomers that produce very similar mass spectra may be identified as individual isomers only if they have sufficiently different GC retention times (i.e., 25% valley between the peaks in question). Otherwise, structural isomers should be identified as isomeric pairs; and
- When analytes coelute, ID criteria may be met, but the spectrum will contain extraneous ions contributed by the coeluting compound.

Because Method 8270C is operating in the full-scan mode, a library search of a mass spectrum may be made for tentative ID, if the following criteria are met:

- Relative intensities of major ions in the reference spectrum should be present in the sample spectrum;
- Relative intensities of the major ions should agree within $\pm 20\%$;
- Molecular ions present in the reference spectrum should be present in the sample spectrum;

- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible contamination or elution of additional compounds; and
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of contamination or coeluting peaks.

Quantitative Analysis

After identification of a compound of interest, quantitative analysis of that compound will be performed on the basis of the integrated abundance of the primary characteristic ion of that compound. If the RSD of the response factor of that compound is $\leq 15\%$, the concentration of that compound in the extract may be determined using the average response factor from the IC curve.

To estimate the concentration of tentatively identified compounds, the same formula is used with a RF of one compared to the nearest eluting IS. The peak areas from the total ion chromatogram should be used. The calculated value should be reported with the qualification that the value is an estimate, with the IS used to determine the estimated concentration.

4.5.3 Determination of MDLs

MDLs that must be achieved for the NATTS Program are presented in Table 4.5-5. MDLs for SVOCs would be most accurately determined by gaseous spiking of the compounds of interest in the field so that the samples would go through the entire sampling and analytical process that field samples experience. This procedure for determination of MDLs is presently not practical, but the closest approximation in the laboratory involves spiking of cleaned certified sorbent so that the samples undergo at least the extraction (and cleanup, if used) and analysis portion of the procedure. The procedures of 40 CFR Part 136 Appendix B are used as a guideline for determination of MDLs. To follow the guidelines of 40 CFR Part 136 Appendix B, the following steps are required:

- Estimate an MDL. This estimate can usually be performed using the calibration standards: if the lowest calibration standard is at a level of 20 ng/μL, the analyst can make some estimate of an MDL from this standard.
- Determine a spiking level for the sorbent matrix. At least seven replicate clean sorbent samples should each be spiked with all of the compounds of interest at a level two to five times the estimated MDLs. For example, if the estimated MDL is 10 ng/μL, the spiking level for the matrix with a 1-mL final extract volume would be gauged to produce a final concentration of compounds of interest in the range of 20 to 50 ng/μL. Surrogate compounds and ISs are spiked at the same level as they are spiked in field samples.
- Prepare and analyze spiked XAD-2[®]; calculate MDLs according to the procedure of 40 CFR Part 136 Appendix B. The calculation of the MDLs is based on the standard deviation of the replicate analyses multiplied by the appropriate value of the Student's t corresponding to a 99% confidence level with n - 1 degrees of freedom.

The selection of the spiking level is a critical factor in the success of the determination. The calculation is based on the reproducibility of the measurement. If the spiking level selected is too low, chromatographic peaks will be more difficult to integrate, and the reproducibility of the measurement (and hence the MDLs) will suffer.

Table 4.5-5. Target MDLs for EPA Method 8270 Analytes: Extraction From Spiked XAD-2 Resin

Compound	MDL (μg)	Compound	MDL (μg)
N-nitrosodimethylamine	6.62	acenaphthylene	4.17
pyridine	11.73	2,4-dinitrophenol	17.00
ethyl methanesulfonate	6.26	4-nitrophenol	9.36
2-picoline	8.10	acenaphthene	5.10
N-nitrosomethylethylamine	6.19	2,4-dinitrotoluene	5.65
methyl methanesulfonate	8.07	2-naphthylamine	4.35
N-nitrosodiethylamine	7.24	dibenzofuran	4.79
phenol	4.50	pentachlorobenzene	5.33
pentachloroethane	6.05	1-naphthylamine	7.10
bis(2-chloroethyl) ether	3.75	diethyl phthalate	7.04
aniline	4.38	2,3,4,6-tetrachlorophenol	4.42
2-chlorophenol	4.78	4-nitroaniline	4.39

Table 4.5-5. Target MDLs for EPA Method 8270 Analytes: Extraction From Spiked XAD-2 Resin

Compound	MDL (µg)	Compound	MDL (µg)
1,3-dichlorobenzene	3.88	4-chlorophenyl phenyl ether	6.25
1,4-dichlorobenzene	4.90	fluorene	4.37
benzyl alcohol	4.96	5-nitro- <i>o</i> -toluidine	3.88
<i>o</i> -cresol (2-methylphenol)	6.17	4,6-dinitro-2-methylphenol	4.20
1,2-dichlorobenzene	4.16	diphenylamine	4.75
<i>bis</i> (2-chloroisopropyl) ether	4.50	azobenzene	1.70
<i>m</i> -, <i>p</i> -cresol (3- and 4-methylphenol)	6.08	phenacetin	5.62
N-nitrosopyrrolidine	7.90	diallate	4.09
N-nitrosodi- <i>n</i> -propylamine	7.44	4-bromophenyl phenyl ether	8.07
<i>o</i> -toluidine	5.25	4-aminobiphenyl	4.75
hexachloroethane	5.74	hexachlorobenzene	4.46
acetophenone	4.57	pronamide	5.54
nitrobenzene	4.11	pentachlorophenol	6.23
N-nitrosopiperidine	5.30	pentachloronitrobenzene	6.76
isophorone	4.00	phenanthrene	5.32
2-nitrophenol	4.60	dinoseb	6.27
2,4-dimethylphenol	3.64	anthracene	6.77
<i>bis</i> (2-chloroethoxy)methane	3.76	carbazole	6.97
2,4-dichlorophenol	5.03	di- <i>n</i> -butyl phthalate	5.21
4-chloroaniline	4.70	benzidine	50.00
1,2,4-trichlorobenzene	4.76	isodrin	4.99
naphthalene	5.59	fluoranthene	5.43
2,6-dichlorophenol	5.18	pyrene	4.84
hexachloropropene	4.94	4-dimethylaminoazobenzene	2.50
hexachlorobutadiene	4.98	chlorobenzilate	4.07
N-nitrosodi- <i>n</i> -butylamine	5.65	3,3'-dimethylbenzidine	27.76
4-chloro-3-methylphenol	5.05	butyl benzyl phthalate	5.37
safrole	4.97	2-acetylaminofluorene	6.74
2-methylnaphthalene	5.69	3-methylcholanthrene	6.90
1,2,4,5-tetrachlorobenzene	5.96	3,3'-dichlorobenzidine	3.79
2,4,6-trichlorophenol	4.86	<i>bis</i> (2-ethylhexyl) phthalate	5.79

Table 4.5-5. Target MDLs for EPA Method 8270 Analytes: Extraction From Spiked XAD-2 Resin

Compound	MDL (µg)	Compound	MDL (µg)
hexachlorocyclopentadiene	5.60	benzo(a)anthracene	4.68
2,4,5-trichlorophenol	5.05	chrysene	4.28
2-nitroaniline	5.31	di- <i>n</i> -octyl phthalate	3.99
isosafrole	4.95	7,12-dimethylbenz(a)anthracene	5.96
2-chloronaphthalene	4.72	benzo(b)fluoranthene	3.69
1,4-naphthoquinone	8.49	benzo(k)fluoranthene	6.07
dimethyl phthalate	4.56	benzo(a)pyrene	1.88
1,3-dinitrobenzene	5.89	indeno(1,2,3-cd)pyrene	5.09
2,6-dinitrotoluene	3.94	dibenz(a,h)anthracene	5.84
3-nitroaniline	3.41	benzo(g,h,i)perylene	7.69

Note: Quantitative data from phenol, cresols, benzyl alcohol, acetophenone, dibenzofuran, and possibly other oxygenated compounds may be biased high because of the potential for oxidation of the XAD-2[®] by ambient ozone during sampling.

4.5.4 Quality Control

QC measures necessary to evaluate the operation of the GC/MS system include:

- Tuning of the GC/MS system to meet DFTPP criteria initially, with verification of the stability of the DFTPP tune every 12 hours of operation;
- IC of the analytical system to meet acceptance criteria, with acceptable performance of the system performance check compounds and the calibration check compounds;
- Acceptable calibration verification every 12 hours of operation; and
- Acceptable stability of RRTs.

The laboratory must perform an initial demonstration of proficiency by analyzing multiple LCSs at an acceptable level of accuracy and precision. The demonstration of proficiency must be repeated as new staff are trained or when significant changes in laboratory instrumentation are made. The LCS consists of cleaned XAD-2[®] spiked with the surrogate

compounds and the compounds of interest. Successful analysis of the LCS demonstrates that the laboratory can perform the sample preparation and analysis successfully in a clean matrix and can be used to document the effect of the matrix on the collected samples.

The analysis of QC samples including a method blank, method spike, and a LCS for each sample batch. The addition of surrogate compounds to each field sample and QC sample is required.

Each laboratory must evaluate surrogate recovery data from individual samples against the surrogate compound control limits developed by the laboratory. Method 8270C includes surrogate compound recovery limits. The values in Table 4.5-6 were established for surrogate compounds in a field dynamic spiking study for stationary source analysis. These values can serve as an approximate guideline until the laboratory establishes its own control limits.

Table 4.5-6. Surrogate Compound Control Limits for SVOC Analysis Using EPA Compendium Method TO-13A/8270C

Surrogate Compound	Estimated Recovery Control Limits (%)
2-fluorophenol	40 to 100
phenol-d ₅	50 to 110
nitrobenzene-d ₅	35 to 95
2-fluorobiphenyl	46 to 106
2,4,6-tribromophenol	33 to 101
terphenyl-d ₁₄	47 to 112

4.5.5 Analysis of Polycyclic Aromatic Hydrocarbons (PAHs) Only—An Alternative Approach

Polycyclic aromatic hydrocarbons (PAHs) make up a subset of the SVOCs presented in Table 4.5-1. There may be situations in which it is desirable to measure only the PAHs. Although the preferred method for collection of semivolatile organic compounds uses XAD-2[®],

certain PAHs only can be collected using PUF. However, prior approval from EPA must be obtained before PAH-specific measurements can be applied to the NATTS Program, if required. An organic compound with a boiling point ≥ 100 °C is considered an SVOC. Within the category of semivolatile organic compounds, PAHs have received increased attention in recent years in air pollution studies because some of the compounds in this class are highly carcinogenic or mutagenic. Specifically, benzo(a)pyrene has been identified as highly carcinogenic. PAHs are primarily products of incomplete combustion processes from natural sources such as wildfires, from industrial processes, transportation, energy production and use, food preparation, smoking tobacco, and disposal activities such as open trash burning. PAHs generally occur as complex mixtures rather than as single compounds. Benzo(a)pyrene (as well as other PAHs) is bioaccumulative, does not break down easily in the environment and is subject to long-range air transport. To understand human risk and the level of human exposure to benzo(a)pyrene and other PAHs, it is necessary to sample and analyze reliably for these compounds. Current methodology requires sampling ambient air with a quartz fiber filter and a sorbent collection module, with subsequent analysis by high resolution gas chromatography coupled with mass spectrometry. EPA Compendium Method TO-13A,¹⁴ “Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS)”, is included in *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, Second Edition (EPA/625/R-96/010b). The complete compendium of methods for ambient air is on-line at www.epa.gov/ttn/amtic/airtox.html ; the specific location of Compendium Method TO-13A is www.epa.gov/ttn/amtic/files/ambient/airtox/to-13arr.pdf .

PAHs encompass a broad range of vapor pressures; the least volatile compounds in the category are present in ambient air substantially distributed between gas and particulate phases. EPA Compendium Method TO-13A¹⁴ sampling methodology permits collection of both phases. However, in the operation of the sampling train, nonvolatile PAHs (PAHs with vapor pressure $< 10^{-8}$ mm Hg) may initially be trapped on the filter but will volatilize to an unknown extent as additional air is pulled through the sampling train: this postcollection volatilization will result in the distribution of the PAHs between the filter and the sorbent¹⁸⁻²³. Because of this postcollection volatilization of collected compounds, separate analysis of the filter will not

accurately reflect the concentrations of the PAHs originally associated with particles; separate analysis of the sorbent will not provide an accurate measurement of the gas phase. EPA Compendium Method TO-13A¹⁴ therefore requires extraction of the filter and sorbent together in order to provide an accurate measurement of total PAH concentrations in ambient air. Because of the relatively low levels of common PAHs in the environment, the methodology suggests the use of a high volume (0.22 m³/min) sampling technique to acquire sufficient sample for analysis. However, the volatility of certain PAHs prevents efficient collection by filter media alone. Consequently, this method utilizes both a filter and a backup PUF cartridge, which provides for efficient collection of most PAHs involving three aromatic rings or higher. A further consideration in sampling SVOCs is the potential loss of lighter SVOCs if sampling occurs during elevated temperatures.

Many of the PAHs have been identified as highly carcinogenic. To understand the extent of human exposure to these PAHs, reliable sampling and analytical methods are necessary. The EPA Compendium Method TO-13A¹⁴ is used to sample and analyze common PAHs. The method involves the use of a combination of quartz filter and sorbent cartridge with subsequent analysis by GC/MS detection. The use of GC/MS as the recommended procedure for analysis of the PAHs was influenced by its sensitivity and selectivity, along with its ability to analyze complex samples.

A wide variety of sorbents such as Tenax[®], XAD-2[®] and PUF^{23,24} have been used to sample common PAHs. All sorbents have demonstrated high collection efficiency. In general, XAD-2[®] resin has a higher collection efficiency for volatile PAHs than PUF, as well as a higher retention efficiency for both volatile and reactive PAHs. PUF cartridges, however, are easier to handle in the field and maintain better flow characteristics during sampling. PUF has demonstrated its capability in sampling organochlorine pesticides, polychlorinated biphenyls and polychlorinated dibenzo-*p*-dioxins but has demonstrated a lower recovery efficiency and storage capability for naphthalene than XAD-2[®].

Filters and PUF cartridges are cleaned in solvents and vacuum dried; PUF can also be purchased precleaned. The filters and PUF cartridges are stored in screw-capped jars wrapped in

aluminum foil (or otherwise protected from light) before careful installation on the sampler. Approximately 300 m³ of air is drawn through the filter and PUF cartridge using a high volume flow rate air sampler or equivalent. The amount of air sampled through the filter and PUF cartridge is recorded, and the filter and cartridge are placed in an appropriately labeled container and shipped along with a blank filter and PUF cartridge and COC forms to the analytical laboratory for analysis.

The filters and PUF cartridges are extracted with the appropriate solvent and prepared to remove potential interferences prior to analysis by GC/MS. The eluent is then analyzed by GC/MS. The analytical system is verified to be operating properly and calibrated with five concentrations of calibration solutions. Other preparation approaches such as accelerated solvent extraction (ASE) may be used if performance equivalent to standard extraction procedures is demonstrated. ASE is safer than conventional extraction procedures and more economical of solvent.

4.5.5.1 Sampling Apparatus and Procedures

Sample collection for quantitative determination of PAHs is accomplished by pulling ambient air at a known and constant flow rate through a quartz fiber filter followed by cartridge containing a PUF plug across a 24-hour collection period.

- High volume sampler. The sample collection is performed using a commercially available PS-1 high volume sampling system capable of maintaining a flow rate of approximately eight standard cubic feet per minute (scfm) through the filter/PUF plug to obtain a total sample volume greater than 325 scm across a 24-hour duration.
- High volume sampler calibrator. The high volume sampler is calibrated using a compatible calibrator to apply multiple levels of simulated resistance to the sampler flow path and characterizing the sampler's performance. The multiple levels of simulated resistance are typically accomplished using individual orifice plates or a variable orifice device.
- Quartz fiber filter. The filter is a 102-mm bindless quartz microfiber filter.

- PUF plugs. The PUF plug is constructed of the polyether type of PUF with a density of 0.022 g/cm^3 . The PUF plug is 3 in. thick and has an outside diameter of approximately $2 \frac{3}{8}$ inches, or is approximately 1/8-in. larger in diameter than the opening in the cartridge into which the PUF plug slides.
- Glass sample cartridge. The cartridge used to contain/secure the PUF plug during sample collection is comprised of a thick-walled glass tube outfitted with a stainless steel screen at the outlet end. The cartridge is sized to accomplish a leak-tight fit in the high volume sampler so that all sample air is channeled through the PUF plug.

4.5.5.2 Sample Collection Procedures

The sampler should be located in an unobstructed area at least 2-m from any obstacle to airflow. The inlet of the high volume sampler must be positioned in the breathing zone, 4 to 10 feet above ground level. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air into the sampling head. When a new sampler is set up or when the sampler is used at a different location, all areas of the sampling apparatus that contact the sample need to be cleared using triple rinses of reagent-grade hexane contained in Teflon wash bottles. All cleaning and washing should be done in a controlled environment to minimize contamination. Solvent should be allowed to evaporate before the PUF sampling module is loaded into the sampler.

Calibration

The high volume sampler is calibrated using a calibrated orifice transfer standard (i.e., high volume sampler calibrator) in accordance with the specifications of EPA Compendium Method TO-13A.¹⁴ The individual orifice plates are placed in the sampling flow stream, and the differential pressure across the orifice plate is documented. Simultaneously, a corresponding Magnehelic pressure reading is recorded. The differential pressure and the Magnehelic readings are used to create a curve that establishes the flow characteristics of each sampler.

Sample Collection

The prepared PUF cartridge is placed and secured into the sampling head of the high volume sampler. The quartz fiber filter is placed and secured onto the inlet of the high volume sampler. The system is activated manually and the desired Magnehelic reading is achieved by adjusting the ball valve located at the exit of the sampling head. The sampler is then programmed to turn on at 12:00 a.m. and turn off at 11:59 p.m. automatically for the 24-hour sampling period. At the end of the sampling period, the sampler is once again activated manually, and a final Magnehelic reading is made without any adjustment to the ball valve. The filter is removed, folded in quarters and placed inside the glass cartridge with the PUF plug. The PUF cartridge is then removed from the high volume sampler and transported to the laboratory.

4.5.6 Analysis Procedures and Issues

A detailed SOP must be prepared to encompass all of the procedures involved with the analysis of PAHs using EPA Compendium Method TO-13A.¹⁴

4.5.6.1 Sample Extraction, Concentration and Cleanup

Field samples should be stored and shipped chilled (<4 °C) in coolers using Blue Ice until the samples are received at the analytical laboratory. After receipt at the analytical laboratory, the samples should be refrigerated at ≤4 °C. Samples should be extracted within seven days after sampling; extracts should be analyzed within 40 days after extraction.

A Soxhlet extraction is performed using approximately 700 mL of 10% diethyl ether in hexane, with the sorbent and filter extracted together in the Soxhlet extractor; the extractor should reflux for 18 hours at a rate of at least three cycles per hour. Prior to extraction the laboratory surrogate standards are spiked into each sample and blank at a level of 1.0 µg/mL. The recovery of the laboratory surrogate is used to monitor for matrix effects or errors in sample preparation and should be in the range of 60 to 120%. The extractor is allowed to cool and is then disassembled. The extract is dried by passing it through a drying column containing ~10 g

of cleaned anhydrous sodium sulfate and is then concentrated using a Kuderna-Danish concentration apparatus followed by nitrogen blow-down to a final volume of 1.0 mL. The extract is transferred to a Teflon-sealed, screw cap amber vial and stored at 4 ± 2 °C until analysis.

To perform a matrix spike analysis, a specific field sample must be taken and designated for this purpose. Matrix spikes are generally not performed for ambient air samples. An LCS in which all of the analytes are spiked onto a clean sorbent matrix and recovered in the laboratory is performed to monitor matrix effects.

A cloudy extract may be purified by solid phase extraction using activated silica gel. If the sample matrix is clean, sample cleanup is not needed. The extract is cleaned up using a succession of solvents with approximately 10 g of cleaned activated silica gel, according to the procedures of EPA Compendium Method TO-13A.¹⁴ The extract eluted from the silica gel cleanup column is concentrated to < 5 mL using a Kuderna-Danish concentrator and then to a final volume of 1 mL using a nitrogen blow-down.

4.5.6.2 GC/MS Analysis

The analysis of the sample extract for PAH is accomplished by operation of the GC/MS system in the electron ionization mode (nominal 70 eV), using selected ion monitoring (SIM) to monitor the compounds of interest at the highest possible level of sensitivity. SIM monitors only the specified ions; the ability to characterize other compounds is precluded. The GC/MS is tuned using a 5-ng/ μ L solution of DFTPP, but the standard tuning criteria for full-scan mode are irrelevant when SIM procedures are used. Since the masses for the PAHs are between 150 and 300, the mass spectrometer should be tuned to maximize the signal for the DFTPP ions above mass 150 (i.e., the mass spectrometer should be tuned to optimize the signal for masses 198, 275, 365, and 442 while maintaining unit resolution between masses 197, 198, and 199 as well as 441, 442, 443).

A stable tune should be established with the highest possible sensitivity for the high masses. The stability of this tune should be demonstrated every 12 hours.

Analysis of Field Samples by GC/MS

Field samples are extracted, cleaned up if necessary and concentrated to a final volume of 1 mL. All sample extracts are allowed to warm to room temperature before analysis (~1 hour). After the GC/MS system has met tuning criteria and has been calibrated (or has met continuing calibration acceptance criteria), field samples are analyzed after the addition of the ISs. When all compounds of interest have eluted from the gas chromatograph, quantitative analysis is performed using retention times and abundances of the primary quantitation ions of ISs and compounds of interest. Note that a secondary ion may be used to perform quantitative analysis only if analytical interference is encountered for the primary quantitation ion. When a sample extract is analyzed that has a compound of interest with a concentration $\geq 20\%$ above the upper range of the calibration curve, the extract must be diluted and reanalyzed. A level of dilution that will keep the compounds of interest within the upper half of the calibration range should be used to ensure that no compound has saturated ions. Since the results of the original analysis are used to estimate the dilution factor required, the level of dilution can be difficult to gauge if the shape of the peak indicates that chromatographic saturation has occurred in addition to mass spectrometric detector saturation. A compound with chromatographic as well as mass spectrometric detector saturation may require sequential dilutions. The sample is diluted with hexane in volumetric glassware, the IS concentration is adjusted and the diluted sample is analyzed.

Quantitative analysis is performed using the mean relative response factor from the most recent initial calibration as follows:

$$Concentration = \frac{A_x I_s V_t D_f}{A_{is} V_i RRF} \quad (4.5-3)$$

where:

Concentration = concentration of the compound of interest, ng/std m³

A_x = area response for the primary ion of the compound of interest

A_{is} = area response for the primary ion of the IS

I_s = amount of IS, ng/mL

\overline{f} = mean relative response factor from the most recent initial calibration

V_i = volume of air sampled, std m³

V_t = volume of final extract, mL

D_f = dilution factor for the extract. If there is no dilution, $D_f = 1$. For a diluted sample, $D_f > 1$.

4.5.6.3 Determination of MDLs

As with SVOC measurement, MDLs for PAHs would be most accurately determined by gaseous spiking of the compounds of interest in the field so that the samples would go through the entire sampling and analytical process that field samples experience. This procedure for determination of MDLs is presently not practical, but the closest approximation in the laboratory involves spiking of cleaned certified sorbent so that the samples experience at least the extraction (and cleanup, if used) and analysis portion of the procedure. The procedures of 40 CFR Part 136 Appendix B are used as a guideline for determination of MDLs. To follow the guidelines of 40 CFR Part 136 Appendix B, the following steps are required:

- Estimate the MDLs. This estimate can usually be performed using the calibration standards: if the lowest calibration standard is at a level of 100 picograms (pg)/ μ L, the analyst can make some estimate of MDLs from this standard.
- Determine a spiking level for the sorbent matrix. At least seven replicate sorbent samples should be spiked with all of the compounds of interest at a level two to five times the estimated MDLs. For example, if the estimated MDL is 50 pg/ μ L, the spiking level for the matrix with a 1-mL final extract volume would be gauged to produce a final concentration of compounds of interest in the range of 100 to 250 pg/ μ L. Surrogate compounds and ISs are spiked at the same level as they are in field samples.
- Prepare and analyze spiked PUF; calculate MDLs. The calculation of the MDLs is based on the standard deviation of the replicate analyses multiplied by the

appropriate value of the Student's t corresponding to a 99% confidence level with n - 1 degrees of freedom. The Student's t values at the 99% confidence level are shown in Table 4.5-7.

Table 4.5-7. Student's t Values at the 99% Confidence Level

Number of Replicates	Degrees of Freedom	t
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764

The selection of the spiking level is a critical factor in determining the success of the determination. The calculation is based on the reproducibility of the measurement. If the spiking level is too low, chromatographic peaks will be more difficult to integrate, and the reproducibility of the measurement (and hence the MDLs) will suffer. A typical set of MDLs for the EPA Compendium Method TO-13A¹⁴ PAH analytes is shown in Table 4.5-8.

Table 4.5-8. Target MDLs for EPA Compendium Method TO-13A Analytes: Extraction from Spiked PUF

Analyte	Method Detection Limit (ng)
Acenaphthene	0.047
acenaphthylene	0.052
anthracene	0.033
benz(a)anthracene	0.029
benzo(a)pyrene	0.040
benzo(e)pyrene	0.020
benzo(g,h,i)perylene	0.020
benzo(b)fluoranthene	0.031
benzo(k)fluoranthene	0.022
chrysene	0.028
coronene	0.018

Table 4.5-8. Target MDLs for EPA Compendium Method TO-13A Analytes: Extraction from Spiked PUF

Analyte	Method Detection Limit (ng)
dibenz(a,h)anthracene	0.020
fluoranthene	0.033
fluorene	0.080
indeno(1,2,3-cd)pyrene	0.028
naphthalene	0.172
perylene	0.027
phenanthrene	0.031
pyrene	0.040

4.5.6.4 QA/QC

Before analysis of any field samples, the laboratory must demonstrate, by analysis of a LRB, that interferences from the analytical system, glassware and reagents are under control. For each batch of field samples (up to 20 samples) an LRB and LCS must be analyzed and must meet acceptance criteria. A field blank should be analyzed at a frequency dependent upon the sampling frequency. For a 6-day sampling frequency, one field blank per quarter is sufficient.

Tuning criteria must be met before the initial 5-point calibration is performed; the initial calibration must meet acceptance criteria.

For each day of analysis, tuning criteria must be met and the calibration check sample must be evaluated to verify the stability of the calibration curve and optimal performance of the chromatograph. IS signal areas must meet project specifications, and surrogate compound recoveries should be within a 60 to 120% recovery window. If significant changes are made to the analytical system (i.e., chromatographic column changed, ion source cleaned, quadrupoles cleaned, etc.), the IC must be repeated.

4.6 OVERVIEW OF EPA COMPENDIUM METHOD TO-9A

Sampling of ancient human tissue shows much lower levels of polychlorinated dibenzo-*p*-dioxins and -furans (PCDDs/PCDFs) than are found today²⁵. Studies of sediment cores in lakes near industrial centers of the United States have shown that dioxin and furan levels were quite low until about 1920²⁶⁻²⁸. Concentrations of these compounds increased beginning in the 1920s until about 1970, when concentrations began to decline. These trends have been shown to correspond to trends in chlorophenol production²⁶. The introduction of dioxin-like compounds into the environment can thus be related to anthropogenic activity. Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofuran (PCDFs) are not commercial chemical products but are trace-level unintentional by-products of most forms of combustion and several industrial chemical processes.

PCDDs/PCDFs are dispersed through the environment by atmospheric transport and are found in the environment as complex mixtures of all isomers.^{27,28} The isomer profiles of PCDDs/PCDFs found in ambient air are similar to those found in combustion sources. For PCDDs/PCDFs related to specific chemical products and by-products, only a few specific and characteristic isomers are detected. The possible numbers of positional isomers for each member of the PCDD/PCDF chemical family (congeners) are shown in Table 4.6-1.

Table 4.6-1. Possible Number of Positional Isomers at Each Chlorine Level

Chlorine Substitution (Number)	Number of Possible Compounds	
	PCDDs	PCDFs
mono (1)	2	4
di (2)	10	16
tri (3)	14	28
tetra (4)	22	38
penta (5)	14	28
hexa (6)	10	16
hepta (7)	2	4
octa (8)	1	1

The 2,3,7,8-substituted PCDDs/PCDFs are considered to be the most toxic isomers, although they account for only a small percentage of the total concentrations found in stack gas emissions from combustion sources and in ambient air. The 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), the most toxic of the PCDDs/PCDFs, is usually found as a very minor component in stack gas emissions and is seldom found in ambient air samples. All of the 2,3,7,8-substituted PCDDs/PCDFs are retained in tissue of life forms such as humans, fish, and wildlife, and the non-2,3,7,8-substituted PCDDs/PCDFs are rapidly metabolized and/or excreted.

Because the PCDDs/PCDFs can be formed by thermal reactions, there has been an increasing interest in ambient air monitoring, especially in the vicinity of combustion and incineration processes such as municipal waste combustors and resource recovery facilities. EPA Compendium Method TO-9A²⁹ (<http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-9arr.pdf>) can be used for NATTS monitoring, if required, to accurately determine the presence or absence of pg/m³ or sub-pg/m³ levels of these compounds in ambient air. The sampling methodology uses a high volume air sampler equipped with a quartz fiber filter and PUF adsorbent for sampling 325 to 400 m³ of ambient air in a 24-hour sampling period. The analytical procedures used for the field samples are based on HRGC coupled with high resolution mass spectrometry (HRMS). EPA Compendium Method TO-9A²⁹ provides accurate quantitative data for tetra- through octa-PCDDs/PCDFs, with total concentrations for each isomeric series as well as accurate specific compound concentrations for a limited number of compounds. Specificity is achieved for quantitative determination of the seventeen 2,3,7,8-substituted PCDDs/PCDFs, with MDLs in the range of 0.01 to 0.2 pg/m³ in ambient air. Concentrations as low as 0.2 pg/m³ can be accurately quantified. The method does not separately quantify gaseous PCDDs/PCDFs and particulate-associated PCDDs/PCDFs because some of the compounds volatilize from the filter and are collected by the PUF adsorbent. PCDDs and PCDFs may be distributed between the gaseous and particle-adsorbed phases in ambient air, so the filter and PUF are combined for extraction in EPA Compendium Method TO-9A.²⁹

Attention has been focused on the determination of PCDDs/PCDFs in ambient air only in recent years. The sample preparation and analysis is time-consuming, complex, difficult and expensive because of the following factors:

- Isotopically labeled standards used in the analysis must incorporate the ^{37}Cl atom as well as ^{13}C , making the standards very expensive to produce and hence to purchase;
- The sample preparation process requires the application of a number of labor-intensive sample cleanup steps to avoid interferences with the analysis, as well as special precautions taken for working with the materials. The 2,3,7,8-TCDD and other 2,3,7,8-substituted isomers are toxic and can pose health hazards if not handled properly. Each of the compounds must be treated as a health hazard, and laboratory staff exposure to these compounds must be minimized. The laboratory staff working with these compounds must follow a strict safety program with an isolated work area, waste handling and disposal procedures, decontamination procedures, and regular wipe testing of the laboratory facilities;
- Because of the high toxicity of specific PCDDs/PCDFs, HRMS must be used to provide the highest possible sensitivity as well as the highest possible level of confidence in the identification of the compound. The instrumentation is complex and expensive, and the computer programs required to reduce the data are also complex and expensive. The analysis must be performed for very low concentrations (pg/m^3 and less), and MDLs must be in the range of 0.01 to 0.2 pg/m^3 to obtain meaningful results for ambient air monitoring purposes.

Quartz fiber filters, PUF plugs and glass adsorbent cartridges are precleaned with appropriate solvents and dried in a clean atmosphere. The PUF is spiked with a known amount of isotopically labeled dioxin standard prior to field deployment. The cartridges and filters are shipped to the field in cleaned, labeled shipping containers. The high volume sampler is put into operation, usually for 24 hours, to sample 325 to 400 m^3 of ambient air. The volume of air sampled is recorded on the COC form shipped to the laboratory with the corresponding filter and PUF. The filter and PUF are combined for sample extraction, the extracts are cleaned up and the sample extracts are subjected to HRGC/HRMS SIM analysis to determine the sampler efficiency, extraction efficiency and the concentrations or the MDLs achieved for the PCDDs/PCDFs. The analytical procedures can be performed to determine only 2,3,7,8-TCDD as the most toxic compound, or the analysis can be performed to determine all possible chlorinated

congeners. The analytical results and the volume of air sampled are used to calculate the concentrations of the respective tetra- through octa-isomers, the concentrations of the 2,3,7,8-chlorine-substituted isomers or the MDLs. The concentrations and/or MDLs are reported in pg/m^3 .

4.6.1 General Description of Sampling Method and Analytical Method Requirements/Capabilities

Sample collection for quantitative determination of PCDDs/PCDFs is accomplished by pulling ambient air at a known and constant flow rate through a quartz fiber filter followed by a cartridge containing a PUF plug for the duration of a 24-hour collection period.

4.6.2 Sampling Procedure and Issues Associated with EPA Compendium Method TO-9A

The equipment listed below is required for the collection of samples for the analysis of PCDD/PCDFs.

- High volume sampler. The sample collection is performed using a commercially available PS-1 high volume sampling system capable of maintaining a flow rate of approximately 8 scfm through the filter/PUF plug to obtain a total sample volume greater than 325 scm across a 24-hour duration.
- High volume sampler calibrator. The high volume sampler is calibrated using a compatible calibrator to apply multiple levels of simulated resistance to the sampler flow path and characterize the sampler's performance. The multiple levels of simulated resistance are typically accomplished using individual orifice plates or a variable orifice device.
- Quartz fiber filter. The filter is a 102-mm bindless quartz microfiber filter.
- PUF plugs. The PUF plug is constructed of the polyether type of PUF with a density of $0.022 \text{ g}/\text{cm}^3$. The PUF plug is 3-in. thick and has an outside diameter of approximately $2 \frac{3}{8}$ in. or approximately $\frac{1}{8}$ -in. larger in diameter than the opening in the cartridge into which the PUF plug slides.

- Glass sample cartridge. The cartridge used to contain/secure the PUF plug during sample collection is comprised of a thick-walled glass tube outfitted with a stainless steel screen at the outlet end. The cartridge is sized to accomplish a leak-tight fit in the high volume sampler so that all sample air is channeled through the PUF plug.
- Preparation of PUF. The PUF used in sampling is a cylindrical plug 6.0 centimeters (cm) in diameter cut from a 3-in. sheet of PUF. Precleaned PUF can be obtained from commercial sources, but at least one PUF plug from a batch should be extracted and analyzed according to EPA Compendium Method TO-9A²⁹ procedures to demonstrate that no contamination of the PUF media has occurred. For an initial cleanup, a number of the PUF plugs are placed in a Soxhlet extractor and extracted with acetone for 16 hours at approximately four cycles per hour. PUF sampling cartridges may be reused. When the cartridges are reused, diethyl ether/hexane (5 to 10% volume/volume) is used as the cleanup extraction solvent. At least one PUF plug from each batch (either commercially cleaned or laboratory cleaned) should be extracted and analyzed according to the preparation and analytical procedures of EPA Compendium Method TO-9A.²⁹ A level of 2 to 20 pg for tetra-, penta- and hexachlorodioxins and 40 to 150 pg for hepta- and octachlorodioxins (similar to the levels detected in the method blank) is acceptable. If levels above these criteria are observed, the entire batch of PUF must be recleaned. If the cleaning process is repeated and the PUF still cannot meet the cleanliness criteria, the batch of PUF (and possibly the sheet from which the plugs were cut) must be discarded. Cartridges are considered clean for up to 30 days from date of certification when stored in their sealed containers. Prior to deployment with the sampling system, the PUF cartridges are spiked with isotopically labeled surrogate compounds, as shown in Table 4.6-2. The surrogate compound solution is added to each PUF sampling cartridge, in the center of the bed of the PUF cartridge, using a microsyringe.

4.6.2.1 Sampling Procedure

The sampler should be located in an unobstructed area at least 2 m from any obstacle to airflow with the inlet positioned in the breathing zone, 4 to 10 feet above ground level. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air into the sampling head. When a new sampler is set up or when the sampler is used at a different location, all areas of the sampling apparatus that contact the sample need to be cleaned using triple rinses of reagent-grade hexane contained in Teflon wash bottles. All cleaning and washing should be done in a controlled environment to minimize contamination. Solvent should be allowed to evaporate before the PUF sampling module is loaded into the sampler.

Table 4.6-2. Native and Isotopically Labeled Standards

Native Compounds	Internal Standards
2,3,7,8-tetrachlorodibenzo- <i>p</i> -dioxin	¹³ C ₁₂ -2,3,7,8-tetrachlorodibenzo- <i>p</i> -dioxin
2,3,7,8-tetrachlorodibenzofuran	¹³ C ₁₂ -1,2,3,7,8-pentachloro- <i>p</i> -dibenzodioxin
1,2,3,7,8-pentachlorodibenzo- <i>p</i> -dioxin	¹³ C ₁₂ -1,2,3,6,7,8-hexachloro- <i>p</i> -dibenzodioxin
1,2,3,7,8-pentachlorodibenzofuran	¹³ C ₁₂ -1,2,3,4,6,7,8-heptachloro- <i>p</i> -dibenzodioxin
2,3,4,7,8-pentachlorodibenzofuran	¹³ C ₁₂ -octachlorodibenzo- <i>p</i> -dioxin
1,2,3,4,7,8-hexachlorodibenzo- <i>p</i> -dioxin	¹³ C ₁₂ -2,3,7,8-tetrachlorodibenzofuran
1,2,3,6,7,8-hexachlorodibenzo- <i>p</i> -dioxin	¹³ C ₁₂ -1,2,3,7,8-pentachlorodibenzofuran
1,2,3,7,8,9-hexachlorodibenzo- <i>p</i> -dioxin	¹³ C ₁₂ -1,2,3,4,7,8-hexachlorodibenzofuran
1,2,3,4,7,8-hexachlorodibenzofuran	¹³ C ₁₂ -1,2,3,4,6,7,8-heptachlorodibenzofuran
1,2,3,6,7,8-hexachlorodibenzofuran	Surrogate Standards
1,2,3,7,8,9-hexachlorodibenzofuran	¹³ C ₁₂ -2,3,4,7,8-pentachlorodibenzofuran
2,3,4,6,7,8-hexachlorodibenzo- <i>p</i> -dioxin	¹³ C ₁₂ -1,2,3,4,7,8-hexachloro- <i>p</i> -dibenzodioxin
1,2,3,4,6,7,8-heptachloro- <i>p</i> -dibenzodioxin	¹³ C ₁₂ -1,2,3,6,7,8-hexachlorodibenzofuran
1,2,3,4,6,7,8-heptachlorodibenzofuran	¹³ C ₁₂ -1,2,3,6,7,8,9-heptachloro- <i>p</i> -dibenzodioxin
1,2,3,4,7,8,9-heptachlorodibenzofuran	Field Standards
octachlorodibenzo- <i>p</i> -dioxin	³⁷ Cl ₄ -2,3,7,8-tetrachlorodibenzo- <i>p</i> -dioxin
octachlorodibenzofuran	¹³ C ₁₂ -1,2,3,7,8,9-hexachloro- <i>p</i> -dibenzodioxin
Recovery Standard	
¹³ C ₁₂ -1,2,3,4-tetrachlorodibenzo- <i>p</i> -dioxin	

Calibration

The high volume sampler is calibrated using a calibrated orifice transfer standard (i.e., high volume sampler calibrator) in accordance with the specifications of EPA Compendium Method TO-9A.²⁹ The individual orifice plates are placed in the sampling flow stream, and the differential pressure across the orifice plate is documented. Simultaneously, a corresponding Magnehelic pressure reading is recorded. The differential pressure and the Magnehelic readings are used to create a curve that establishes the flow characteristics of the sampler.

Sample Collection

The prepared PUF cartridge is placed and secured into the sampling head of the high volume sampler. The quartz fiber filter is placed and secured onto the inlet of the high volume sampler. The system is activated manually, and the desired Magnehelic reading is achieved by adjusting the ball valve located at the exit of the sampling head. The sampler is then programmed to turn on at 12:00 a.m. and turn off at 11:59 p.m. automatically for the 24-hour sampling period. At the end of the sampling period, the sampler is once again activated manually, and a final Magnehelic reading is made without any adjustment to the ball valve. The filter is removed, folded in quarters and placed inside the glass cartridge with the PUF plug. The PUF cartridge is then removed from the high volume sampler and transported to the laboratory.

4.6.3 Analytical Procedures and Issues

A detailed SOP must be prepared to encompass all the procedures involved in the analysis of field samples. The most important member of the compound class measured for the NATTS Program is 2,3,7,8-TCDD (CAS No. 1746-01-6).

4.6.3.1 Equipment, Materials, Reagents and Standards

The analysis is performed using HRGC/HRMS. The GC must be programmable and designed for use of capillary chromatographic columns. The injection technique selected and the injection volume must be used consistently throughout the series of analyses. The capillary column must be fitted directly into the ion source of the mass spectrometer. Since graphite ferrules can adsorb PCDDs/PCDFs, Vespel[®] or equivalent inert ferrules must be used. The MS is operated in the electron ionization mode, using the isotope dilution SIM procedures specified in EPA Compendium Method TO-9A,²⁹ with a total cycle time of 1 second or less. The static resolving power of the MS must be maintained at 10,000 or greater (10% valley definition). The data system must control the MS, data acquisition and data processing, with the capability of

controlling and switching to different sets of ions according to EPA Compendium Method TO-9A²⁹ protocol.

Capillary chromatography columns are needed to perform the analysis, either the columns specified in EPA Compendium Method TO-9A²⁹ or alternatives that have been demonstrated to meet the method performance requirements.

Standard laboratory equipment such as hoods, rotary evaporator, balances, etc., is specified in EPA Compendium Method TO-9A.²⁹

Standard laboratory reagents and high purity solvents required for performance of the method are described in EPA Compendium Method TO-9A.²⁹ The native and isotopically labeled dioxin/furan standards required for performance of EPA Compendium Method TO-9A²⁹ are shown in Table 4.6-2. The compounds listed in Table 4.6-2 are used in the preparation of calibration standards, sample fortification solutions, recovery standard spiking solution, sampler field fortification solution, and matrix/method spike solutions.

An additional set of dioxin/furan standards is used to define the first and last compound at each chlorination level to elute from the chromatographic column. The exact standard used for this purpose depends upon the chromatographic columns selected.

4.6.3.2 Sample Preparation

Samples collected in the field should be shipped and stored at a temperature <4 °C until receipt at the analytical laboratory. At the laboratory, the samples should be refrigerated at ≤ 4 °C. Extraction of the samples must be performed within seven days of sampling, and the extracts must be analyzed within 40 days after extraction.

Glassware Cleanup

For preparation of dioxin/furan samples, each piece of glassware should go through the cleaning process separately, except for oven baking. Each vessel should be washed three times

with hot tap water, twice with acetone and twice with hexane prior to being baked for 16 hours at 450 °C in a forced air oven that is vented to the outside. The PTFE stopcocks should be cleaned as described above, except for oven baking. All glassware should be rinsed with acetone and hexane immediately before use.

Acid/Base Cleanup for Extract of Quartz Fiber Filters, PUF Plugs

The PUF plug and the quartz fiber filter are removed from the glass sample cartridge and placed in a Soxhlet extractor. An aliquot of the isotopically labeled sample fortification solution (a solution of the ISs, as shown in Table 4.6-2) is added to the sample prior to extraction. EPA Compendium Method TO-9A²⁹ originally specified benzene as the extracting solvent, but because of the health hazards associated with the use of benzene, toluene should be used as the extraction solvent. After a 16-hour extraction and solvent exchange into a final volume of 25 mL of hexane, acid-base cleanup is performed using 2N potassium hydroxide for a maximum of four washes until no color is visible in the aqueous layer, a partition against sodium chloride solution, and acid wash using concentrated sulfuric acid, until no color is visible in the aqueous layer, up to a maximum of four washes. After partitioning against sodium chloride solution, dry the extract and concentrate using a Kuderna-Danish concentrator and a steam bath to a final volume of 1 to 2 mL. The extract is ready for alumina column cleanup at this point, but it can be sealed and stored in the dark, if necessary. Method instructions call for acid/base cleanup with repeated acid/base washes (up to a maximum of four) to ensure removal of color from the aqueous layer. If color remains after the acid/base cleanup (probably yellow or brown), a silica column cleanup is required before the alumina cleanup.

Silica Column Cleanup for Extract of Quartz Fiber Filters, PUF Plugs

If silica column cleanup is required, silica gel columns are prepared according to the instructions of EPA Compendium Method TO-9A.²⁹ The prepared columns are stored in an oven set at 220 °C until ready for use (or at least overnight). Silica columns should be removed from the oven when needed and placed in a desiccator until they have equilibrated to room

temperature, then used immediately. The silica gel column is eluted with hexane, and the eluate is subjected to alumina column cleanup.

Alumina Column Cleanup for Extract of Quartz Fiber Filters, PUF Plugs

The alumina column is prepared according to EPA Compendium Method TO-9A²⁹ instructions and prewashed with methylene chloride. Methylene chloride is forced from the alumina column with a stream of dry nitrogen, and prepared columns are stored in an oven set at 225 °C until they are ready for use (at least overnight). Columns should be removed from the oven only when needed, placed in a desiccator over anhydrous calcium sulfate until they have equilibrated to room temperature, and used immediately. The hexane extract is placed into the column and eluted according to the instructions of EPA Compendium Method TO-9A.²⁹ After alumina column cleanup, the extract is ready for carbon column cleanup.

Carbon Column Cleanup for Extract of Quartz Fiber Filters, PUF Plugs

The carbon column is prepared using silica gel and carbon according to the instructions of EPA Compendium Method TO-9A,²⁹ eluted according to the Method, and all elution solvents are archived. When the extract has been eluted with toluene, add tetradecane and concentrate to a final volume of 5 mL using a stream of dry nitrogen and a water bath maintained at 60°C. The recovery standard, ¹³C₁₂-1,2,3,4-TCDD, is added after the carbon column cleanup is complete; the extract may then be stored in the dark at room temperature. Immediately prior to analysis, the extract is concentrated to 30 µL using a stream of nitrogen at room temperature. Immediately prior to analysis, the sample is diluted to a final volume of 100 µL with toluene.

4.6.3.3 Interferences and Contamination

As in all chromatographic analytical methods, any compound with a similar mass eluting from the HRGC column within ±2 seconds of a compound of interest is a potential interference. Any compound eluting from the HRGC column in a very high concentration will decrease overall instrument sensitivity in a given retention time window. If the interfering compound has

a sufficiently high concentration, the mass assignments in the retention time window may be changed and the compound of interest may not be observed at all. Compounds that are chemically similar and hence extracted with PCDDs/PCDFs are also common interferences. These interfering compounds include polychlorinated biphenyls (PCBs), methoxybiphenyls, polychlorinated diphenyl ethers, polychlorinated naphthalenes, the pesticides DDE and DDT, etc. Cleanup procedures in EPA Compendium Method TO-9A²⁹ are carefully designed to remove most of these types of substances, but the cleanup procedures are not guaranteed to be 100% efficient in all situations. The chromatographic resolution of the capillary column and the mass resolution of the mass spectrometer are also helpful in removing interferences from the compounds of interest. Polychlorinated diphenyl ethers are extremely difficult to resolve from PCDFs because of their chemical similarity, because they elute in the same retention time windows as PCDFs, and because of the similarity of their mass spectrometric fragmentation pattern.

Because the analysis is performed at such low concentration levels, minimization of potential interferences is critical. High purity reagents and solvents must be used, and all glassware and equipment must be scrupulously cleaned. All materials used in the laboratory procedures must be monitored and analyzed frequently to ensure that they are not contaminated.

4.6.3.4 Preparation of the Analytical System

The HRGC/HRMS system is operated in the electron ionization (EI) mode using SIM detection. Before analysis of a set of samples is initiated, the instrument must achieve a static mass resolution of 10,000 (10% valley, tuning at mass 292.9825 of perfluorokerosene (PFK)), with corrective action implemented if the instrument does not meet the requirements. Instrument mass resolving power is verified according to the procedures of EPA Compendium Method TO-9A.²⁹ To avoid problems with mass drifts over the long chromatographic elution time required for the dioxin/furan analysis, a lock mass ion for the reference compound (PFK) is used to tune the MS. An acceptable lock-mass ion at any mass between the lightest and heaviest ion in each mass window can be used to monitor and correct any mass drifts of the MS. The level of PFK in the ion source should be kept at the lowest level possible to allow effective monitoring of

changes in sensitivity. If the level of PFK in the instrument is too high, high background signals will be observed and the ion source will become contaminated. Contamination decreases instrument sensitivity and requires downtime for instrument maintenance. Table 10 of EPA Compendium Method TO-9A²⁹ shows the five mass windows used to monitor the dioxins/furans (tetrachloro- through octachloro-, one window for each level of chlorination), the accurate masses monitored to four decimal places (different accurate masses based on the combination of masses 35/37 for chlorine and masses 12/13 for carbon), a PFK lock mass, and a PFK QC mass. Accurate masses for the diphenyl ether isomers are also included at the appropriate retention times. The total time for each SIM cycle should be one second or less for data acquisition, including the sum of the mass ion dwell times and electrostatic analyzer voltage reset times (i.e., 1 second start-to-start).

Two HRGC columns have been used successfully in the EPA Compendium Method TO-9A²⁹ analysis since 1984:

- DB-5 (60 m). Provides an efficient analysis for total concentrations of PCDDs/PCDFs, specific isomers (total tetra-, penta-, hexa-CDDs/CDFs, four heptachlorodibenzofuran isomers, two heptachlorodibenzodioxin isomers, octachlorodibenzodioxin, and octachlorodibenzofuran) and determination of MDL.
- SP-2331 (60 m). Provides demonstrated and confirmed resolution of 2,3,7,8-substituted tetra-, penta-, and hexa-CDDs/CDFs.

Other capillary columns may be used if the performance satisfies the specifications for resolution of PCDDs/PCDFs. After the capillary column has been selected and the HRMS parameters are optimized, an aliquot of the column performance solution should be analyzed to determine and confirm SIM parameters, retention time windows, and chromatographic resolution of the compounds. The chromatographic peak separation between 2,3,7,8-TCDD and the coeluting isomers must be resolved with a valley of 25% or more. The retention order of the compounds will be determined by the chromatographic column used.

4.6.3.5 Determination of MDLs

The MDL is defined as the amount of an analyte required to produce a signal with a peak area at least 2.5 times the area of a background signal level measured at the retention time of interest. MDLs are calculated for total PCDDs/PCDFs and for each 2,3,7,8-substituted congener. Ambient levels of total PCDDs/PCDFs are usually observed in the range of 0.3 to 2.9 pg/m³. To generate meaningful data for ambient air, the MDL for tetra-, penta-, and hexa-CDDs/CDFs should be in the range of 0.02 to 0.15 pg/m³. Trace levels of heptachlorodibenzodioxins and octachlorodibenzodioxin (0.05 to 0.25 pg/m³) are usually detected in the method blank.

The MDL is calculated according to Eq. 4.6-1.

$$MDL = (2.5 \times A_x \times Q_{is}) / (A_{is} \times V_{std} \times mRRF) \quad (4.6-1)$$

where:

MDL = concentration of unlabeled PCDD/PCDF, pg/m³

A_x = sum of integrated ion abundances of the quantitation ions for the unlabeled PCDDs/PCDFs which do not meet the ID criteria of 2.5 × area of noise level at the analyte retention time

A_{is} = sum of the integrated ion abundances of the quantitation ions for the ¹³C₁₂-labeled IS

Q_{is} = quantity of the ¹³C₁₂-labeled IS spiked into the sample prior to extraction, pg

V_{std} = standard volume of ambient air sampled, std m³

mRRF = mean relative response factor for the unlabeled PCDD/PCDF.

If response signals for one or both quantitation ions at the retention time of the 2,3,7,8-substituted isomer (or at the retention time of non-2,3,7,8-substituted isomers) are absent, the instrument noise level is measured at the expected retention time of the analyte and multiplied by

2.5, inserted into Eq. 4.6-1, and calculated and reported as not detected (ND) at the specific MDL.

Response signals at the same retention time as the 2,3,7,8-substituted isomers or the other isomers that have a signal-to-noise ratio in excess of 2.5:1 but do not satisfy the identification criteria are calculated and reported as ND at the elevated MDL and discussed in the narrative that accompanies the analytical results.

4.6.3.6 IC for Analysis of Field Samples

After the HRGC/HRMS SIM operating conditions have been optimized, an initial 5-point calibration is performed using calibration solutions with the concentrations shown in Table 4.6-3.

Table 4.6-3. Composition/Concentrations of the IC Solutions

Calibration Solution	Concentrations (pg/ μ L)				
	1	2	3	4	5
Unlabeled Analytes					
2,3,7,8-tetrachlorodibenzodioxin	0.5	1.0	5.0	50	100
2,3,7,8-tetrachlorodibenzofuran	0.5	1.0	5.0	50	100
1,2,3,7,8-pentachlorodibenzodioxin	2.5	5.0	25	250	500
1,2,3,7,8-pentachlorodibenzofuran	2.5	5.0	25	250	500
2,3,4,7,8-pentachlorodibenzofuran	2.5	5.0	25	250	500
1,2,3,4,7,8-hexachlorodibenzodioxin	2.5	5.0	25	250	500
1,2,3,6,7,8-hexachlorodibenzodioxin	2.5	5.0	25	250	500
1,2,3,7,8,9-hexachlorodibenzodioxin	2.5	5.0	25	250	500
1,2,3,4,7,8-hexachlorodibenzofuran	2.5	5.0	25	250	500
1,2,3,6,7,8-hexachlorodibenzofuran	2.5	5.0	25	250	500
1,2,3,7,8,9-hexachlorodibenzofuran	2.5	5.0	25	250	500
2,3,4,6,7,8-hexachlorodibenzodioxin	2.5	5.0	25	250	500
1,2,3,4,6,7,8-heptachlorodibenzodioxin	2.5	5.0	25	250	500

Table 4.6-3. Composition/Concentrations of the IC Solutions

Calibration Solution	Concentrations (pg/ μ L)				
	1	2	3	4	5
1,2,3,4,6,7,8-heptachlorodibenzofuran	2.5	5.0	25	250	500
1,2,3,4,7,8,9-heptachlorodibenzofuran	2.5	5.0	25	250	500
octachlorodibenzodioxin	5.0	10	50	500	1000
octachlorodibenzofuran	5.0	10	50	500	1000
Internal Standards					
¹³ C ₁₂ -2,3,7,8-tetrachlorodibenzodioxin	100	100	100	100	100
¹³ C ₁₂ -1,2,3,7,8-pentachlorodibenzodioxin	100	100	100	100	100
¹³ C ₁₂ -1,2,3,6,7,8-hexachlorodibenzodioxin	100	100	100	100	100
¹³ C ₁₂ -1,2,3,4,6,7,8-heptachlorodibenzodioxin	100	100	100	100	100
¹³ C ₁₂ -octachlorodibenzodioxin	200	200	200	200	200
¹³ C ₁₂ -2,3,7,8-tetrachlorodibenzofuran	100	100	100	100	100
¹³ C ₁₂ -1,2,3,7,8-pentachlorodibenzofuran	100	100	100	100	100
¹³ C ₁₂ -1,2,3,4,7,8-hexachlorodibenzofuran	100	100	100	100	100
¹³ C ₁₂ -1,2,3,4,6,7,8-heptachlorodibenzofuran	100	100	100	100	100
¹³ C ₁₂ -2,3,4,7,8-pentachlorodibenzofuran	60	80	100	120	140
¹³ C ₁₂ -1,2,3,4,7,8-hexachlorodibenzodioxin	60	80	100	120	140
¹³ C ₁₂ -1,2,3,6,7,8-hexachlorodibenzofuran	60	80	100	120	140
¹³ C ₁₂ -1,2,3,6,7,8,9-heptachlorodibenzodioxin	60	81	100	120	140
Field Standards					
³⁷ Cl ₄ -2,3,7,8-tetrachlorodibenzodioxin	100	100	100	100	100
¹³ C ₁₂ -1,2,3,7,8,9-hexachlorodibenzodioxin	100	100	100	100	100
Recovery Standard					
¹³ C ₁₂ -1,2,3,4-tetrachlorodibenzodioxin	50	50	50	50	50

Quantification relationships between labeled and unlabeled standards are shown in Tables 15, 16, and 17 of EPA Compendium Method TO-9A.²⁹ After the calibration solutions have been analyzed, the relative response factors for each unlabeled compound relative to its corresponding ¹³C₁₂-labeled IS are calculated according to Eq. 4.6-2.

$$RRF(I) = (A_x \times Q_{is}) / (Q_x \times A_{is}) \quad (4.6-2)$$

where:

A_x = sum of the integrated ion abundances of the quantitation ions for unlabeled PCDDs/PCDFs

A_{is} = sum of the integrated ion abundances of the quantitation ions for the $^{13}\text{C}_{12}$ -labeled ISs.

RRFs for $^{13}\text{C}_{12}$ -labeled PCDD/PCDF ISs relative to the $^{37}\text{Cl}_{4-2,3,7,8}$ -tetrachloro-dibenzodioxin recovery standard are calculated according to Eq. 4.6-3.

$$RRF(II) = (A_{is} \times Q_{rs}) / (Q_{is} \times A_{rs}) \quad (4.6-3)$$

where:

A_{rs} = integrated ion abundance for the quantitation ion of the $^{37}\text{Cl}_{4-2,3,7,8}$ -TCDD recovery standard

Q_{is} = quantity of the $^{13}\text{C}_{12}$ -labeled IS injected, pg

Q_x = quantity of the unlabeled PCDD/PCDF analyte injected, pg

Q_{rs} = quantity of the $^{37}\text{Cl}_{4-2,3,7,8}$ -TCDD injected, pg.

The RRFs are dimensionless quantities. The average relative response factors for the five concentration levels of the calibration standards are calculated by dividing the mean of the five RRFs by five.

Acceptance Criteria for the Initial Calibration

For an acceptable calibration, the analytical data must satisfy the acceptance criteria contained in Tables 19 and 20 of EPA Compendium Method TO-9A.²⁹ The isotope ratios must be within the acceptable range, and the percent RSD for the response factors should be less than the values shown in Table 21 of EPA Compendium Method TO-9A.²⁹ The signal-to-noise ratio

for the $^{13}\text{C}_{12}$ -labeled standards must be 10:1 or more; the signal-to-noise ratio for the unlabeled standards must be 5:1 or more.

Continuing Calibration

At the beginning of each day a continuing calibration analysis should be performed to check and confirm the continuing stability of the calibration. An aliquot of one of the calibration standards (a mid-range standard) is used to perform the continuing calibration check. The continuing calibration analysis must meet the criteria for acceptability of the isotope ratios and the signal-to-noise ratios for the initial calibration. The continuing stability of the calibration should also be verified at the end of the day. The percent difference for the continuing calibration check is calculated using Eq. 4.6-4.

$$\%Difference = [(RRF_{cc} - mRRF)/mRRF] \times 100 \quad (4.6-4)$$

where:

RRF_{cc} = RRF for a specific analyte in the continuing calibration standard

$mRRF$ = mean response factor from the IC curve.

4.6.3.7 Analytical Procedure

An aliquot of the cleaned up sample extract is analyzed with the HRGC/HRMS system using the optimized instrument parameters and the exact masses that have been established for the dioxin/furan analysis. The following criteria are used for the identification of PCDDs/PCDFs in samples:

- The integrated ion abundance for $M/(M+2)$ or $(M+2)/(M+4)$ shall be within $\pm 15\%$ of the theoretical value. Acceptable control limits for the ion abundance ratios are shown in Tables 19 and 20 of EPA Compendium Method TO-9A.²⁹
- The ions monitored for a given analyte must maximize within 2 seconds of each other.

- The retention time for the 2,3,7,8-substituted analytes must be within 3 seconds of the corresponding $^{13}\text{C}_{12}$ -labeled IS or surrogate standard.
- The ID of 2,3,7,8-substituted isomers that do not have corresponding $^{13}\text{C}_{12}$ -labeled standards must be done by comparison to the analysis on the same chromatographic column of a standard that contains the specific congeners. The RRT of the analyte must be within 0.005 RRT units of the comparable RRTs of the analyte and the nearest eluting internal standard found in a separate analysis.
- The signal-to-noise ratio for the monitored ions must be >2.5 .
- The analysis shall show that polychlorinated diphenyl ethers are not present. Any polychlorinated diphenyl ethers that elute within ± 2 secs of PCDF peaks indicate a positive interference, especially if the intensity of the polychlorinated diphenyl ether peak is 10% or more of the PCDF peak.

Peak areas for the ions of $^{13}\text{C}_{12}$ -labeled PCDDs/PCDFs, $^{37}\text{Cl}_4$ -2,3,7,8-TCDD, unlabeled PCDDs/PCDFs, and the respective RRFs are used for quantitative analysis:

- $^{37}\text{Cl}_4$ -2,3,7,8-TCDD is spiked into the extract prior to final concentration. Calculated relative response factors are used to determine the sample extraction efficiencies (% recoveries) for the nine $^{13}\text{C}_{12}$ -labeled ISs, which were spiked into the sample prior to extraction .
- The $^{13}\text{C}_{12}$ -labeled PCDD/PCDF ISs and response factors are used for quantitative calculation of unlabeled PCDDs/PCDFs and for determination of MDLs. (However, $^{13}\text{C}_{12}$ -octachlorodibenzodioxin is used for octachlorodibenzofuran). Each $^{13}\text{C}_{12}$ -labeled IS is used to quantify all of the PCDDs/PCDFs in its isomeric group.
- The $^{37}\text{Cl}_4$ -2,3,7,8-TCDD spiked onto the PUF prior to sampling is used to determine the collection efficiency for the sampling period.

4.6.3.8 Calculations

Extraction Efficiency

The extraction efficiencies (% recovery) of the nine $^{13}\text{C}_{12}$ -labeled PCDDs/PCDFs measured in the extract are calculated using the Eq. 4.6-5.

$$\%R_{is} = [A_{is} \times Q_{rs} \times 100] / [Q_{is} \times A_{rs} \times RRF(II)] \quad (4.6-5)$$

where:

$\%R_{is}$ = percent recovery (extraction efficiency)

A_{is} = sum of the integrated ion abundances of the quantitation ions for the $^{13}\text{C}_{12}$ -labeled IS

A_{rs} = sum of the integrated ion abundances of the quantitation ions for the $^{37}\text{Cl}_4$ - or the $^{13}\text{C}_{12}$ -labeled recovery standard

Q_{is} = quantity of the $^{13}\text{C}_{12}$ -labeled IS added to the sample before extraction, pg

Q_{rs} = quantity of the $^{37}\text{Cl}_4$ - or $^{13}\text{C}_{12}$ -labeled recovery standard added to the sample extract before analysis, pg

$RRF(II)$ = calculated mean RRF for the labeled IS relative to the appropriate labeled recovery standard (Eq. 4.6-3).

Analyte Concentration

The concentration of each 2,3,7,8-substituted PCDD/PCDF that has met ID criteria is calculated using Eq. 4.6-6.

$$C_x = (A_x \times Q_{is}) / [A_{is} \times V_{std} \times RRF(I)] \quad (4.6-6)$$

where:

C_x = concentration of unlabeled PCDD/PCDF congener(s), pg/m³

A_x = sum of the integrated ion abundances of the quantitation ions for the unlabeled PCDDs/PCDFs

A_{is} = sum of the integrated ion abundances of the quantitation ions for the respective $^{13}\text{C}_{12}$ -labeled IS

Q_{is} = quantity of the $^{13}\text{C}_{12}$ -labeled IS added to the sample before extraction, pg

V_{std} = standard volume of air sampled, std m³

$RRF(I)$ = calculated mean RRF for an unlabeled 2,3,7,8-substituted PCDD/PCDF (Eq. 4.6-2).

4.6.4 Quality Assurance/Quality Control

Certified analytical standards, both native compounds and isotopically labeled standards, are available through Cambridge Isotope Laboratories and from a number of other distributors. IC and continuing calibration analyses must meet EPA Compendium Method TO-9A²⁹ acceptance criteria. Compounds must meet EPA Compendium Method TO-9A²⁹ ID criteria. All field samples, method blanks, field blanks, and LCSs must be spiked with ¹³C₁₂-labeled ISs prior to extraction. Sample preparation, analysis, and data evaluation are performed on a set of 12 samples consisting of 9 field samples, field blank, method blank, fortified method blank, or an LCS. The ¹³C₁₂-1,2,3,4-TCDD standard is spiked onto the PUF plugs prior to shipping them to the field for sampling in order to determine and document the sampling efficiency. QA/QC requirements for the data are summarized in Table 4.6-4.

Table 4.6-4. QA/QC Requirements for EPA Compendium Method TO-9A Data

Criterion	Requirement
Satisfy ID criteria	Integrated ion abundance ratio within ±15% of theoretical ions monitored for a given analyte maximize within two sec of each other Retention time for 2,3,7,8-substituted analytes must be within three sec of the corresponding ¹³ C ₁₂ -labeled IS or surrogate 2,3,7,8-isomers without ¹³ C ₁₂ -standards meet method ID criteria Signal-to-noise ratio for monitored ions >2.5 Absence of polychlorinated diphenyl ethers
Recoveries for ¹³ C ₁₂ -labeled tetra-, penta-, hexa-CDDs/CDFs	50 to 120%
Recoveries for ¹³ C ₁₂ -labeled heptachlorodibenzodioxin and octachlorodibenzodioxin	40 to 120%
Accuracy achieved for PCDDs/PCDFs in method spike at 0.25 to 2.0 pg/m ³	70 to 130%
Precision achieved for duplicate method spikes or quality assurance samples	±30%
Recovery of PUF prespike	50 to 120%
Method blank contamination	Free of contamination that would interfere with field sample results
MDL range for method blank and field blank (individual isomers)	0.02 to 0.25 pg/m ³

4.7 AEROSOL BLACK CARBON MEASUREMENT PROCEDURE

Carbon is one of the most abundant constituents of ambient particulate matter. Carbon can be present as organic carbon (OC), which is volatile, and as elemental carbon (EC), which is nonvolatile. Particulate EC is ubiquitous in the atmosphere, present at levels ranging from 0.05 to 300 ng/m³ in remote areas³⁰⁻³⁵ and up to 13.3 µg/m³ in urban areas.³⁵ The value of 13.3 µg/m³ can go up or down depending upon method and sampling interval.

Black Carbon (BC) is produced only by combustion processes involving carbonaceous material; BC is not generated by any known atmospheric reactions.³⁰⁻³² BC is not degraded under atmospheric conditions, and the only important sinks for BC are wet and dry deposition^{30,35,36}. BC is predominantly present in submicron particles,^{30,36-39} and can have a lifetime in the atmosphere ranging from several days to several weeks, depending upon the meteorology.³⁵ Ambient measurement data indicate that long-range transport becomes important^{30,31,32,35} because of the long lifetime for BC. BC can be regional in nature, especially in remote areas, but local sources are usually dominant.^{30,35} The levels of BC can exceed 30 to 40 µg/m³ in areas with a large diesel influence. The brown coloration of polluted urban airsheds is due to absorption by the soot component of combustion emissions, i.e., traffic. BC plays an important role in atmospheric chemistry because of its catalytic properties^{30,35,36,40} and affects visibility by light extinction.^{35,37,41,42} Because of its absorption of light, BC is potentially climate-altering.^{35,37,42}

Aerosol BC is most obvious in diesel exhaust but is emitted from all combustion sources together with other species such as toxic and carcinogenic organic compounds. BC is strongly optically absorbing. The aethalometer is an instrument that measures suspended carbonaceous particulates: the aethalometer measures ONLY the optically absorbing BC aerosol fraction of a sampled airstream, in near-real-time using a continuous filtration and optical transmission technique. In the urban environment, the aethalometer measurements show the direct emissions patterns according to the diurnal cycle of traffic (weekdays vs. weekends, etc.). In the more remote locations, the time-resolved data obtained from the aethalometer measurements reflect medium- or long-range transport of emissions from the source area to the receptor point (i.e.,

meteorology). Optical scattering, usually the larger component of visibility extinction, is strongly affected by natural phenomena such as changes in humidity, natural biogenic and sea-spray sources, etc., and is therefore not a good tracer of anthropogenic impact.

The aethalometer was developed as an effective real-time analyzer for measuring particle light absorption; results are reported as BC concentration in the atmosphere. The aethalometer collects aerosol continuously on a quartz fiber filter tape, and determines the increment of optically absorbing material collected per unit volume of sampled air. The optical measurement is ratiometric and no external calibration materials are required: quartz filter tape is the only material used. The aethalometer uses an incremental optical absorption technique to respond rapidly and with high sensitivity to the presence of optically absorbing aerosol species that are collected on an absolute quartz fiber filter. The aethalometer operates at a wavelength of 880 nm (in the near-IR range).

4.7.1 Overview of BC Measurement

The aethalometer collects the aerosol continuously on a quartz fiber filter, and determines the increment of optically absorbing material collected per unit volume of sampled air. Since BC is the dominant optically absorbing material in the submicron size range, this measurement is interpreted as a mass of BC according to calibrations performed by intercomparison with other chemical analysis techniques. The optical measurement is ratiometric and no external calibration materials are required: filter tape is the only material used. The aethalometer uses an incremental optical absorption technique to respond rapidly and with high sensitivity to the presence of optically absorbing aerosol species that are collected on an absolute quartz fiber filter.

4.7.2 General Description of Measurement Method

The principle of the aethalometer is to measure the attenuation of a beam of light transmitted through a filter while the filter is continuously collecting an aerosol sample. The measurement is made at successive regular intervals of a time base period. By using the appropriate value of the optical absorbance cross-section for the particular combination of filter

and optical components, the BC content of an aerosol deposit can be determined at each measurement time. The increase in optical attenuation from one period to the next is due to the increment of aerosol BC collected from the airstream during the period. Dividing this increment by the volume of air sampled during that time determines the mean BC concentration in the sampled airstream during the period. For a short time base relative to the time scale of other variations in a particular air mass, the measurements appear to be continuous. If the mean concentration does not vary greatly from one measurement period to the next, the period average is a reasonable representation of the time behavior of the actual BC concentration during the period.

The objectives of the aethalometer hardware and associated software are:

- To collect the aerosol sample with as few losses as possible on an appropriate filter material;
- To measure the optical attenuation of the collected aerosol deposit as accurately as possible;
- To calculate the rate of increase of the BC component of the aerosol deposit and to interpret this rate of increase as a BC concentration in the airstream; and
- To display and record the data, and to perform necessary instrument control and diagnostic functions.

The aethalometer is fully automatic, completely self-contained, operates automatically upon power-up, and can be left unattended for long periods of time. The configuration of the aethalometer includes a filtration and analysis chamber with automatically advancing quartz fiber tape, sample aspiration pump, air mass flow meter or controller (a typical flow rate is 5 Lpm), and temperature-stabilized optics and electronics. The instrument is operated by an embedded computer that controls all instrument functions and records data; an analog output is available for use with data acquisition systems to allow remote polling of the data.

Measurement of aerosol BC for NATTS requires the application of an aethalometer in a “big spot” configuration (Magee Scientific designation of “-ER” after the model number). For

NATTS application, BC measurements must be made using a Magee Scientific AE-16 nonportable aethalometer with a BGI PM_{2.5} inlet (SCC 1.829). Any aethalometer model can be “big spot” if “-ER” is affixed to the model number. The AE-16-ER model incorporates the “big spot” on the tape for analytical measurements—a larger impaction area on the tape than the standard model. The BGI cyclone is designed to perform a cut to exclude particulate matter larger than 2.5 µm in aerodynamic diameter when operated at the prescribed flow rate of 5.0 Lpm.

4.7.3 Interferences

The “blackness” measurement for BC is sensitive only to the amount of carbon thus defined and measured. The measurement is insensitive to any amounts of extractable organic carbon or other aerosol species that frequently contribute substantially to the total aerosol mass, yet are not optically absorbing, implying that BC is the only aerosol species that is optically absorbing in the visible spectrum and that a measurement of visible light absorption may be interpreted directly in terms of a mass of BC. This observation is generally valid for aerosol samples taken from sources and in urban and many remote areas but is not valid when the sample contains a very large amount of mineral dust. Dust has an absorption cross section that is smaller than that of BC by a factor of 100 to 1000. If the amount of mineral dust is 100 to 1000 times greater than the amount of BC, a comparable optical absorption may be produced. This interference cannot be eliminated in the real-time measurements of the aethalometer, though it can be determined in a subsequent analysis of the filter sample.

It is also important to protect the BC aerosol inlet from two macroscopic contaminants, rain and insects. The quartz fiber filter will clog and will dramatically change its optical properties if it becomes wet, so it is very important that rain, spray, or any other water be excluded. Magee Scientific strongly recommends using a trap if there is any possibility of rain or other water entry. It is also necessary to exclude insects from the inlet, since a small mosquito sucked onto the filter can cause an extremely large change in optical transmission and will certainly ruin the data collected in that period.

4.7.4 Operational Procedure

The following section applies only to the configuration of the single-channel aethalometer, Model AE-16-ER. Performance specifications of both the multichannel and portable aethalometer configurations are derived from the specifications listed here. The aethalometer can adequately measure an increment of less than 1 ng of BC on its filter. At a flow rate of 5 Lpm and a time base of 5 min and with a resolution corresponding to $0.04 \mu\text{g}/\text{m}^3$ of BC, 2% of a typical urban concentration of $2 \mu\text{g}/\text{m}^3$ of BC can be measured. Time base and airflow rate may be varied to optimize sensitivity vs. time resolution from 5 min. System specifications are shown in Table 4.7-1.

Table 4.7-1. Aethalometer Specifications (Model AE-16-ER) for NATTS

Parameter	Specification
Filtration Medium	Quartz fiber tape, 15-m tape rolls. Sample collection proceeds on an 1.67 cm^2 oval spot until a threshold BC loading density is reached, at which point the tape advances. Each roll of tape accommodates 1500 spots.
Pumping and Sample Airflow Rate	Includes a 1 to 10 Lpm mass flow meter. Normal sample flow range is 5 Lpm. Vacuum is provided either by an internally mounted diaphragm pump or an external pump or other suction source.
Optics and Electronics	Stabilized solid-state light source at 880 nm, 24-bit A/D conversion of photometric signals. Active temperature stabilization of electronics.
Operator Interface	Display panel with keypad, status lights, and 4-line screen.
Computer	Embedded computer runs automatically upon power-up; recovers from power failures. Calculates BC concentrations directly in ng/m^3 .
Data Processor	The data processing system (J. Turner, Washington University) performs a unit conversion to $\mu\text{g}/\text{m}^3$.
Electrical Specifications	120 or 240 vAC, 50/60 Hz, 60 watts maximum
Ambient Particulate Inlet	The ambient particulate inlet used with the aethalometer is a BGI "Photometer" Cyclone (Model SCC 1.829), featuring dry sampling (no oil or grease). This unit has a $2.5\text{-}\mu$ cut at 5 Lpm. The SCC model also has a very low-pressure drop at design flow rates, and requires a vertical inlet tube. The cyclone is held to this tube by a pair of internal O-rings. The cleaning frequency of the SCC is greater than 30 days of continuous operation, desirable for continuous particulate monitors.

4.7.4.1 Filtration Medium

The aethalometer is normally operated with web-reinforced quartz fiber filter tape. This material has a deep mat of optically scattering fibers within which the aerosol particles are collected, with the goal of nullifying any effect on optical transmission by light scattering from the particles that have been collected. The measurement is therefore sensitive only to incremental light absorption. The aethalometer must use a deep fibrous type of filter for correct operation. Since the quartz fiber material is thermally stable to high temperatures, the fiber may be heat treated by firing to 600 °C to remove all combustible carbonaceous compounds from the filter prior to use. In manufacture, the quartz fiber material is laid down upon a reinforcing web of cellulosic material to provide mechanical strength: the pure quartz material itself is extremely brittle and friable, with little mechanical strength. The material must be handled with some care and requires the use of the web underlayer to perform automatic tape handling.

Aerosol is collected on an area of quartz fiber filter at a moderate face velocity. A “high sensitivity” (HS) sampling head provides a collecting spot area of 0.5 cm², whereas the “extended range” (ER) sampling head collects on a spot of 1.67 cm² (i.e., 3.3 times larger). The optimal sampling rate for NATTS application is 5 Lpm. The rate of accumulation of BC on the spot is proportional to both the BC concentration in the airstream and to the airflow rate. The greatest sensitivity is achieved by using the highest airflow rate through the smaller high sensitivity (HS) spot (i.e., for rural or remote areas). However, in areas of higher concentration (such as urban areas), the filter will become overloaded more rapidly, leading to a necessity for changing the filter to avoid optical saturation. The time required to change the spot on the filter leads to interruption of data collection. In urban areas or when sampling streams with high BC concentration, good instrument performance is achieved using an instrument with the ER head at lower flow rates, with the benefit of less frequent filter changes, where time resolution of 5 min is acceptable. The ER inlet disperses the sample over a spot area that is 3.3 times larger than the HS inlet to reduce the rate at which aerosol optical density accumulates and therefore prolongs the life of each spot. When the HS inlet is used, filter tape advances may be quite frequent in an urban area, leading not only to a greater consumption of tape but also to a greater loss of data when the instrument is inactive during tape advance and reinitialization.

The aethalometer filter must be changed periodically to avoid overload and saturation of the optical absorption. As the aerosol deposit accumulates, the optical transmission through the filter spot diminishes, but the digitization resolution of the measuring electronics and the amplitude of electronic noise remain constant. The relative importance of noise and measurement error increase as the loading of the aerosol deposit increases. The aethalometer automatically advances the tape to provide a fresh filtration spot before the aerosol BC becomes too large. The limit is set at an optical attenuation value of 75 (an optical absorption depth of 0.75), corresponding to a surface loading of aerosol BC of approximately $4 \mu\text{g}/\text{cm}^2$ on the spot. When this attenuation value is reached, the program halts temporarily to advance the filter tape and reinitializes automatically when the fresh spot is in place before resuming measurements. This reinitialization process takes a certain amount of time during which the output of valid data is suspended. The tape advance itself may be set in software to “1” or “2” spots, depending upon user preference for spot spacing. Each spot advance requires 1 min since the tape drive motors move extremely slowly in order not to tear or stretch the tape. In addition to this time, the algorithm allows for a period of stabilization before valid data are reported for analysis on the fresh spot. Realistically, if the time base is set to 5 min, a tape advance will result in the loss of up to 15 min of data, based on the fact that the fresh filter tape surface requires time to equilibrate with the ambient composition and humidity of the sampled airstream as distinguished from the storage environment inside the chassis. For this reason, the time base should be set to no longer than 5 min in urban locations (where tape advances may be more frequent because of the higher loadings of BC) in order not to lose any more data than necessary.

An additional feature of the aethalometer that can be used to avoid overloading and to prolong the life of the tape in an urban environment is the “tape saver” feature. The tape saver controls a flow bypass valve that can divert the flow of particulate-laden sample air away from the filter spot for a controllable fraction of each time base period. This feature reduces the amount of sample accumulation in high aerosol concentrations by a known fraction that is accounted for in the BC calculation algorithm. Use of the tape saver prolongs the life of each filter tape spot and thus reduces the consumption of tape and the interruptions to data collection due to tape advance and instrument reinitialization. At a time base setting of 5 min, time saver

options of “X3” and “X10” are available: the instrument periodically switches a valve to divert airflow to bypass the filter tape spot for a certain fraction of the time, although the airflow still passes through the flow meter. The X3 setting varies the aerosol collection time from 50% at low BC concentrations to 30% at high BC concentrations; the X10 setting varies the aerosol collection time from 50% at low BC concentrations to 10% at high BC concentrations.

Each 15-m roll of tape provides approximately 1500 spots. Each spot lasts from hours in cities at high BC concentrations to several months at remote locations, so changing the tape roll is required only occasionally. The display screen of the computer shows an estimate of the percentage of the tape roll remaining and provides a warning when the value falls below 10%. The Magee Scientific manual (*The Aethalometer*, 2003-04, by A.D.A. Hansen; Magee Scientific Company, Berkeley, CA) provides a thorough description of the tape-changing process.

4.7.4.2 Operating Protocol for BC with Magee Scientific Model AE-21 Aethalometer

This protocol addresses performing BC measurements using the Magee Scientific aethalometer with a 5-Lpm BGI “Photometer” Cyclone (Model 1.829) PM_{2.5} inlet for the NATTS Program. The instrument is operated with tape-saver mode off and sample flow reported at 25°C [not the instrument default of 70 °F]. Standard “Magee” BC calibration [“sigma”] value is used (16.6m²/g-C).

Daily or Every Site Visit:

- Check the aethalometer display for normal operation (reasonable readings for time and flows, no error messages, error lights, etc.).

Once Each Week:

- Check the system date and time on the aethalometer display and on the data logger PC. The aethalometer time should be within 1 min of the site’s master time source. If the time is reset, record the time error before changing the time, and the

date and time you changed the time. The aethalometer must be "stopped" to change the time. A security code must be entered to stop the aethalometer and perform certain other system operating tasks; the default code is 111 and should not be changed. If there is a clear trend in the system time error (for example, a system typically might gain 1 min each week), set the time somewhat off in the opposite direction of the trend to reduce the need for frequent system time changes.

- Check the sample flow on the aethalometer display and record it in the log. The sample flow should be 5.0 ± 0.3 Lpm. Adjust sample flow (with the valve on the pump or from the keyboard, depending on the aethalometer model) if necessary, and record the after adjustment value in the log sheet.
- The cyclone requires cleaning approximately once per month.
- Check the filter tape supply. Change filter tape if the thickness of the roll is less than 1/8 in. Re-tension the tape roll takeup spool if needed. Inspect the used filter tape spots that are visible for distinct and uniform borders between the exposed and unexposed areas. If obvious poor seals are noted, contact Magee Scientific.

Once Each Month:

- While the aethalometer is in its normal run mode, perform an external flow check. Do not stop data collection on the aethalometer to do this test because stopping data collection can change the flows. The tape saver function must be off to perform this flow check procedure.
- Measure the sample flow at the inlet of the fine mass impactor using a BIOS flow meter, dry test meter, rotameter, or other calibrated volumetric (e.g., not standard temperature and pressure (STP)) flow measurement device with a range of 3 to 8 Lpm. Wet flow devices are not recommended because they cannot be used below freezing and often have a relative humidity-dependent error due to water vapor. The external flow meter **must** be at ambient temperature for readings to be valid. An STP flow device can be used if the temperature is within 5 °C of 25 °C; in this case skip the next step.
- Record the flow from the aethalometer display. Correct the external volumetric flow measurement to standard conditions of 25 °C and 29.92 in. Hg as follows:
$$\text{STP flow} = \text{actual flow} * [298/(273 + \text{ambient T, } ^\circ\text{C})] * [\text{station BP, in.}/29.92]$$
- Calculate the percent error of the aethalometer flow compared to the external flow standard.

$$\% \text{ error} = 100 * (\text{aethalometer display} - \text{external STP flow}) / \text{external STP flow}$$

If the flow difference is more than 7%, corrective action may be necessary.

- Leak check the aethalometer by disconnecting the inlet hose at the rear of the instrument and blocking the inlet on the back. Record the lowest flow reading observed on the flow meter display; it should be less than 2.5 Lpm. Reconnect the sample line.
- Change the aethalometer data disk. The aethalometer does not need to be interrupted to change the data disk as long as the change is done during the first 3 min of any 5-min measurement cycle [based on the aethalometer's internal clock]. Before changing the disk, start by labeling a new disk with the site and start date/time (local standard time). Remove the old data disk and insert the new disk. **Immediately put the write protect tab on the old disk**, and record the end date/time (Standard Time) on the disk label. Return the disk to the central laboratory.

Operational Issues and Options:

- Failure to Advance: To avoid the failure to advance, set spots per advance to two rather than one.

An example of a field data sheet is shown in Figure 4.7-1.

For each tape roll change of the aethalometer, the stainless steel filter support mesh screen should be cleaned. Remove the locking screws attaching the top of the inlet cylinder to the lifting plate, and carefully lift it up and away from the base. Clean any accumulation of quartz fiber from the top of the mesh screen. When replacing the inlet cylinder, check carefully that it is properly seated on the base. The flow is measured by a thermal mass flow meter inserted directly downstream of the filter spot. This flow meter reads out airflow corrected to 70 °F and 1013 millibars (MB).

The optical sampling and analysis cylinder should be removed and cleaned once every year or two or at any time there has been the possibility that foreign material such as insects, macroscopic dust, or tape fluff has been drawn into the instrument. This schedule may be

accelerated in areas with high aerosol loading: a good guideline is to perform the cleaning every second time a roll of tape is installed. The disassembly and cleaning procedure takes less than 30 minutes, requires no special tools, requires no special skills, and the instrument may be reassembled without concerns about critical alignment or repositioning of components. A detailed procedure is supplied in the aethalometer manual.

Aethalometer Instrument

Field Data Sheet

Site Name: _____ Magee Scientific AE-____ Serial #: _____ Date: _____

Weekly Checks:	Week 1	Week 2	Week 3	Week 4
Actual Date, Time				
Inst. Date, Time				
Time reset: (min)				
Green Light (✓)				
Flow (sLpm)				
Tape Supply (✓)				
Tape Tension (✓)				
Filter Seals (✓)				
Clean Inlet, Date				
Operator Initials				

Operator Comments: _____

Monthly Check: Date: _____ Operator Initials: _____

Configuration: Compare to Printed Message Text Log. Inst. settings correct? Y/N _____

Flow Check: (Audit device Serial #: _____ Flow: sLpm _____) (Flow: _____)

(Flow measurement can be performed inside) Flow at 5 sLpm Y/N: _____

Leak Check: (Block inlet on rear of Inst. for 30 seconds.) Less than 1.5 (Lpm) Y/N: _____

Change Data Diskette: Do this during first 3 minutes of 5-min cycle. Label diskette with site and data date range. Write protect and send diskette back to central office.

Note: flow standard conditions are T = 20°C and P = 29.92 in. Hg

Note: Inspect recent collection areas on tape for sharp definition indicating a good filter seal.

Figure 4.7-1. Example of a Field Data Sheet for Aethalometer Measurements

4.7.5 Validation

The measurement method is differential-ratiometric and the optical analysis does not require any validation. The only periodic check is to validate the response of the air mass flow meter that monitors the sample flow rate. Usually this calibration check is done once every six months. If there is concern about stability of the optical subsystem, the sensor and reference channel voltages on a clear filter spot can be compared to those reported on the data sheet shipped with the instrument.

4.7.6 Accuracy/Sensitivity

Sensitivity is proportional to sample airflow rate and inversely proportional to the integrating time base. At typical conditions (5 Lpm flow, 5 minutes time base), the typical noise level is $<0.1 \mu\text{g}/\text{m}^3$. Data can be generated at short time bases and then averaged over longer periods to recover higher sensitivity equivalent to longer integrating times. The time base should always be set to 5 minutes. Accuracy of sample flow is equal to the accuracy of airflow meter used, typically 2%. Absolute relationship to chemical determination of BC on collocated filter samples depends upon chemical method and aerosol composition.

4.7.7 Data Processing

Data processing software has been developed by the Air Quality Laboratory at Washington University in St. Louis in collaboration with George Allen (Northeast States for Coordinated Air Use Management (NESCAUM)) to postprocess the raw data files obtained directly from the aethalometer. The software is available through jrturner@seas.wustl.edu and is discussed in Section 5 of this document (“Data Management”). This program can process data from 1- or 2-channel configurations of the aethalometer.

Raw data are obtained from the aethalometer in 5-min intervals. This program uses the raw data file(s) as input and generates two processed data files as output: a 5-min data output file (similar to the raw data file but with additional formatting and data validation); and a 1-hour

average output file, which also includes data validation. Both output files are in comma-delimited format which can easily be imported into spreadsheets or other data analysis packages. BC concentrations are reported as ng/m^3 in the raw data files and $\mu\text{g/m}^3$ in the postprocessed output files. A log file is also generated which provides important documentation concerning the postprocessing.

The maximum file size that can be processed is determined by the number of 5-min intervals between the two extreme time stamps in the input file. The software can handle up to one million intervals corresponding to a maximum time span of 9.5 years. The processor cannot handle time stamps prior to January 1, 2000.

4.8 OVERVIEW OF METEOROLOGICAL MONITORING METHODS

Meteorology is a critical element in the formation, transport, and ultimate disposition of many pollutants. Consequently, meteorological data are essential to the development and evaluation of control strategies and the assessment of trends. Other types of evaluations that depend on meteorological data include modeling, diagnostic analysis, emissions trading, and health effects analysis. Accordingly, measurement of meteorological parameters is a requirement of the NATTS Program. In support of NATTS, meteorological monitoring must address the parameters presented in Table 4.8-1.

Table 4.8-1. Overview of Meteorological Monitoring Requirements

Question	Answer
Where to monitor?	Measurements are to be made directly at each NATTS Program site, or at a location in close proximity to the site that has been determined to still be representative of the site.
How to monitor?	Measurements are to be in situ and continuous.
What parameters?	Required measurement parameters are Wind Direction, Wind Speed, Temperature, Dew Point, Solar Radiation, Barometric Pressure, and Precipitation.
What interval?	Raw data collection frequency is 1 minute, and minimum sample frequency is hourly.
What levels?	Measurements are to be made at 10 m above ground level (AGL) for Wind Direction and Wind Speed. Measurements of all the other parameters are to be made at 2-m AGL.

Detailed guidance for the required meteorological monitoring parameters is available through the EPA document, “Meteorological Monitoring Guidance for Regulatory Modeling Applications.”⁴³ Recommended procedures for quality assurance and audit activities for the meteorological monitoring system are found in *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV: Meteorological Measurements, Version 1.0 (Draft)*.⁴⁴

4.8.1 System Specifications for Meteorological Measurements

System specifications for the measurements are shown in Table 4.8-2. The data acquisition system should sample the meteorological sensors at 10-sec intervals. Data for all variables should be processed to obtain 1-hour averages. The data acquisition system clock should have an accuracy of ± 1 minute per week.

Table 4.8-2. System Specifications for Surface Meteorological Measurements

Parameter	Method	Reporting Units	Operating Range	Resolution
Wind Speed	Cup, Propellor, or Sonic Anemometer	m/s	0.5 – 50 m/s	0.1 m/s
Wind Direction	Vane or Sonic Anemometer	Degrees	0 – 360° (540)	1°
Temperature	Thermistor	°C	-30 – 50 °C	0.1 °C
Dew Point	Psychrometer or Hygrometer	°C	-30 – +30°C	0.1°C
Solar Radiation	Pyranometer	Watts/m ²	0 – 1100 W/m ²	10 W/m ²
Barometric Pressure	Aneroid Barometer	mb	600 – 1100 mb	0.5 hPa
Precipitation	Tipping Bucket, Weighing Rain Gauge	mm/hour	0 – 250 mm/hour	0.25 mm

4.8.1.1 Siting Considerations

Surface meteorological measurements for the NATTS Program should be made directly at the NATTS Program site where practical. If not practical, surface meteorological measurements should be made at an alternate location that is in close proximity to the NATTS site so that data obtained is representative. For general application, the site should be located in a level, open area away from the influence of obstructions such as buildings or trees. The area surrounding the site should have uniform surface characteristics.⁴⁵ Although it may be desirable to collocate the surface meteorological measurements with the ambient air quality measurements, collocation of the two functions may not be possible at all monitoring sites without violating one or more of the above criteria. Siting and exposure requirements specific to each of the surface meteorological variables are discussed in subsequent sections.

Surface meteorological measurements in urban areas present special difficulties because compliance with siting and exposure criteria may be precluded by the close proximity of buildings and other structures. In all cases, specific site characteristics should be well documented, especially where surface characteristics and/or terrain are not uniform and when standard exposure and siting criteria cannot be met.

As a general rule, meteorological sensors should be sited at a distance beyond the influence of obstructions such as buildings and trees. This distance depends on the variable being measured as well as the type of obstruction. Another general rule is that meteorological measurements should be representative of the type of meteorological conditions in the area of interest. However, a quantitative method does not exist for determining meteorological representativeness absolutely—there are no generally accepted analytical or statistical techniques to determine representativeness of meteorological data or monitoring sites. Representativeness has been defined as “the extent to which a set of measurements taken in a space-time domain reflects the actual conditions in the same or different space-time domain taken on a scale appropriate for a specific application.”⁴⁶ For use in air quality modeling applications, meteorological data should be representative of conditions affecting the transport and dispersion of pollutants in the area of interest as determined by the locations of the sources and receptors being modeled. In many instances, multiple meteorological monitoring sites may be required to adequately represent spatial variations. In selecting monitoring sites, secondary considerations such as accessibility and security must be considered but cannot be allowed to compromise the quality of the meteorological data. In addition to routine maintenance and quality assurance activities, annual site inspections should be performed to verify the siting and exposure of the sensors.

Wind instruments must be placed while taking into account the purpose of the measurements. The instruments should be located over level, open terrain at a height of 10 m above the ground and at a distance of at least ten times the height of any nearby obstruction.

Complex terrain refers to any site where terrain effects on meteorological measurements may be significant. Terrain effects include aerodynamic wakes, density-driven slope flows, channeling, flow accelerations over the crest of terrain features, etc. These flows primarily affect wind speed and wind direction, but temperature and humidity measurements may also be affected. A siting decision in complex terrain will almost always represent a compromise. Monitoring options in complex terrain range from a single tall tower to multiple tall towers supplemented by data from one or more remote sensing platforms. Since each complex terrain

situation has unique features, no specific recommendations will cover all cases. However, the recommended steps in the siting process are relevant to all situations:

1. Define the variables needed for the specific application.
2. Develop as much information as possible to assess what terrain influences are likely to be important: examine topographic maps, estimate plume rise, and analyze any available site-specific meteorological data. An evaluation by a meteorologist based on a site visit would be desirable.
3. Examine alternative measurement locations and techniques while considering advantages and disadvantages of each technique/location.
4. Optimize network design by balancing advantages and disadvantages.

Guidance and concerns specific to the measurement of wind speed, wind direction, and temperature difference in complex terrain are addressed in the EPA guidance document.⁴³

Coastal locations feature unique meteorological conditions associated with local scale land-sea breeze circulations. To provide representative measurements for the entire area of interest, multiple meteorological monitoring sites are needed: one site at a shoreline location and additional inland sites perpendicular to the orientation of the shoreline. Where terrain in the vicinity of the shoreline is complex, measurements at additional locations such as bluff tops may also be necessary.

Urban areas are characterized by increased heat flux and surface roughness, effects that vary horizontally and vertically within the urban area and alter the wind pattern relative to the outlying rural areas. Close proximity of buildings in downtown urban areas often precludes strict compliance with standard sensor exposure guidance. In general, multiple sites are needed to provide representative measurements in a large urban area, especially true for ground-level sources where low-level local influences such as street canyon effects are important and for multiple elevated sources scattered over an urban area.

4.8.1.2 Wind Speed and Wind Direction

Wind speed determines the amount of initial dilution experienced by a plume and is used in the calculation of plume rise associated with point source releases. Wind speed and wind direction are essential to the evaluation of transport and dispersion processes of all atmospheric pollutants. Wind speed is measured with mechanical sensors (cup or propeller anemometers) or nonmechanical sensors (sonic anemometers). Wind direction for meteorological measurements purposes (defined as the direction from which the wind is blowing) is typically measured with a wind vane and configured to indicate degrees clockwise from true north or a sonic anemometer.

The standard height for surface layer wind measurements is 10-m above ground level.⁴⁴ The location of the site for wind measurements should ensure that the horizontal distance to obstructions (e.g., buildings, trees, etc.) is at least ten times the height of the obstruction. In urban areas (where the “ten times” criterion may not be met), a protocol should be provided to invalidate the measurements for the problem directions. Evans et al.⁴⁵ provide a discussion of the validity of 10-m wind data in an urban setting where the average obstruction height is of the same order as the wind measurement height.

An open-lattice tower is the recommended structure for monitoring of meteorological variables at the 10-m level. In the case of wind measurements, certain precautions are necessary to ensure that the measurements are not significantly altered by turbulence in the immediate wake of the meteorological tower. To avoid such tower effects, the wind sensor should be mounted on a mast a distance of at least one tower width above the top of the tower or, if the tower is higher than 10-m, on a boom projecting horizontally from the tower. In the latter case, the boom should extend a distance at least twice the diameter/diagonal of the tower from the nearest point on the tower. The boom should project into the direction that provides the least distortion for the most important wind direction (i.e., into the prevailing wind).

There are several types of open-lattice towers: fixed, tilt-over, and telescopic. A fixed tower is usually assembled as a 1-piece structure from several smaller sections. This type of tower must be sturdy enough to be climbed safely to install and service the instruments. Tilt-

over towers are also 1-piece structures but are hinged at ground level. This type of tower has the advantage of allowing the instruments to be serviced at ground level. Telescopic, 10-m towers are usually composed of three sections, each approximately 4 m in length. The top section is the smallest in diameter and fits inside the middle section which in turn fits inside the base section. The tower can be extended to a height of 10-m by use of a hand crank located at the lowest section. The top of the tower can be lowered to a height of about 4 m to provide easy access to the wind sensors. Telescopic and tilt-over towers are not generally recommended for heights above 10-m. Regardless of which type of tower is used, the structure should be sufficiently rigid and properly guyed to ensure that the instruments maintain a fixed orientation at all times. Instrumentation for monitoring wind speed and direction should never be mounted on or near solid structures, such as buildings, stacks, water storage tanks, cooling towers, etc., because all such structures create significant distortions in the flow field.

A sensor with a high accuracy at low wind speeds and a low starting threshold is recommended for ambient monitoring applications. Lightweight materials (e.g., molded plastic or polystyrene foam) should be used for cups and propeller blades to achieve a starting threshold (lowest speed at which a rotating anemometer starts and continues to turn and produce a measurable signal when mounted in its normal position) of $\leq 0.5 \text{ m s}^{-1}$. Wind vanes or tail fins should also be constructed from lightweight materials. The starting threshold (lowest speed at which a vane will turn to within 5 degrees of the true wind direction from an initial displacement of 10 degrees) should be $\leq 0.5 \text{ m s}^{-1}$. Overshoot must be $\leq 25\%$ and the damping ratio should lie between 0.4 and 0.7.

4.8.1.3 Temperature

Temperature affects photochemical reaction rates and consequently is an essential variable for ambient monitoring applications. Thermistor resistance temperature detectors (RTD) are among the required for NATTS monitoring. These sensors provide accurate measurements and maintain a stable calibration over a wide temperature range. The RTD operates on the basis of the resistance changes of certain metals, usually platinum or copper, as a function of temperature.

The standard height for surface layer ambient temperature measurements is 2-m above ground level.^{45,46} If a tower is used, the temperature sensor should be mounted on a boom that extends at least one tower width/diameter from the tower. The measurement should be made over a uniform plot of open, level ground at least 9-m in diameter. The surface should be covered with nonirrigated or unwatered short grass or, in areas which lack a vegetation cover, natural earth. Concrete, asphalt, and oil-soaked surfaces and similar surfaces should be avoided to the extent possible. The sensor should be at least 30-m from any paved area. Other areas to avoid include large industrial heat sources, roof tops, steep slopes, hollows, high vegetation, swamps, snow drifts, standing water, and air exhausts. The distance to obstructions for accurate temperature measurements should be at least four times the obstruction height. In urban areas, extraneous energy sources (e.g., tunnels and subway entrances, roof tops, etc.) should be very deliberately avoided.

Temperature measurements should be accurate to ± 0.1 °C over a range of -30 to + 50 °C with a resolution of 0.1 °C. The time constant (63.2%) should be ≤ 60 sec. Solar heating is usually the greatest source of error; consequently, adequate shielding is needed to provide a representative ambient air temperature measurement. Ideally, the radiation shield should block the sensor from view of the sun, sky, ground, and surrounding objects. The shield should reflect all incident radiation and not reradiate any of that energy toward the sensor. A forced aspiration shield is needed for temperature/relative humidity measurements at 2-m. The best type of shield provides forced aspiration at a rate of at least 3 m s^{-1} over a radiation range of -100 to $+1100 \text{ W/m}^2$. Errors in temperature should not exceed ± 0.25 °C when a sensor is placed inside a forced aspiration radiation shield. The sensor must be protected from precipitation and condensation; otherwise evaporative effects and other forms of radiational heating or cooling will lead to a depressed temperature measurement (i.e., wet bulb temperature).

4.8.1.4 Precipitation

Precipitation data are used for consistency checks in data review and validation. Precipitation measuring devices include the tipping bucket rain gauge and the weighing rain gauge. Both types of gauge measure total liquid precipitation and may also be used to measure the precipitation rate, but the tipping bucket is preferable for that application. The tipping bucket rain gauge is probably the most common type of instrument in use for meteorological programs; a single and multiple test must be performed with the tipping bucket. The rain gauge should be located on level ground in an open area. Obstructions should not be closer to the instrument than two to four times their height. The area around the rain gauge should be covered with natural vegetation. The mouth of the rain gauge should be level and should be as low as possible but still precluding in-splashing from the ground (30 cm above ground level is the recommended minimum height). A wind shield/wind screen (such as an Alter-type wind shield, consisting of a ring with approximately 32 free-swinging, separate metal leaves) should be used to minimize the effects of high wind speeds.

4.8.1.5 Solar Radiation

Solar radiation refers to the electromagnetic energy in the solar spectrum (0.10 to 4.0 μm wavelength). The latter is commonly classified as UV (0.10 to 0.40 μm), visible light (0.40 to 0.73 μm), and near-IR (0.73 to 4.0 μm) radiation. About 97% of the solar radiation reaching the outer atmosphere of earth lies between 0.29 and 3.0 μm .⁴⁷ A portion of this energy penetrates through the atmosphere and is either absorbed or reflected at the surface of the earth. The rest of the solar radiation is scattered and/or absorbed in the atmosphere before reaching the surface of the earth. Solar radiation measurements are used in heat flux calculations that estimate atmospheric stability and in modeling photochemical reactions.

Energy fluxes in the spectrum of solar radiation are measured using a pyranometer. These instruments are configured to measure what is referred to as global solar radiation (i.e., direct plus diffuse (scattered) solar radiation). The sensing element of the typical pyranometer is protected by a clear glass dome to prevent entry of energy (wavelengths) outside the solar

spectrum (i.e., long-wave radiation). The glass domes used on typical pyranometers are transparent to wavelengths in the range of 0.28 to 2.8 μm .

Solar radiation measurements should be taken in a location with an unrestricted view of the sky in all directions. In general, locations should be avoided that have obstructions which could cast a shadow or reflect light on the sensor; light-colored walls or artificial sources of radiation should also be avoided. The horizon as viewed from the pyranometer should not exceed five degrees. Sensor height is not critical for pyranometers. Consequently, tall platforms or rooftops are typical locations. Regardless of where the pyranometer is sited, it is important to ensure that the level of the instrument is maintained and that the glass dome is cleaned as necessary.⁴⁸ To facilitate leveling, the pyranometers should be equipped with an attached circular spirit level.

Manufacturer's specifications should match the requirements of the World Meteorological Organization for either a secondary standard or first class pyranometer (see Table 4.8-3), especially if the measurements are to be used for estimating heat flux.⁴⁷ Photovoltaic pyranometers (which usually fall under second class pyranometers) may be used for ambient air monitoring applications on a case-by-case basis. The cost of photovoltaic-type sensors is significantly less than the cost of thermocouple-type sensors. However, their spectral response is limited to the visible spectrum. An Eppley precision spectral pyranometer (PSP) is the best instrument to measure global solar radiation due to a better cosine response, but a thermopile sensor should be used instead of a Licor silicon cell.

Table 4.8-3. Classification of Pyranometers

Characteristic	Units	Secondary Standard	First Class	Second Class
Resolution	W/ m ²	±1	±5	±10
Stability	%FS year ⁻¹	±1	±2	±10
Cosine Response	%	< ±3	< ±7	< ±15
Azimuth Response	%	< ±3	< ±5	< ±10

Table 4.8-3. Classification of Pyranometers

Characteristic	Units	Secondary Standard	First Class	Second Class
Temperature Response	%	±1	±2	±5
Nonlinearity	%FS	±0.5	±2	±5
Spectral Sensitivity	%	±2	±5	±10
Response Time (99%)	seconds	< 25	< 60	< 240

4.8.1.6 Barometric Pressure

Barometric pressure (station pressure) is used in all calculations of fundamental thermodynamic quantities (e.g., air density). There are two basic types of instruments available for measuring atmospheric pressure: the mercury barometer and the aneroid barometer. The Hg barometer measures the height of a column of mercury supported by the atmospheric pressure but does not offer the convenience of automated data recording. An aneroid barometer uses a pressure transducer as a sensor. There are numerous commercially available pressure transducers that meet specifications for a monitoring program; values can be recorded either in the analog or digital mode. Ideally, the pressure sensor should be located in a ventilated shelter about 2-m above ground level. The height of the station above mean sea level and the height of the pressure sensor above ground level should be documented. If needed, the pressure can then be adjusted to standard height. An aneroid or pressure transducer is needed to measure station barometric pressure.

If the pressure sensor is placed indoors, accommodations should be made to vent the pressure port to the outside environment. One end of a tube should be attached to the pressure port of the sensor, and the other end should be vented to the outside of the trailer or shelter so that pressurization due to the air-conditioning or heating system is avoided. The wind can often cause dynamic changes of pressure in a room in which a sensor is placed

4.8.2 Additional Beneficial Meteorological Information

Although not a requirement of the NATTS Program, upper air meteorological measurements and derived meteorological variables such as stability, mixing height, and turbulence are highly desirable for use in data interpretation. If available, these measurements and variables should be obtained.

The most widely used technologies for monitoring upper-air meteorological conditions include radiosondes and ground-based remote sensing platforms including sodar (sound detection and ranging), radar (radio detection and ranging), and radio acoustic sounding system (RASS). The design of a program for performing upper-air monitoring will depend upon region-specific factors. The optimal design for a given region is expected to be some combination of remote sensing and conventional atmospheric soundings. In special cases, the upper-air monitoring plan may be augmented with data from aircraft and/or tall towers. Data from existing sources (e.g., the National Weather Service (NWS) upper-air network) should be considered and integrated with the ambient air trends monitoring plan. Site selection is extremely critical for a boundary layer wind profiler and sodar system. Ambient noise considerations and tall obstructions will affect sodar measurements.

Upper-air wind speeds and wind directions are vector-averaged measurements. Remote sensing systems (e.g., Doppler sodar) provide continuous measurements of wind speed and wind direction as a function of height. These data are needed to provide wind data with the necessary temporal and vertical resolution to evaluate changes in transport flow fields coincident with the evolution of the convective boundary layer. Such evaluations can aid in the diagnosis of conditions associated with extreme ozone concentrations, for example. The capabilities of the various platforms for upper-air meteorological monitoring (towers, balloon systems, and remote sensors) are compared in Table 4.8-4.

Table 4.8-4. Capabilities and Limitations of Meteorological Measurement Systems for Vertical Profiling of the Lower Atmosphere

Variable	Tower	Sodar ³	Mini-sodar	Radar	Radar with RASS	Radiosonde	Tethersonde
	Typical Maximum Height/Range (m above ground level)						
Wind Speed	100 ¹	600	300	2 - 3 km	2 - 3 km	>10 km	1000
Wind Direction	100 ¹	600	300	2 - 3 km	2 - 3 km	> 10 km	1000
Wind Sigmas ²	100 ¹	600	300	2 - 3 km	2 - 3 km	NM	NM
Relative Humidity	100 ¹	NM	NM	NM	NM	> 10 km	1000
Temperature	100 ¹	NM	NM	NM	1.2 km	> 10 km	1000
Typical Minimum Height (m above ground level)							
Wind Speed	10	50	10	100	100	10	10
Wind Direction	10	50	10	100	100	10	10
Wind Sigmas ²	10	50	10	100	100	NM	NM
Relative Humidity	2	NM	NM	NM	NM	10	10
Temperature	2	NM	NM	NM	100	10	10
Typical Resolution (m)							
Wind Speed	2 - 10	25	10	60 - 100	60 - 100	5 - 10	10
Wind Sigmas ²	2 - 10	25	10	60 - 100	60 - 100	NM	NM
Relative Humidity	2 - 10	NM	NM	NM	NM	5 - 10	10
Temperature	2 - 10	NM	NM	NM	60 - 100	5 - 10	10

NM = Not measured; no capability for this variable.

¹Typically meteorological towers do not exceed 100 m. However, radio and TV towers may exceed 600 m.

²The standard deviation of horizontal and vertical wind components.

³The sodar system antenna must be properly oriented with respect to true north, and 10 m wind direction must have proper alignment and integrity.

Conventional atmospheric soundings obtained using rawinsondes or their equivalent are needed to provide atmospheric profiles with the necessary vertical resolution for estimating the mixing height and for use in initializing the photochemical grid models used for evaluating control strategies. Such soundings should extend to the top of the convective boundary layer (CBL) or 1000 m, whichever is greater, and should include measurements of wind speed, wind direction, temperature, and humidity. Four soundings per day are needed to adequately characterize the development of the atmospheric boundary layer. These soundings should be acquired just prior to sunrise when the atmospheric boundary layer is usually the most stable, in

mid-morning when the growth of the boundary layer is most rapid, during mid-afternoon when surface temperatures are maximum, and in late afternoon when the boundary layer depth is largest. Soundings obtained from a NWS upper-air station may be used to obtain part of this information depending on the time of the sounding and the location of the NWS site.

4.8.2.1 Siting and Exposure for Upper-Air Measurements

The upper-air measurements are intended for more macro-scale application than are the surface meteorological measurements. Consequently, the location of the upper-air site need not be associated with any particular surface monitoring site. Factors that should be considered in selecting a site for the upper-air monitoring include whether the upper-air measurements for the proposed location are likely to provide the necessary data to characterize the meteorological conditions associated with the parameters of interest, and the extent to which data for the proposed location may augment an existing upper air network. Near lake shores and in coastal areas, where land/sea/lake breeze circulations may play a significant role in pollutant formation and transport, additional upper-air monitoring sites may be needed. This consideration would also apply to areas located in complex terrain. All of the above are necessary components of the DQOs for an upper air monitoring plan.

4.8.2.2 Tall Towers

In some instances it may be possible to use existing towers located in monitoring areas to acquire vertical profiles of atmospheric boundary layer data. Radio and television transmission towers, which may be as tall as 600 m, can be equipped with in situ meteorological sensors at many levels. An advantage to using a tower is the ability to run an unattended data acquisition system. Also, data can normally be collected under all weather conditions. However, the main disadvantage of using a tower is the inability to determine the mixed layer height during most of the day. When moderate to strong convective conditions exist, the mixed layer height easily exceeds the height of the tallest towers. Another disadvantage is the potentially high cost of maintenance, especially during instances when the instrumentation needs to be accessed for adjustments or repairs.

4.8.2.3 Balloon Systems

Balloon-based systems include rawinsonde (sometimes called radiosonde) and tethered systems. The rawinsonde consists of a helium-filled balloon, an instrumental package, a radio transmitter, and a tracking device. The instrument package includes sensors for measuring atmospheric temperature, relative humidity, and barometric pressure. Data from ground-based radar, used to track the balloon, are processed to determine wind speed and direction. Typical specifications for the sensors used in rawinsondes are shown in Table 4.8-5.

Table 4.8-5. Manufacturer’s Specifications for Sensors Used in Rawinsondes

Sensor	Range	Accuracy	Resolution
Pressure	1080 to 3 mb	±0.5 mb	0.1 mb
Temperature	-90° to +60°C	±0.2°C	0.1°C
Relative Humidity	5 - 100%		

Unlike surface measurements, there is no equivalent to system accuracy for upper-air meteorological measurements from rawinsondes. Consequently, to assess the quality of rawinsonde measurements, the NWS uses a special statistical parameter called the “functional precision,” defined as the root-mean-square (rms) difference between measurements made by identical instruments at as nearly as possible the same time and same point in the atmosphere⁴⁹. The functional precision of NWS radiosonde measurements is shown in Table 4.8-6.

Table 4.8-6. Functional Precision of Rawinsonde Measurements

Variable	Functional Precision
Wind Speed (at the same height)	± 3.1 m/s
Wind Direction (at the same height)	± 18 degrees [\leq 3.1 m/s] ± 14 degrees [5.1 m/s] ± 9 degrees [10.3 m/s] ± 6 degrees [15.4 m/s] ± 5 degrees [20.6 m/s]
Temperature (at the same pressure)	±0.6°C
Dew Point Depression (at the same pressure)	±3.3°C
Height (at the same pressure)	±24 m

A tethersonde system is comprised of a tethered balloon with one or more instrument packages attached to the tether. The instrument package includes a radio transmitter and sensors to measure atmospheric temperature, relative humidity, barometric pressure, wind speed, and wind direction. Data are telemetered to the ground by radio or by conductors incorporated within the tethering cable. Tether sondes are capable of providing data up to about 1000-m in good conditions. Use of a tethersonde is limited by wind speed; they can be used reliably only in light-to-moderate wind conditions (5-m/s at the surface to 15 m/s aloft). Tethered balloons are also considered a hazard to aviation and thus are subject to Federal Aviation Administration (FAA) regulations. A permit is required to operate such a system. A tethersonde system is an excellent way to conduct a performance check on PAI-LR under proper meteorological conditions. The tethersonde provides a check on 15-min average wind speed and wind direction. Sodar PAI-LR measures from 100-m to 2000-m above ground level.

4.8.2.4 Ground-Based Remote Sensors

Ground-based remote sensors have become effective tools for acquiring upper-air information and have played an increasingly important role in atmospheric boundary layer studies. For the NATTS Program, ground-based systems are the preferred approach for upper-air meteorological monitoring and estimation of mixing heights. There are two basic types of remote sensing systems used to acquire 3-component wind velocity profiles: radar and sodar. Radars (also called wind profilers) transmit an electromagnetic signal (~ 915 megahertz (MHz)) into the atmosphere in a predetermined beam width which is controlled by the configuration of the transmitting antenna. Sodars (also called acoustic sounders) transmit an acoustic signal (~ 2 - 5 kilohertz (KHz)) into the atmosphere in a predetermined beam width, which is also controlled by the transmitting antenna. The radar has a range of approximately 150 - 3000-m with a resolution of 60 - 100 m. The sodar has a range of about 50 - 1500 m with a resolution of about 25 - 50-m.

Both systems transmit their respective signals in pulses. Each pulse is both reflected and absorbed by the atmosphere as it propagates upward. The vertical range of each pulse is

determined by how high it can go before the signal becomes so weak that the energy reflected back to the antenna can no longer be detected. As long as the reflected pulses can be discerned from background noise, meaningful wind velocities can be obtained by comparing the Doppler shift of the return signal to that of the output signal. A positive or negative Doppler shift indicates whether the radial wind velocity is moving toward or away from the transmitting antenna. The attenuation of a transmitted pulse is a function of signal type, signal power, signal frequency and atmospheric conditions. Radar signal reflection depends primarily on the presence of an index of refraction gradient in the atmosphere which varies with temperature and humidity. Sodar signal reflection depends primarily on the presence of small-scale atmospheric turbulence. The reflected signals received by either a radar or sodar are processed in a system computer by signal conditioning algorithms.

To obtain a profile of the 3-component wind velocity, one vertical beam and two tilted beams are needed. The two tilted beams are usually between 15 and 30 degrees from the vertical. These two beams are also at right angles to each other in azimuth. For example, one tilted beam may be oriented toward the north while the second tilted beam points east. Each antenna transmits a pulse and then listens for the reflected signal in succession. After all three antennas perform this function, enough information is available to convert the radial velocities into horizontal and vertical wind velocities by using simple trigonometric relationships.

Radars and sodars may use monostatic or phased array antenna configurations. Monostatic systems consist of three individual transmit/receive antennas. Phased array systems consist of a single antenna array which can electronically steer the beam in the required directions. Vertical panels (also known as clutter fences) are usually placed around the antennas. This placement effectively acts to block any stray side-lobe echoes from contaminating the return signal of a radar. For sodars, these panels cut down on the side-lobe noise, which may be a nuisance to nearby residents and also prevents any background noise that may contaminate the return signal.

A RASS uses a combination of electromagnetic and acoustic pulses to derive a virtual air temperature profile. A RASS usually consists of several acoustic antennas placed around a radar

system. The antennas transmit a sweep of acoustic frequencies vertically into the atmosphere. Concurrently, a radar beam is emitted vertically into the atmosphere. The radar beam will most strongly reflect off the sound wave fronts created by the acoustic pulses. The virtual air temperature is computed from the speed of sound which is measured by the reflected radar energy. The typical range of a RASS is approximately 150 - 1500-m with a resolution of 60 - 100-m.

Unlike in situ sensors that measure by direct contact, remote sensors do not disturb the atmosphere. Another fundamental difference is that remote sensors measure a volume of air rather than a fixed point in space. The thickness of the volume is a function of the pulse length and frequency used. The width of the volume is a function of beam spread and altitude. Siting of these profilers is sometimes a difficult task. Artificial and natural objects located near the sensors can potentially interfere with the transmission and return signals, the result of which is corrupted wind velocity data.

Since sodars use sound transmission and reception to determine the overlying wind field, a clear return signal with a sharply defined atmospheric peak frequency is required. Thus, consideration of background noise may put limitations on where a sodar can be located. External noise sources can be classified as active or passive and as broadband (random frequency) or narrowband (fixed frequency). General background noise is considered active and is broadband. If loud enough, it can cause the sodar software to reject data because it cannot find a peak or because the signal-to-noise ratio is too low. The net effect is to lower the effective sampling rate due to the loss of many transmission pulses. A qualitative survey should be conducted to identify any potential noise sources. A quantitative noise survey may be necessary to determine whether noise levels are within the minimum requirements of the instrumentation.

Examples of active, broadband noise sources include highways, industrial facilities, power plants, and heavy machinery. Some of these noise sources have a pronounced diurnal, weekly or even seasonal pattern. A noise survey should at least cover diurnal and weekly patterns. Examination of land-use patterns and other sources of information may be necessary to determine whether any seasonal activities may present problems.

Examples of active, fixed-frequency noise sources include rotating fans, a backup beeper on a piece of heavy equipment, birds and insects. If these noise sources have a frequency component in the sodar operating range, that frequency component may be misinterpreted as good data by the sodar. Some of these sources can be identified during the site selection process. One approach to reducing the problem of fixed-frequency noise sources is to use a coded pulse (i.e., the transmit pulse has more than one peak frequency). A return pulse would not be identified as data unless peak frequencies were found in the return signal the same distance apart as the transmit frequencies.

Passive noise sources are objects either on or above the ground (e.g., tall towers, power transmission lines, buildings, trees) that can reflect a transmitted pulse back to the sodar antenna. Although most of the acoustic energy is focused in a narrow beam, side-lobes do exist and are a particular concern when antenna enclosures have degraded substantially. Side-lobes reflecting off stationary objects and returning at the same frequency as the transmit pulse may be interpreted by the sodar as a valid atmospheric return with a speed of zero. It is not possible to predict precisely which objects may be a problem. Anything in the same general direction in which the antenna is pointing and higher than 5 to 10 m may be a potential reflector. It is therefore important to construct an "obstacle vista diagram" prior to sodar installation that identifies the direction and height of potential reflectors in relation to the sodar. This diagram can be used after some data have been collected to assess whether or not reflections are of concern at some sodar height ranges. Note that reflections from an object at a distance X from an antenna will show up at a height $X \cos(\alpha)$, where α is the tilt angle of the antenna from the vertical.

The radar, sodar and RASS antennas should be aligned and tilted carefully as small errors in orientation or tilt angle can produce unwanted biases in the data. True north should also be established for antenna alignment. Installation of the antennas should not be permanent since problems are very likely to arise in siting the profilers in relation to the tower and other objects that may be in the area. One final consideration is the effect of the instrument on its surroundings. The sound pulse from a sodar and RASS is quite audible and could become a

nuisance to residents who might happen to live near the installation site. This audible pulse should be a consideration in the siting process because of the potential irritation to nearby residents.

4.8.2.5 Estimation of Mixing Height

In addition to the meteorological variables that are measured directly, estimates are also required of the depth of the mixed layer (i.e., mixing height). The mixing height is a derived variable indicating the depth through which vertical mixing of pollutants occurs. Reliable estimates of the mixing height are essential to dispersion modeling. Light detection and ranging (LIDAR) systems are good techniques for determining the mixing height. LIDAR results can be compared to the sodar mixing height (which is derived from an algorithm).

The EPA recommended method for estimating mixing height requires measurement of the vertical temperature profile.^{50,51} In this method, the afternoon mixing height is calculated as the height above the ground of the intersection of the dry adiabatic extension of the maximum surface temperature with the 12 a.m. morning temperature profile. This concept of a mixing layer in which the lapse rate is roughly dry adiabatic is well founded on general theoretical principles and on operational use in regulatory dispersion modeling over the last two decades. Comparisons of mixing height estimates based on the Holzworth method with several other techniques indicate that all methods perform similarly in estimating the maximum afternoon mixing depth. The Holzworth method is normally preferred because of its simplicity. Available methods for determining mixing heights are summarized in Table 4.8-7.

Table 4.8-7. Methods Used to Determine Mixing Heights

Platform	Variable Measured	Advantages/Limitations
Aircraft LIDAR	Inert tracer	Consistent with the definition of mixing height as used in dispersion modeling. Labor intensive, not practical for routine applications.
Rawinsonde	Potential temperature	Relatively robust for estimating the daytime (convective) mixing depth. Limited by the noncontinuous nature of rawinsonde launches.
Sodar	Turbulence Acoustic	For continuous monitoring of boundary layer conditions. Range, however, is limited for sodar; estimates of the mixing height are

Table 4.8-7. Methods Used to Determine Mixing Heights

Platform	Variable Measured	Advantages/Limitations
	backscatter	possible only when the top of the mixed layer is within the range of the sodar. Good for monitoring the nocturnal surface-based temperature inversion—although different from mixing height, nocturnal inversion is equally important for modeling nocturnal dispersion conditions.
Radar wind profiler	Refractive index	For continuous monitoring of boundary layer conditions
RASS	Virtual temperature	Virtual temperature profile obtained using a RASS is used to estimate the convective mixing height in the same way that temperature data are used (limited to the range of the RASS, approximately 1 km).

The mixing height determined with Holzworth's procedure from 00Z and 12Z NWS rawinsonde should be compared with sodar PAI-LR mixing height or RASS or LIDAR mixing height.

4.9 INNOVATIVE METHODS FOR AMBIENT AIR MONITORING

This section discusses several innovative methodologies that are potentially applicable to the NATTS network. These methodologies are **NOT** presently accepted by EPA for application to the NATTS Program. Many of them are not documented thoroughly and have not achieved the level of acceptance and recognition that a numbered EPA method confers. Prior EPA approval is required for the use of any of these methodologies in the NATTS Program. The effect on consistency of data resulting from the application of these methods, in place of the accepted NATTS measurement methods, must be assessed.

The prospective user of the alternative methodology must also demonstrate performance equivalent to the currently accepted methodology and produce the necessary documentation (i.e., formally written protocol, SOPs). Specific requirements for demonstrating equivalency of methodology will be defined by EPA. These innovative methods are considered to be nonroutine in nature. Nonroutine methods are more research oriented, more difficult to operate and maintain, and usually require a specially trained or skilled operator. Nonroutine methods may also be new technologies not yet fully field tested or evaluated.

4.9.1 *Aldehydes and Ketones*

EPA Compendium Method TO-11A⁸ has been specifically disqualified for the sampling and analysis of acrolein, a compound of special concern. Extensive development and evaluation of candidate methodologies is therefore being performed to elucidate a methodology that will be effective for the sampling and analysis of acrolein, as well as other carbonyl compounds. One such methodology has been reported by Zhang et al. at Rutgers University featuring the design and evaluation of a tube-type diffusive sampler that uses dansylhydrazine (DNSH)-coated solid sorbent to collect aldehydes and ketones.⁵² The derivatized carbonyl compounds are analyzed using a sensitive HPLC-fluorescence technique.

The Rutgers diffusive sampler was evaluated using test atmospheres in the laboratory and was also evaluated in the field where results were compared to the application of the

conventional EPA Compendium TO-11A⁸ derivatization method using silica gel sampling cartridges coated with DNPH. The comparative evaluation results indicate that the diffusive sampler is a valid passive sampler for 24 - 48 hour collection of carbonyl compounds in indoor, outdoor or personal air. Use of a passive sampler for outdoor ambient air monitoring has the advantage of removing concerns over the supply of power. Aldehyde/ketone samplers currently employed use DNPH-coated sorbents as the sampling medium for collecting carbonyl compounds as DNPH derivatives (hydrazones). These DNPH derivatives are subsequently extracted and analyzed by HPLC using a UV detector.

The passive sampler reported by the Rutgers team uses a fluorogenic reagent, DNSH, to derivatize the carbonyl compounds. The DNSH derivative has shown enhanced sensitivity and selectivity compared to the DNPH methodology because the DNSH derivatives can be determined using HPLC combined with fluorescence detection, a more sensitive and selective detection method than the UV detection method.

Tubes were prepared for sampling by coating a commercially available C₁₈ cartridge with approximately 0.5 mg of DNSH. A dynamic dilution system was used in the laboratory to generate humidified test atmospheres containing formaldehyde, acetaldehyde, propionaldehyde, acrolein, acetone, crotonaldehyde, hexaldehyde and benzaldehyde, compounds selected for testing because of their importance in determining human health risk. When the coated sampling tubes were used to collect ambient air, the tubes were placed in the selected location with the barrel end uncapped and completely exposed. At the end of the sampling period, the barrel end of the sampling cartridge was recapped, the capped sampling tubes were wrapped individually with aluminum foil and placed in a cooler and the tubes were shipped to the laboratory as soon as possible.

Prior to extraction of the derivatized compounds, the capped tubes, wrapped in aluminum foil, were placed in an oven at 60°C for 1 hour to drive the reversible DNSH derivatization reactions in the direction of derivative formation. After the heating period, the cooled tubes were extracted with acetonitrile and analyzed. Extracts were found to be stable under refrigeration at 4°C for at least 7 days; extended time periods have not been tested. The analytical detection

limits for the DNSH derivatives from this study ranged from 5 - 26 pg on column, with acrolein showing a detection limit of 26 pg, as determined by using 3 times the standard deviation from the analysis of acetonitrile extracts of six randomly selected blank, coated sampling cartridges. It has not been determined how this method of determining MDL compares to the procedure using 40 CFR Part 136 Appendix B, so this MDL cannot be compared to the MDLs quoted for EPA Compendium Method TO-11A.⁸

The effects of temperature, relative humidity, face velocity, carbonyl concentrations and sampling duration on the sampling rates were evaluated. A series of experiments was conducted in which the coated sorbent cartridges were exposed to known concentrations of the eight carbonyl compounds in the test atmosphere; recoveries ranged from 60% for acrolein to 107% for propionaldehyde. Relatively low recoveries for acrolein and crotonaldehyde (~76%) were attributed to possible instability of the derivatives.

The performance of the DNSH-coated passively exposed cartridges and actively exposed DNPH cartridges was evaluated comparatively in the field by taking collocated samples on a 48-hour basis. The two methods were shown to agree reasonably well for formaldehyde, acetaldehyde, acetone, and propionaldehyde. On average, the difference between the two methods was within 40% for these four compounds. It is expected that the DNSH-coated tubes can be used outdoors without an O₃ scrubber in high O₃ environments on the basis of a study that found that O₃ (up to 300 ppb) is not a significant interference as long as DNSH is in substantial excess over the carbonyl compounds being derivatized. The O₃ seems to cause only partial oxidation of the DNSH reagent but had no effect on carbonyl-DNSH derivatives.

The use of the DNSH derivative (and of the passive sampling approach) appears to offer some advantages and looks promising for derivatization/analysis of acrolein, but extensive research remains to be performed to determine the range of applicability of the method and comparability to the currently accepted EPA Compendium TO-11A⁸ DNPH derivatization method. The preliminary results indicating comparability of the two methodologies for a few compounds to within approximately 40% is not sufficient to demonstrate that the two methods

are equivalent. Use of the DNSH derivative in the active sampling mode has not been evaluated, and MDLs have not been determined according to the Federal Register methodology.

4.9.2 Remote Sensing Applications

Monitoring using several types of remote sensors is potentially applicable to the requirements of the NATTS network. Several of these monitoring systems are presently in use for specialized applications. Factors presently affecting practical application of these types of systems in the NATTS Program are:

- Sensitivity. MDLs for remote sensing systems are typically not consistent with the MDLs achieved with manual technologies currently proposed for use for NATTS;
- Engineering Units. Remote sensing monitoring systems report results as concentration per meter (path integrated) rather than volumetric concentration, as required by NATTS (i.e., $\mu\text{g}/\text{m}^3$ of air sampled);
- Equipment Cost. The purchase price for these monitoring systems is relatively high, as opposed to the moderate cost of most manual sampling systems. However, operational costs may well be less for the remote sensing systems; and
- Complexity. The level of expertise and training currently required for operation of these relatively complex systems in the field is much greater than the expertise and training required to operate a manual collection system.

4.9.2.1 Optical Measurements of Trace Gases for NATTS

UV differential optical absorption spectroscopy (UV-DOAS) measures gases by the absorption of light. An emitter projects a beam of light to a receiver along path lengths typically hundreds of meters. Specific gases absorb light from known parts of the spectrum (i.e., UV visible and IR wavelength ranges). This absorption is recorded using a computer-controlled spectrometer.

With respect to NATTS, UV-DOAS monitoring may be applicable for formaldehyde and benzene. The issues of sensitivity and engineering units, as discussed above, should be

addressed to accomplish practical application of this monitoring approach, but if these issues are resolved, the UV-DOAS would provide true continuous monitoring data. The continuous data would provide many more data points compared to counterpart manual sampling approaches and would allow a better assessment of long-term, temporal, and diurnal trends to be made.

Fourier transform IR (FTIR) spectroscopy as applied to open-path monitoring of atmospheric gases is gradually evolving from monitoring efforts conducted by highly trained individuals experienced in the fields of instrument development and spectroscopy to routine operation of monitoring efforts by trained technicians. EPA Compendium Method TO-16 was written to provide guidance to users for the acquisition of data in a standardized way and to process those data to obtain path-integrated atmospheric gas concentrations. The FTIR can potentially measure the concentration of a large number of atmospheric gases, so the methodology is generalized. (EPA Compendium Method TO-16: Long-Path, Open-Path Fourier Transform Infrared Monitoring of Atmospheric Gases (EPA/625/R-96/010b, <http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-16r.pdf>)

The method is set up in two parts:

- Initial data acquisition after the system has been set up by the manufacturer to produce data that will form the basis of a quality assurance data set; and
- Routine data acquisition to produce time sequences of atmospheric gas concentration data.

In routine monitoring applications as well as during the initial setup, it is required that the ambient temperature and the relative humidity be monitored on a continuous basis so that the water vapor concentration as a function of time can be determined. These data should be acquired at the site where the FTIR data are taken; use of data taken at airports that may be miles away is not adequate.

Trace gas monitoring using FTIR-based, long-path, open-path systems has a number of significant advantages over the traditional methods:

- Integrity of the sample is assured since no sampling actually occurs;
- Multigas analysis is possible with a single field spectrum;
- Path-integrated pollutant concentrations are obtained;
- Spatial survey monitoring of industrial facilities is possible if scanning optics are used;
- Co-adding of spectra to improve detection capabilities is easily performed;
- Rapid temporal scanning of line of sight or multiple lines of sight is possible; and
- Monitoring of otherwise inaccessible areas is possible.

The potential for water vapor interference in FTIR measurement operations can be impacted by the area that is chosen for positioning the FTIR—for example, near large bodies of water when atmospheric conditions may be moisture-laden. Water vapor interference is especially critical when looking at compounds that are within the same absorption band as water.

The ultimate significance of remote sensing with FTIR systems is a matter of cost-effectiveness and of technological advances needed in at least two important areas:

- Improvement in the characteristics of the instrumentation to enhance sensitivity and ease of use; and
- Development of “intelligent” software to improve the means for short-term adjustment of background and water vapor spectra to account for the continual variation of ambient conditions that can adversely affect the accuracy and precision of FTIR-based systems.

It is recommended that on-site meteorological conditions, wind speed and direction, be measured during FTIR measurements.

In addition to EPA Compendium Method TO-16, additional guidance for operation of FTIR ambient air monitoring systems is available in *Open-Path Monitoring Guidance*

Document. EPA 600/4-96-040. U.S. Environmental Protection Agency, April 1996; also available at <http://www.epa.gov/ttn/amtic/files/ambient/other/lnspath/r-96-040.pdf> .

4.9.3 Particle Characterization: Photoacoustic Analyzer

It may be desirable to measure aerosol light absorption by means that do not require the use of filters, and that can observe the aerosol closer to its natural state. The photoacoustic methodology is one way of performing this measurement.^{53,54} A photoacoustic analyzer detects and quantifies BC particles in real time, similarly to an aethalometer. A photoacoustic analyzer measures light absorption at a laser wavelength of 1047 nm. BC absorbs very strongly at this wavelength, in contrast to other aerosols and gases. Sample air is pulled continuously through an acoustical waveguide, and the laser also passes through the waveguide. When BC absorbs light, it is heated. This heat transfers very rapidly to the surrounding air in a time that is much shorter than the period of laser-beam modulation, so all of the heat from light absorption comes out of the particles during each acoustic cycle. Upon heating, the surrounding air expands and generates a pressure disturbance (i.e., an acoustical signal) that is measured with a microphone attached to the waveguide. Since BC aerosols absorb light throughout the entire particle volume, the light absorption measurement is also a measure of BC mass concentration. The photoacoustic analyzer measures particles in a flowing airstream without the need to collect the particles on a filter or filter tape, and the photoacoustic analyzer has a very large dynamic range (130 decibels (dB)), making it suitable for a wide range of measurements.

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