# TECHNICAL ASSISTANCE DOCUMENT
# FOR THE
# NATIONAL AIR TOXICS TRENDS STATIONS PROGRAM

## Revision 2

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## TABLE OF CONTENTS

**Page**

## TABLE OF CONTENTS (Continued)

**Page**

## TABLE OF CONTENTS (Continued)

**Page**

## TABLE OF CONTENTS (Continued)

**Page**

## TABLE OF CONTENTS (Continued)

**Page**

## LIST OF TABLES

**Page**

## LIST OF TABLES (Continued)

**Page**

## LIST OF TABLES (Continued)

**Page**

## LIST OF FIGURES

**Page**

## REFERENCES AND RESOURCES

**Page**

## ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| ACN | acetonitrile |
| ACS | American Chemical Society |
| AGP | Advanced gradient pump |
| AGL | Above ground level |
| AIRS | Aerometric Information Retrieval System |
| amu | atomic mass unit |
| AQS | Air Quality Subsystem (of the Aerometric Information Retrieval System) |
| ASE | accelerated solvent extraction |
| BFB | 4-bromofluorobenzene |
| CAA | Clean Air Act |
| CAL | Calibration standards |
| CBL | Convective boundary layer |
| CBV | Continuing blank verifications |
| cc | cubic centimeter |
| CCB | continuing calibration blank |
| CCC | Continuing calibration certification |
| CCV | continuing calibration verification |
| CDX | Central Data Exchange |
| CFR | Code of Federal Regulations |
| COA | Certification of Analysis |
| COC | chain of custody |
| $Cr^{+6}$ | hexavalent chromium |
| CV | coefficient of variation |
| DFTPP | decafluorotriphenylphosphine |
| DI | deionized |
| DL | Detection limit |
| DNPH | 2,4-dinitrophenylhydrazine |
| DPC | 1,5-diphenylcarbohydrazide |
| DQI | data quality indicator |
| DQO | data quality objective |

**ACRONYMS AND ABBREVIATIONS (Continued)**

| | |
|---|---|
| EPA | U.S. Environmental Protection Agency |
| eV | electron volts |
| FAA | Federal Aviation Administration |
| FAEM | Flexible approaches to environmental measurement |
| FID | flame ionization detector |
| FRM | Federal Reference Method |
| g | gram(s) |
| GC | gas chromatograph/gas chromatography |
| GC/MS | gas chromatograph/mass spectrometer, gas chromatography/mass spectrometry |
| GC/MS/SIM | Gas chromatography/mass spectrometry/selection ion monitoring |
| GPRA | Government Performance Results Act |
| HAP | hazardous air pollutant |
| Hg | mercury |
| HPLC | high performance liquid chromatography |
| $I_2$ | iodine |
| IC | initial calibration; ion chromatography |
| ICB | initial calibration blank |
| ICP/MS | inductively coupled plasma/mass spectrometry |
| ICS | interference check standard |
| ICV | initial calibration verification |
| ID | identification |
| in. | inch(es) |
| IR | infrared |
| IS | internal standard |
| KHz | kilohertz |
| KI | potassium iodide |
| km kilom | eter |
| L | liter(s) |
| LCS | laboratory control standard; laboratory control spike; laboratory control sample |
| LIDAR | light detection and ranging |

**ACRONYMS AND ABBREVIATIONS (Continued)**

| | |
|---|---|
| LFB | laboratory fortified blank |
| LIMS | Laboratory Information Management System |
| Lpm | liters per minute |
| M | Molar |
| m | meter(s) |
| $m^3$ | Cubic meters |
| mAu | Milliamp units |
| MB | method blank |
| MDL | method detection limit |
| mg m | illigram(s) |
| MHz | megahertz |
| min | minute(s) |
| mL m | illiliter(s) |
| mm m | illimeter(s) |
| mM m | illimolar |
| MQO | measurement quality objective |
| MRRT | mean relative retention time |
| MS | mass spectrometer/mass spectrometry; matrix spike |
| MS/MSD | matrix spike/matrix spike duplicate |
| µg | microgram(s) |
| µL | microliter(s) |
| µm m | icrometer(s) |
| n | number |
| NAMS | National Air Monitoring Station |
| NATA | National Air Toxics Assessment |
| NATTS | National Air Toxics Trends Stations |
| ng | nanogram(s) |
| NIST | National Institute of Standards and Technology |
| nm nanom | eter |
| $NO_X$ | oxides of nitrogen |
| NWS | National Weather Service |

**ACRONYMS AND ABBREVIATIONS (Continued)**

| | |
|---|---|
| $O_2$ | oxygen |
| $O_3$ ozone | |
| OAQPS | Office of Air Quality Planning and Standards (EPA) |
| o.d. | Outer diameter |
| $OH^s$ | Hydroxide ion |
| PAH | polycyclic aromatic hydrocarbon, polynuclear aromatic hydrocarbon |
| PAMS | Photochemical Assessment Monitoring Stations |
| PBMS | Performance-based measurement system |
| PDR | Post-column Derivatizing Reagent |
| PE | performance evaluation |
| pg | picogram(s) |
| $PM_{2.5}$ | particulate matter with an aerodynamic diameter ≤ 2.5 microns |
| $PM_{10}$ | particulate matter with an aerodynamic diameter ≤ 10 microns |
| ppbv | parts per billion (by volume) |
| PQL | Practical quantitation limit |
| PSP | precision spectral pyranometer |
| psig | pounds per square inch gauge |
| PT | Proficiency Test |
| PTFE | polytetrafluoroethylene |
| PUF | polyurethane foam |
| QA | quality assurance |
| QAAR | Quality Assurance Annual Report |
| QAPP | Quality Assurance Project Plan |
| QC | quality control |
| QCS | quality control specifications |
| QL | Quantitaiton limit |
| QMP | quality management plan |
| RASS | radio acoustic sounding system |
| RB | reagent blank |
| RD | Raw Hourly, Daily and Sub-Hourly |
| RF | response factor |

**ACRONYMS AND ABBREVIATIONS (Continued)**

| | |
|---|---|
| RH | Relative humidity |
| rms | root mean square |
| RP | Raw Precision |
| RPD | relative percent difference |
| RRF | relative response factor |
| RRT | relative retention time |
| RSD | relative standard deviation |
| RTD | resistance temperature detector |
| scfm | standard cubic feet per minute |
| scm | standard cubic meters |
| SD | standard deviation |
| SIM | selected ion monitoring |
| SOP | standard operating procedure |
| SQL | Sample quantitation limit |
| SRM | standard reference material |
| SSQC | secondary source quality control |
| SVOC | semivolatile organic compound |
| TAD | technical assistance document |
| TO | toxic organic<br>*(EPA Compendium for the Determination of Toxic Organic Compounds in Ambient Air*, Second Edition. EPA/625/R-96/01b) |
| TSA | technical systems audit |
| TSP | total suspended particulate |
| UATS | Urban Air Toxics Strategy |
| UV | Ultraviolet |
| UV-VIS | Ultraviolet - visible |
| VOC | volatile organic compound |
| v/v | Volume per volume |

# SECTION 1
# INTRODUCTION

## 1.0 BACKGROUND AND OVERVIEW

There are currently 188 hazardous air pollutants (HAPs)[1], or air toxics, regulated under the Clean Air Act (CAA) that have been associated with a wide variety of adverse health effects, including cancer and neurological effects. These air toxics are emitted from multiple sources, including major stationary, area, and mobile sources, resulting in population exposure to these pollutants. U.S. Environmental Protection Agency (EPA) Government Performance Results Act (GPRA) commitments specify a goal of reducing air toxics emissions by 75 percent from 1993 levels to significantly reduce the potential for human health risk.

The National Air Toxics Trends Station (NATTS) Program ambient monitoring network was developed to fulfill the need for long-term ambient air toxics (a.k.a. HAPs) monitoring data that is acquired using consistent measurement approaches and of known and high quality. The principle purpose of this 27 site network is tracking trends in ambient HAP levels to help assess progress toward emission and risk reduction goals. This Technical Assistance Document (TAD) provides the sampling, analysis, and data reporting standards required of all entities responsible for implementing the NATTS program.

## 1.1 DATA CONSISTENCY

The objective of the NATTS is to successfully detect trends in HAPs concentrations with uniform certainty across the national set of monitoring sites, at the targeted level (i.e., a coefficient of variation (CV) of 15 percent over rolling three year periods). Using a 1-in-6-day monitoring frequency, the monitoring approach must show a combination of precision, accuracy, and sensitivity appropriate for the concentration ranges at a set of fixed monitoring sites each selected with consistent siting criteria. This level of performance is currently substantiated for a limited number of HAPs that have been monitored successfully over several years using the

methods presented in Section 4 of this document. These HAPs have National Institute of Standards and Technology (NIST)-based calibration standards or equivalent and have standardized monitoring calibration procedures. Continuous review of the status of methods will be used to assess the appropriateness of application to NATTS monitoring needs.

## 1.2 TARGET ANALYTES

A key component for the air toxics monitoring network is the designation of HAPs that will be measured. It is not practical to measure all HAPs at all locations. Recognizing the practical limitations on air toxics regulatory programs, the CAA amendments required EPA to develop a subset of the 188 toxics identified in Section 112 with the greatest impact on the public and the environment in urban areas. This subset of the 188 air toxics consists of the 33 HAPs identified in the Integrated Urban Air Toxics Strategy (UATS)[3] commonly referred to as the "Urban HAP List" and all other HAPs for which risk factors have been developed by EPA. Because this list of analytes reflects a variety of possible exposure periods (acute/chronic), pathways (inhalation, dermal, ingestion), and types of adverse health effects (cancer/noncancer), the toxics monitoring network should attempt to address the full list. Considering the chemical properties of these HAPs, they can be grouped into several general categories, including volatile organic compounds (VOCs), metals, carbonyl compounds, and semivolatile organic compounds (SVOCs) including the polycyclic aromatic hydrocarbons (PAHs).

"Analytes of Principle Interest" for the NATTS Program were selected and are presented in Table 1.1-1. Nineteen of the 62 analytes presented in Table 1.1-1 must be monitored at all NATTS sites because these entries are the major risk drivers based on a relative ranking performed by EPA. These 19 analytes are referred to as the "Method Quality Objectives (MQO) Core Analytes." The remaining 43 entries must be reported to NATTS if the corresponding methods are being conducted at the site.

**Table 1.1-1. NATTS Analytes of Principle Interest**

| Compound | Class | Method | Cancer Risk $10^{-6}$ (µg/m$^3$) | Non-Cancer Risk [Hazard Quotient=0.1] (µg/m$^3$) |
|---|---|---|---|---|
| **Acrolein** | VOC | TO-15 | | **0.00200** |
| **Perchloroethylene (tetrachloroethylene)** | | | **0.17000** | **27.00000** |
| **Benzene** | | | **0.13000** | **3.00000** |
| **Carbon tetrachloride** | | | **0.06700** | **19.00000** |
| **Chloroform** | | | | **9.80000** |
| **Trichloroethylene** | | | **0.50000** | **60.00000** |
| **1,3-Butadiene** | | | **0.03000** | **0.20000** |
| **Vinyl Chloride** | | | **0.11000** | **10.00000** |
| Acetonitrile | | | | 6.00000 |
| Acrylonitrile | | | 0.01500 | 2.00000 |
| Bromoform | | | 0.91000 | |
| Carbon Disulfide | | | | 70.00000 |
| Chlorobenzene | | | 100.00000 | |
| Chloroprene | | | | 0.70000 |
| *p*-Dichlorobenzene | | | 0.09100 | 80.00000 |
| *cis*-1,3-Dichloropropene | | | 0.30000 | 2.00000 |
| *trans*,1,3-Dichloropropene | | | 0.30000 | 2.00000 |
| Ethyl Acrylate | | | 0.07100 | |
| Ethylbenzene | | | | 100.00000 |
| Hexachloro-1,3-Butadiene | | | 0.00220 | 9.00000 |
| Methyl Ethyl Ketone | | | | 500.00000 |
| Methyl Isobutyl Ketone | | | | 300.00000 |
| Methyl Methacrylate | | | | 70.00000 |
| Methyl tert-Butyl Ether | | | 3.80000 | 300.00000 |
| Methylene Chloride | | | 2.10000 | 100.00000 |
| Styrene | | | | 100.00000 |
| 1,1,2,2-Tetrachloroethane | | | 0.01700 | |
| Toluene | | | | 40.00000 |
| 1,1,2-Trichloroethane | | | 0.06300 | 40.00000 |
| 1,2,4-Trichlorobenzene | | | | 20.00000 |
| *m*-,*p*-Xylene | | | | 10.00000 |
| *o*-Xylene | | | | 10.00000 |
| **Formaldehyde** | Carbonyl | TO-11A | **180.00000** | **0.98000** |
| **Acetaldehyde** | | | **0.45000** | **0.90000** |

**Bold** indicates required MQO Core Analytes.

[1] Method IO-3.5 measures Total Chromium only; determination of hexavalent chromium requires a specialized sampling and analytical methodology.

**Table 1.1-1. NATTS Analytes of Principle Interest (Continued)**

| Compound | Class | Method | Cancer Risk $10^{-6}$ (µg/m$^3$) | Non-Cancer Risk [Hazard Quotient=0.1] (µg/m$^3$) |
|---|---|---|---|---|
| **Nickel compounds ($PM_{10}$)** | Metals | IO-3.5 | **0.00210** | **0.00900** |
| **Arsenic compounds ($PM_{10}$)** | | | **0.00023** | **0.00300** |
| **Cadmium compounds ($PM_{10}$)** | | | **0.00056** | **0.00200** |
| **Manganese compounds ($PM_{10}$)** | | | | **0.00500** |
| **Beryllium compounds ($PM_{10}$)** | | | **0.00042** | **0.00200** |
| **Lead compounds ($PM_{10}$)** | | | | **0.15000** |
| Antimony | | | | 0.02000 |
| Chromium[1] | | | 0.00008 | 0.01000 |
| Cobalt | | | | 0.01000 |
| Mercury | | | | 0.03000 |
| Selenium | | | | 2.00000 |
| **Hexavalent chromium (TSP)** | Metals | EPA Method | **0.00008** | **0.00081** |
| **Napthalene** | PAH | TO-13A | **0.02940** | **0.02900** |
| **Benzo(a)pyrene** | | | **0.00091** | **0.30000** |
| Acenaphthene | | | | 0.30000 |
| Acenaphthylene | | | | 0.30000 |
| Anthracene | | | | 0.30000 |
| Benz(a)anthracene | | | 0.00910 | 0.30000 |
| Benzo(B)fluoranthene | | | 0.00910 | 0.30000 |
| Benzo(e)pyrene | | | | 0.30000 |
| Benzo(k)fluoranthene | | | 0.00910 | 0.30000 |
| Chrysene | | | 0.09100 | 0.30000 |
| Dibenz(a,h)anthracene | | | 0.00910 | 0.30000 |
| Fluoranthene | | | | 0.30000 |
| Fluorene | | | | 0.30000 |
| Indeno(1,2,3-cd)pyrene | | | 0.00910 | 0.30000 |
| Phenanthrene | | | | 0.30000 |
| Pyrene | | | | 0.30000 |

**Bold** indicates required MQO Core Analytes.
[1] Method IO-3.5 measures Total Chromium only; determination of hexavalent chromium requires a specialized sampling and analytical methodology.

## 1.3 SITE CONSIDERATIONS

Information on air toxics compounds is needed for both urban and rural areas. Urban-oriented information is needed to address the range of population exposures across and within

urban areas, whereas rural data are needed for characterization of exposures of non-urban populations, to establish background concentrations and to better assess environmental impacts. The ratio of urban and suburban to rural sites across the NATTS Program monitoring network is 20 to seven. Given that the NATTS program objectives are premised upon long term ambient air measurements, the sites must necessarily be considered and treated as permanent. Therefore, NATTS Program participants must use monitoring sites established and maintained in the same location and collect data year-round for many years using the methods and frequency guidelines specified in this TAD. For manual sampling, the default frequency for sample collection at NATTS Program collection locations is one sample every six days, as determined by the requirements of the NATTS data quality objectives (DQOs).

## 1.4 SHORT SUMMARY OF EACH SUBSEQUENT CHAPTER

The remainder of this technical assistance document incorporates the following sections:

- "Issues Concerning the NATTS Program" (Section 2) includes guidance and rationale for consistency in site selection, sample collection and analysis procedures to ensure that DQOs for exposure assessment and trends are met.
- "Quality Assurance and Quality Control" (Section 3) includes the general approach and specific requirements for consistency in the quality control (QC) and quality assurance (QA) recommended for the NATTS monitoring. Specific MQOs are provided for sample analysis procedures as criteria for performance-based methodology.
- "Measurement Methods for the NATTS Program" (Section 4) describes the application of existing methods for the collection and analysis of NATTS Program samples, with specifications and criteria to resolve ambiguities in the Compendium Methods used for NATTS Program monitoring and ensure the consistency of measurement approach.
- "Data Validation and Management" (Section 5) provides guidance for data review and consistency. This section provides information and guidance on procedures to ensure data are consistent, validated, reported, archived and entered into the

Aerometric Information Retrieval System-Air Quality Subsystem (AIRS-AQS) data base in a consistent and equivalent manner for each of the participating NATTS participants.

## Section 1
## References and Resources

1. Smith, R.L.; French, C.L.; Murphy, D.L.; Thompson, R. *Selection of HAPs Under Section 112(k) of the Clean Air Act: Technical Support Document*; Integrated Urban Air Toxics Strategy (UATS), July 28, 1999.

# SECTION 2
# ISSUES CONCERNING THE NATTS PROGRAM

Current EPA GPRA commitments specify a goal of reducing air toxics emissions by 75 percent from 1993 levels in order to significantly reduce the risk to Americans of cancer and other serious adverse health effects caused by airborne air toxics. To assess progress toward that goal, EPA has initiated numerous activities aimed at providing the best technical information regarding air toxics emissions, ambient concentrations, and health impacts. One key element of the full air toxics assessment process is the long-term monitoring of ambient concentrations of air toxics compounds at sites throughout the nation using consistent techniques/method to generate representative high quality data to allow analysis of patterns and trends in ambient air toxics measurements.

## 2.0 CONSISTENCY OF DATA

The ability to detect and evaluate trends on a nationwide basis requires standardized operation of the NATTS Program based upon four key components:

- Strict and specific DQOs for the program;
- Specified measurement methods performed in a standardized manner across the network;
- Strict and specific MQOs for the monitoring methods specified; and
- Stability of monitoring sites including location and operation over the specified period of time.

Standardization to specific methods and operations, and then assessing those operations against a specific set of MQOs, will yield consistency of data among the sites included in a monitoring network to allow evaluation of trends nationwide. To provide data usable for establishing trends at a given area, a monitoring site must be operating in the same location for an extended period of time (i.e., years). To know within the specified limits of error whether the

concentrations of air toxics compounds have decreased by 75 percent in a given urban area since 1993, the same site must be performing the same measurements at the same frequency from 1993 (the baseline year) until the present. To perform a nationwide evaluation of trends, consistency of data among all of the sites in the monitoring network is essential: monitoring sites must be performing the measurements using identical sampling and analytical methods in the same way over the specified long-term period, meeting the same quality specifications and reporting data in the same way. This consistency will be achieved by performing the same measurements in the same way (as specified in Section 4 of this document) and meeting the same quality specifications at every site. The function of this guidance document is to provide guidelines for standardization of the sampling, analytical, quality assurance, and reporting methodology.

## 2.1 ESTABLISHING MONITORING OBJECTIVES: THE ROLE OF DATA QUALITY OBJECTIVES AND THE QUALITY ASSURANCE PROJECT PLAN

The components essential to the systematic planning process that will result in monitoring data of the quality, quantity and consistency required to achieve program goals are DQOs, MQOs and a Quality Assurance Project Plan (QAPP). The project DQOs provide the answer to the critical question of how good the data must be in order to achieve Program goals. DQOs are used to develop the criteria that a data collection design should satisfy, including when to collect samples, where to collect the samples, the tolerable level of decision errors for the study, and how many samples to collect. Using the DQO process assures that the type, quantity, and quality of environmental data used in decision making will be appropriate for the evaluation of national trends in ambient air toxics measurements. DQOs for the overall trends monitoring network have been determined by EPA (see Section 3 of this document). Individual monitoring sites may have additional DQOs as dictated by local priorities, but local DQOs cannot be less stringent than the EPA DQOs. MQOs for the 19 NATTS MQO Core Compounds (as presented in Table 1.1-1) are also found in Section 3.

EPA policy requires that all projects involving the generation, acquisition, and use of environmental data be planned and documented and have an Agency-approved QAPP prior to

the start of data collection. The primary purpose of the QAPP is to provide an overview of the project, describe the need for the measurements, and define QA/QC activities to be applied to the project, all within a single document. The QAPP should be sufficiently detailed to provide a clear description of every aspect of the project and include information for every member of the project staff, including site operators, laboratory staff, and data reviewers. The QAPP facilitates communication among clients, data users, project staff, management, and external reviewers. Effective implementation of the QAPP assists project managers in keeping projects on schedule and within the resources budgeted. State and local organizations must develop their own QAPPs that meet their specific needs.

## 2.2 ACHIEVING MONITORING OBJECTIVES

The monitoring network must be designed to address all the needs of the NATTS Program and to satisfy the following objectives:

- Measure the MQO Core Compounds and other Analytes of Principle Interest for the NATTS Program. As shown in Table 1.1-1, monitoring methods for the MQO Core Compounds have been specified and are regularly being applied through the EPA's National Monitoring Programs.

- Ensure nationally consistent and representative data of high and known quality. To ensure nationally consistent data of high quality, the correct execution of sampling and analytical methodology is required (as presented in Section 4 of this document). The methods specified consider the threshold concentrations at which adverse health effects have been documented and provide sufficient sensitivity to obtain an adequate limit of detection. The field and laboratory monitoring operating procedures provide for appropriate QA, data management, and reporting practices.

- Collect a sufficient amount of data to estimate annual average concentrations at each monitoring site. The NATTS Program specification to estimate annual average concentrations at each monitoring site is to collect a minimum of one 24-hour sample every six days. This will result in at least 61 samples per year (together with the requisite number of duplicates, replicates, etc).

- Complement existing programs. The NATTS Program network will be integrated with existing programs to achieve efficiencies of scale to the extent that

methodologies and operations are compatible. The NATTS Program will maximize the use of existing platforms and take advantage of mobile monitoring and saturation monitoring resources, where appropriate.

- Reflect community-oriented population exposure. Stationary monitors will be sited to be representative of average concentrations within a 0.5- to 4-kilometer (km) area (i.e., neighborhood scale). These neighborhood-scale measurements are more reflective of typical population exposure, can be used to estimate long-term population risk, and are the primary component of the NATTS Program. If a different scale of measurement is used, the monitors should represent typical population exposure as well as exposure in communities near air toxics emission sources that may be impacted disproportionately.

- Represent geographic variability. A truly national network must represent a variety of conditions and environments that will allow characterization of different emissions sources and meteorological conditions. The NATTS Program supports population risk characterization, understanding of the relationships between emissions and air quality under different circumstances, and allows for tracking of changes in emissions. National assessments must reflect the differences among cities and between urban and rural areas for selected HAPs, so the network will:

  - Include cities with high population risk (both major metropolitan areas and other cities with potentially high anticipated air toxics concentrations);

  - Distinguish differences within and between geographic regions (to describe characteristics of areas affected by high concentrations vs. low concentrations);

  - Reflect the variability among pollutant patterns across communities; and

  - Include background monitoring.

The initial focus of the NATTS Program has been on community-oriented locations and reflects a population-oriented approach. The NATTS Program emphasizes fixed station, long-term monitoring using specified consistent methods to allow the assessment of trends.

# SECTION 3
# QUALITY ASSURANCE AND QUALITY CONTROL

Site specific NATTS monitoring plans and associated QA program elements for field and laboratory efforts, as approved by EPA, have been designed to ensure data comparability across the entire NATTS Program network.

## 3.0 NATTS PROGRAM QUALITY MANAGEMENT PLAN

Since the NATTS Program has specific objectives that are dependent on obtaining consistent, representative, and high and known quality data across the nation, EPA headquarters assumed responsibility for the development of the Quality Management Plan (QMP) for this program. Similar to the particulate matter with an aerodynamic diameter of ≤ 2.5 micrometers (μm) ($PM_{2.5}$) speciation QMP, the NATTS QMP provides a set of minimum requirements that will be followed by all monitoring organizations participating in the NATTS. The QMP covers the technical elements applicable to the program. The Office of Air Quality Planning and Standards (OAQPS) began development of the NATTS QMP in 2002 and submitted it for review to the major program stakeholders. The final approved NATTS Program QMP was approved and implemented in 2005.

## 3.1 NATTS PROGRAM QUALITY ASSURANCE REQUIREMENTS

The NATTS Program is designed within EPA's "Flexible Approaches to Environmental Measurement" (FAEM) – the evolution of EPA's Performance-Based Measurement Systems (PBMS) approach. The FAEM allows specific methods or approaches to be required by EPA, but also allows for small deviations in the way that the specified methods are performed as long as the resulting data meet data quality acceptance criteria. Deviations must be documented in associated site specific QAPPs and approved by EPA prior to the initiation of monitoring.

This section describes the major QA elements associated with implementing, operating, assessing, and reporting for the NATTS programs. The following QA elements are addressed:

- Data Quality Objectives;
- Quality Assurance Project Plans;
- Standard operating procedures (SOPs);
- Technical assessments;
- Data verification/validation;
- Data Quality Indicators (DQIs); and
- Method Quality Objectives.

### *3.1.1 NATTS Data Quality Objectives*

The DQO process provides a general framework for ensuring that the data collected by EPA meet the needs of decision makers and data users. The process establishes the link between the specific end use(s) of the data with the data collection process and the data quality (and quantity) needed to meet the program's goals. The result of the DQO process is a series of requirements used as the basis for the detailed planning in a project-specific QAPP. The primary trends objective of the NATTS Program is:

> ***To be able to detect a 15 percent difference (trend) between two successive 3-year annual mean concentrations (rolling averages) within acceptable levels of decision error.***

Being able to detect this trend allows evaluation of the effectiveness of HAP reduction strategies. This is not to say that the NATTS data cannot be used for other purposes. However, the development of the NATTS quality system DQIs (detectability, precision, bias, and completeness), and their resultant MQOs were based upon attaining this objective.

In 2001 a workgroup representing data users, decision-makers, state and local agency staff, and monitoring and laboratory personnel developed the DQOs through a series of

conference calls. Since it would not be reasonable to develop DQOs for every toxic compound measured in the NATTS, and in the interest of simplicity and consistency in the MQOs, the highest risk drivers, at that time, were selected for the development of the DQOs: benzene, 1,3-butadiene, arsenic, chromium, acrolein, and formaldehyde. This information was based on variability and uncertainty estimates from the 10-city Pilot Study, which suggests that the specified air toxics trends DQOs will be met for monitoring sites that satisfy the goals of:

- A 1-in-6 day sample collection rate;
- An 85 percent sample collection completeness; and
- A 15 percent measurement CV.

These results were explicitly developed for benzene (urban and rural); 1,3-butadiene (urban and rural); arsenic (urban and rural); chromium (urban only); acrolein (urban only); and formaldehyde (urban and rural).

To ensure nationally consistent data of appropriate quality (meeting the DQOs), the methods specified in Section 4 of this document consider the following DQIs:

- Detectability—being able to measure the concentration ranges required for the program;
- Completeness—being able to collect the quantity of data necessary without a high level of maintenance;
- Precision—being repeatable to an acceptable level; and
- Bias—being able to maintain a concentration that does not systematically deviate from the true concentration.

Section 4 of the NATTS TAD provides specifications for the consistent use of sampling and analysis methods for the NATTS Program. Through QAPP reviews and technical systems audits (TSAs), operational deviations that could affect the quality of the data will be identified and discussed to ensure that the methods continue to meet the DQOs.

### *3.1.2 Quality Assurance Project Plan Development*

As with the QMP, QAPPs are required for any environmental data operation using EPA funds. The purpose of the QAPP is to document planning results for environmental data operations and to provide a project-specific "blueprint" for obtaining the type and quality of environmental data needed for a specific decision or use. The QAPP documents how QA and QC are applied to an environmental data operation to assure that the results obtained are of the type and quality needed and expected to meet the program specific DQOs. All aspects of planning, implementation, operation, assessment, and reporting must be addressed in the QAPP.

The NATTS Program participants are required to develop QAPPs for their monitoring organization. To provide consistency in the development of the quality system, the OAQPS QA team developed a model QAPP that was distributed to the NATTS managers in late 2002. This document was designed and written to be a guide for the NATTS managers to develop their individual QAPPs. The EPA regional offices are required to review and approve these QAPPs. **However, it must be noted that review must specifically consider whether the plan will allow the NATTS Program DQOs to be met, and not just whether a good technical approach is being proffered, before plan approval is provided. The NAATS DQOs take precedent over any regional, state, local, or tribal objectives.** The most valuable resource for preparation of a site-specific QAPP is EPA's QA guidance document, *Model Quality Assurance Project Plan for the National Air Toxics Trends Stations*. (Available at http://www.epa.gov/ttn/amtic/files/ambient/airtox/nattsqapp.pdf).

This document represents a model QAPP for the NATTS. The OAQPS staff developed this model QAPP as an example of the type of information and detail necessary for the documents that will be submitted by state, local, or tribal air toxics monitoring programs involved in the NATTS. This model QAPP was generated using the EPA QA regulations and guidance as described in EPA QA/R-5, *EPA Requirements for Quality Assurance Project Plans*, and the accompanying document, EPA QA/G-5, *Guidance for Quality Assurance Project Plans*. All pertinent elements of the QAPP regulations and guidance are addressed in the model QAPP.

Chapter 7 of the model QAPP describes the DQOs for the NATTS. Since all NATTS sites will be part of the trends network, OAQPS requires that the DQOs be identical. The SOPs listed in the table of contents of the model QAPP are a guidance document developed for OAQPS for the NATTS. This TAD was developed by Eastern Research Group, Morrisville, NC, and is available at the following Internet web site: http://www.epa.gov/ttn/amtic/airtxfil/html.

### *3.1.3 Standard Operating Procedures*

As part of the QAPP development process, NATTS participants are required to develop SOPs with specific details on how they are performing the specified methods. As an example, it is not appropriate to simply reference EPA Toxic Organic (TO) Compendium Method 15 in the QAPP as the method for use since there are a number of options included in that method. SOPs must show that the method is being performed with the approach specified.

If subcontractors are used by the NATTS monitoring organization, they must submit their SOPs to the NATTS monitoring organization for incorporation into the QAPP prior to EPA regional office review and approval.

### *3.1.4 Technical Assessments*

An assessment is an evaluation process used to measure performance or effectiveness of a system and its elements. Assessment is an all-inclusive term used to denote audits, performance evaluations (PE), proficiency tests (PT), management systems audits, peer review, inspection, or surveillance.

The following information outlines the components of the NATTS technical assessments. Due to the one-year duration of local scale projects grants, it is not anticipated that external TSAs would be performed on the monitoring activities of these grants. The laboratory TSAs, PTs, and calibration certification will be made available only if the laboratories used in the local scale projects happen to be participating in the NATTS Program; otherwise the local scale

projects will not be included in these external assessment activities. These assessments could be made available if the timing of grant activity could be coordinated with funding and planning for these assessments for the NATTS.

***TSAs—***A TSA is a thorough, systematic, on-site, qualitative audit of facilities, equipment, personnel, training, procedures, recordkeeping, data validation, data management, and reporting aspects of the NATTS Program.

- Laboratory TSA—EPA, using contractors and EPA regional offices, will attempt to perform five to seven audits a year of the laboratories performing analysis for the NATTS Program. It is expected that audits of all laboratories would be completed in three years. An audit check sheet will be developed to provide a consistent evaluation across all laboratories. Reports on these audits will be included in an annual QA report.

- Field TSA—The EPA regional offices will perform TSAs on field activities during their normal TSA audit schedules.

- Internal TSA—Monitoring organizations as part of the internal quality system procedures may perform TSAs of the environmental data operations as described in their QAPP.

***PTs —***A PT is a type of assessment in which a sample, the composition of which is unknown to the analyst (i.e., Single Blind), is provided to test whether the analyst/laboratory can produce analytical results within the specified acceptance criteria. OAQPS proposes the use of bi-annual PT studies for the NATTS Program laboratories using the following process:

- Decide on the **audit constituents** and the **concentration levels**;

- Find an independent organization to develop the PT samples. The organization (vendor) that creates the PT samples must not perform analysis for any of the NATTS state or local agencies;

- The independent organization/vendor will certify the audit concentration and constituents through the NIST. Proficiency test materials will be developed that would be sent to NIST for analysis and certification. The appropriate confidence limit window would be identified. This information would be reported from NIST to OAQPS for review/approval of audit. Contractor payment for an audit

set would be dependent on the NIST/contractor concentration comparison. Failure would require development of a new PT audit. OAQPS may or may not have to develop an independent contract with NIST to ensure analysis and reporting to OAQPS.

### *3.1.5 Verification and Validation*

Verification is confirmation by examination and provision of objective evidence that **specified requirements** have been fulfilled. Validation is confirmation by examination and provision of objective evidence that the particular requirements **for a specific intended use** are fulfilled. It is the responsibility of the state, local and tribal monitoring organizations and their contractors that operate, collect and analyze the samples to perform the data validation and verification of the data before submission to the AQS national data base. The procedures for validation and verification should be detailed in their QAPPs and therefore reviewed by the EPA regional offices.

In addition, the VOCDat software tool, which is free and available to the public, was developed through EPA funding. This tool can be used to validate data and get the data into a format that can be sent to the AQS. [VOCDat is available at http://www.sonomatech.com/sti/software_projects_vocdat.htm.]

Due to the fact that the DQOs (a specific intended use) have been identified, OAQPS, with the help of the EPA regions and NATTS stakeholders, has developed consistent data verification and validation criteria similar to the validation templates developed for the $PM_{2.5}$ program. OAQPS has incorporated the verification/validation templates into their QMP.

### *3.1.6 Assessment of Data Quality Indicators*

A quality assessment is used to determine whether the type, quantity, and quality of data needed to support a decision (the DQO) have been achieved.

OAQPS will hire a contractor to create a quality assurance annual report (QAAR). The QAAR will document the information on the DQIs and independent assessments (TSAs and PTs) that are performed within a calendar year. These results will then be compared against the MQO criteria for this program. The annual report will be used by OAQPS, EPA regional offices, and NATTS stakeholders to assess the status of the program. If problems are identified, corrective steps by the NATTS state and local agencies with the input of the EPA regional offices will be undertaken.

After the first three years of NATTS monitoring (and every year after that), a more interpretive assessment will be performed to determine whether the assumptions and data quality requirements used to develop the DQOs are being achieved.

## 3.2 QUALITY SYSTEM DEVELOPMENT FOR THE TOXICS PROGRAM

The Science Advisory Board, results from 1996 National Air Toxics Assessment (NATA) analyses, and the national data analysis project completed in 2001 suggest that the National Toxics Monitoring Program needs to develop and administer a quality system with the goal of producing data of adequate quality. The objective of the National Toxics Monitoring Program quality system is to identify the tolerable levels of uncertainty and implement mechanisms for the control and assessment of data quality to maintain uncertainty within these tolerable levels.

Figure 3.3-1 provides a simple paradigm for development of a quality system for a monitoring program. The term “uncertainty” is used generically to describe the sum of all sources of error associated with a given portion of the measurement system. Overall data uncertainty is the sum of total population uncertainty and total measurement uncertainty. Population uncertainty is defined as the natural spatial and temporal variability in the population of the data being evaluated and is identified by the DQI called representativeness. Total measurement uncertainty is the total error associated with the data collection operation and is

defined by the DQIs: precision, bias completeness, comparability and detectability. As Figure 3.2-1 illustrates, development of the quality system involves three stages:

- **Formulation of the DQOs—**to define the quality of data needed to make a correct decision an acceptable percentage of the time. Section 3.2.1 provides a description of the DQOs. The quality is defined through quantification of the **DQIs**;

- **Formulation of MQOs**—to identify the number and type of QC samples with the acceptance criteria for those samples so that the user can control and assess the quality of the data;

- **Performance based on DQIs**—to determine by statistical assessment if the MQOs and DQOs are met and to provide descriptions of data uncertainty. If the MQOs and DQOs are not met, the DQI assessment would help to determine whether modifications to the DQOs are necessary or more QC is required.

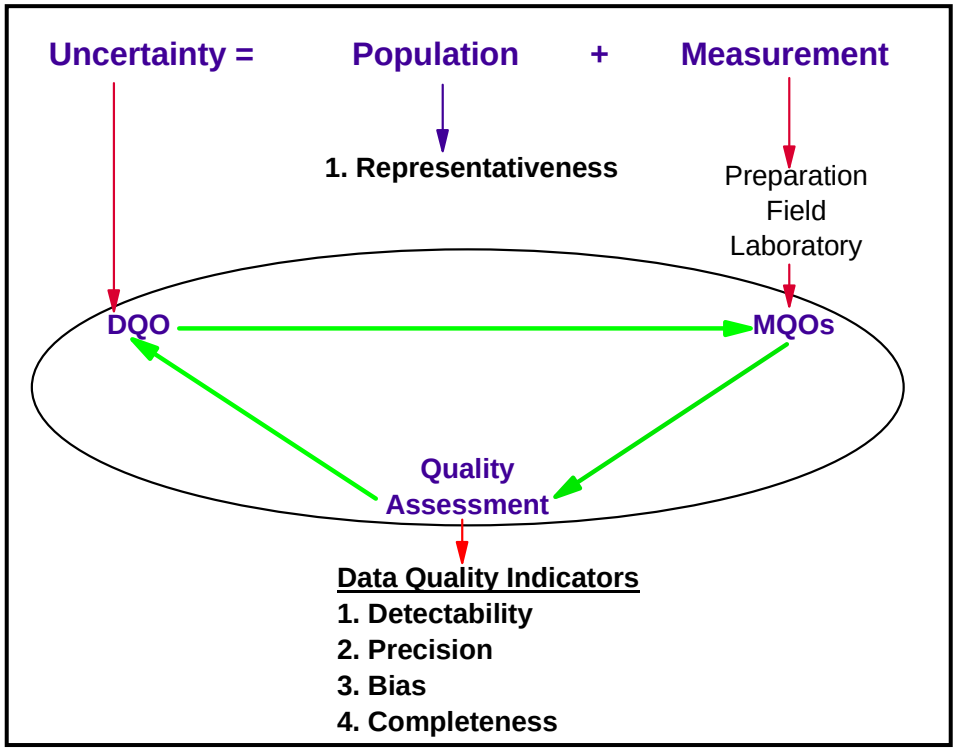


**Figure 3.2-1. Quality System for the Toxics Program**

### *3.2.1 Data Quality Indicators*

Controlling and assessing data quality to achieve the DQOs requires the ability to define the appropriate DQIs and identify measurements that can be made to provide estimates of these indicators. In addition, these DQIs can be used as metadata elements in a comprehensive data base. The important DQIs include:

**Representativeness—**Representativeness is a measure of the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. The current NATTS network has been based on a number of logistical and resource constraints that has limited its size. In addition, since there have been some constraints on how these sites were identified, the personnel developing the NATTS made the assumption that these sites accurately and precisely represent a characteristic of the population necessary to determine a national trend. During the development of the DQOs, the NATTS pilot data were used to provide measurements of population parameters. To achieve the NATTS DQOs, a sampling frequency of one day in six is required.

**Precision—**Precision assesses whether the data collection approach is repeatable. This step is important for determining whether the measurement system is under control. The estimate of precision (and bias) must be inclusive of the total data collection system, i.e., the estimate should include imprecision related to field, preparation, handling and laboratory operations. Precision will be assessed through the use of duplicate or collocated sampling, duplicate filters and a number of laboratory techniques. To achieve the NATTS DQOs, total precision should be controlled to <15 percent CV.

**Bias—**Bias assesses whether there a systematic deviation from the true concentration being reported. Bias will be assessed through the operation of a proficiency testing program and standards certifications which will provide assessments of laboratory bias issues. Laboratory

performance audits will also be conducted as the approach/procedures/equipment to accomplish this effort are developed.

**Completeness—**Completeness assesses whether enough information is being collected to ensure confidence in the conclusion or decisions made with the data. To achieve the NATTS DQOs, a completeness level of 85 percent or greater is required.

**Sensitivity—**Sensitivity assesses whether the management activities allow quantification, with the appropriate level of certainty, of a significant (acceptable) number of values from a monitoring site. Target minimum Method Detection Limits (MDLs) have been established for the NATTS Program and are presented with each specified method in Section 4 of this document.

**Comparability—**Comparability assesses whether the data from one site compares to the data from another site and/or sites across the nation. This comparability is achieved by consistently performing specified methods, and by setting DQOs and establishing the correct MQOs for the DQIs above. If the methods are consistent and the acceptance criteria are achieved, the data should be comparable.

### *3.2.2 Measurement Quality Objectives*

Measurement quality objectives are identified to control and assess various elements of a data collection activity and provide the metric used to assess some of the DQIs above. Thorough the implementation of the MQOs for the specified methods, and by achieving the acceptance limits for those MQOs, the assumption can be made that the DQOs will be met.

The highest risk drivers selected for the development of the DQOs include the following compounds:

- Acrolein, benzene, 1,3-butadiene, carbon tetrachloride, chloroform, tetrachloroethylene, trichloroethylene, and vinyl chloride (VOCs, analyzed by gas chromatography/mass spectrometry/Selective Ion Monitoring (GC/MS/SIM));
- Arsenic, beryllium, cadmium, lead, manganese, and nickel (a metal, analyzed by inductively coupled plasma/mass spectrometry (ICP/MS));
- Hexavalent chromium ($Cr^{6+}$) (a metal, analyzed by ion chromatography (IC));
- Acetaldehyde and formaldehyde (carbonyl compounds, analyzed by high performance liquid chromatography (HPLC)); and
- Benzo(a)pyrene and naphthalene (PAHs, analyzed by GC/MS/SIM).

MQOs for these compounds are summarized in Tables 3.2-1, 3.2-2, 3.2-3, 3.2-4, and 3.2-5 respectively.

**Table 3.2-1. VOC MQOs for the NATTS Program**

| MQO Parameter | Requirement | Acceptance Criteria |
|---|---|---|
| Precision | Duplicate samples or Collocated samples. Duplicate samples are taken simultaneously through the same collection system. Collocated samples are taken simultaneously through 2 separate collection systems at the same location.<br>10 % of total samples – 6 per year for 1-in-6 day sampling. | <15% CV |
| Bias | Performance Evaluation samples. 2 per calendar year. | +/- 25% for each analyte/sample |
| Completeness | Valid samples collected compared to samples planned. | >85% |
| Sensitivity | Experimentally determined MDL conducted per the specifications of 40 Code of Federal Regulations (CFR) Part 136, Appendix B. Determined annually, or after any major instrument change.<br>Minimum of 7 low level canister standards analyzed over a 2-day period (minimum). | Benzene: 0.130 $\mu g/m^3$<br>1,3-Butadine: 0.100 $\mu g/m^3$<br>Acrolein: 0.100 $\mu g/m^3$<br>Vinyl Chloride: 0.110 $\mu g/m^3$<br>Trichloroethylene: 0.500 $\mu g/m^3$<br>Tetrachloroethylene: 0.170 $\mu g/m^3$<br>Chloroform: 0.500 $\mu g/m^3$ |

**Table 3.2-2. Metals MQOs for the NATTS Program**

| MQO Parameter | Requirement | Acceptance Criteria |
|---|---|---|
| Precision | Collocated samples. Collocated samples are taken simultaneously through 2 separate collection systems at the same location.<br>10 % of total samples – 6 per year for 1-in-6 day sampling. | <15% CV |
| Bias | Performance Evaluation samples. 2 per calendar year. | +/- 25% for each analyte/sample |
| Completeness | Valid samples collected compared to samples planned. | >85% |
| Sensitivity | Experimentally determined MDL conducted per the specifications of 40 CFR Part 136, Appendix B. Determined annually, or after any major instrument change.<br>Minimum of 7 low level filters analyzed over a 2-day period (minimum). | Arsenic: 0.0010 $\mu g/m^3$<br>Beryllium: 0.00042 $\mu g/m^3$<br>Cadmium: 0.0056 $\mu g/m^3$<br>Lead: 0.0010 $\mu g/m^3$<br>Manganese: 0.0010 $\mu g/m^3$<br>Nickel: 0.0021 $\mu g/m^3$ |

**Table 3.2-3. Hexavalent Chromium MQOs for the NATTS Program**

| MQO Parameter | Requirement | Acceptance Criteria |
|---|---|---|
| Precision | Collocated samples. Collocated samples are taken simultaneously through 2 separate collection systems at the same location.<br>10 % of total samples – 6 per year for 1-in-6 day sampling. | <15% CV |
| Bias | Performance Evaluation samples. 2 per calendar year. | +/- 25% for each analyte/sample |
| Completeness | Valid samples collected compared to samples planned. | >85% |
| Sensitivity | Experimentally determined MDL conducted per the specifications of 40 CFR Part 136, Appendix B. Determined annually, or after any major instrument change.<br>Minimum of 7 low level filters analyzed over a 2-day period (minimum). | Hexavalent Chromium: 0.0043 $ng/m^3$ |
| Sample Flow Rate Accuracy | Sampler indicated sample flow rate compared to measured sample flow rate using a primary standard flow measurement device. | +/- 10% |

**Table 3.2-4. Carbonyl Compounds MQOs for the NATTS Program**

| MQO Parameter | Requirement | Acceptance Criteria |
|---|---|---|
| Precision | Duplicate samples or Collocated samples. Duplicate samples are taken simultaneously through the same collection system. Collocated samples are taken simultaneously through 2 separate collection systems at the same location.<br>10 % of total samples – 6 per year for 1-in-6 day sampling. | <15% CV |
| Bias | Performance Evaluation samples. 2 per calendar year. | +/- 25% for each analyte/sample |
| Completeness | Valid samples collected compared to samples planned. | >85% |
| Sensitivity | Experimentally determined MDL conducted per the specifications of 40 CFR Part 136, Appendix B. Determined annually, or after any major instrument change.<br>Minimum of 7 low level cartridge standards analyzed over a 2-day period (minimum). | Formaldehyde: 0.100 µg/$m^3$<br>Acetaldehyde: 0.100 µg/$m^3$ |
| Sample Flow Rate Accuracy | Sampler indicated sample flow rate compared to measured sample flow rate determined using a primary standard flow measurement device. | +/- 10% |

**Table 3.2-5. PAH MQOs for the NATTS Program**

| MQO Parameter | Requirement | Acceptance Criteria |
|---|---|---|
| Precision | Collocated samples. Collocated samples are taken simultaneously through 2 separate collection systems at the same location.<br>10 % of total samples – 6 per year for 1-in-6 day sampling. | <15% CV |
| Bias | Performance Evaluation samples. 2 per calendar year. | +/- 25% for each analyte/sample |
| Completeness | Valid samples collected compared to samples planned. | >85% |
| Sensitivity | Experimentally determined MDL conducted per the specifications of 40 CFR Part 136, Appendix B. Determined annually, or after any major instrument change.<br>Minimum of 7 low level cartridge standards analyzed over a 2-day period (minimum). | Naphthalene: 0.029 µg/$m^3$<br>Benzo(a)pyrene: 0.00091µg/$m^3$ |

To help in achieving NATTS MQOs, there are many method specific technical specification/criteria for both sample collection and analysis that must be adhered to as closely as possible. Summaries of primary technical specifications/criteria are presented in Tables 3.2-6, through 3.2-10

**Table 3.2-6. Technical Specifications/Criteria for VOC Measurements**

| Parameter | Requirement | Acceptance Criteria Detail and Flag |
|---|---|---|
| ***Field Sampling*** | | |
| Sampler Certification Challenge | Representative selection of analytes at a typical/practical level in humidified Zero Air or Nitrogen. Performed prior to field deployment, annually thereafter, and/or after any major component repair. | ± 20% per analyte |
| Sampler Certification Zero | Humidified Zero Air or Nitrogen. Performed prior to field deployment, annually thereafter, and/or after any major component repair. | ≤0.2 parts per billion by volume (ppbv)[1] per analyte or MDL, whichever is greater |
| Sampling Period | 24 hours | ± 1 hour |
| Canister Cleanliness Certification | One canister per batch cleaned | ≤0.2 ppbv per analyte or MDL, whichever is greater |
| ***Analysis*** | | |
| Holding Time (Days) | 30 days from sampling | Not Applicable |
| Mass Spectrometer (MS) Tune Check (4-bromofluorobenzene) | Daily or every 24 hours | Meets Method TO-15 criteria (Table 3) |
| Initial Calibration Levels Frequency | Multipoint calibration:<br>5 or 6 points, ranging from 0.25 to 15 ppbv<br>At least quarterly or after failure to meet acceptance criteria or after major change in instrumentation. | Relative standard deviation (RSD) of response factor ≤ 30%<br>Relative retention time (RRT) for analytes ± 0.06 retention time units from mean retention time in multipoint calibration |
| Continuing Calibration Check Frequency | Daily | ± 30% bias from mean response factor from multipoint calibration |
| Second Source Calibration Check Frequency | Following the calibration curve | ± 30% bias from mean response factor from multipoint calibration |
| Laboratory System Blank Frequency | Clean canister filled with humidified air Daily, prior to sample analysis | ≤ 0.2 ppbv per analyte or MDL, whichever is greater |
| Internal Standards Frequency | Every standard, blank, and sample | Area response within ± 40% of most recent calibration check<br>Retention time ± 0.33 min of most recent calibration check |
| Duplicates Analysis Frequency | Replicate laboratory analysis of duplicate or collocated field samples | < 25% relative percent difference (RPD) for analytes > 5 × MDL |

**Table 3.2-7. Technical Specifications/Criteria for Metals Measurements**

| Parameter | Requirement | Acceptance Criteria |
|---|---|---|
| ***Field Sampling*** | | |
| Sampling Period | 24 hours | ± 1 hour |
| Glassware/Plasticware Preconditioning | Washed in 1:1 nitric acid in a clean room, double-wrapped in sealed plastic bags. | Not Applicable |
| Filter Type: Quartz for High Volume, Teflon for low Volume | 1 per filter lot change | Not Applicable |
| Field Blanks | 1 per month | Not Applicable |
| ***Analysis*** | | |
| Holding Time | 180 days, stored at 15 to 30 °C | Not Applicable |
| Reporting Units | Total ng or $ng/m^3$ | Not Applicable |
| Extraction Efficiency | Using NIST Standard Reference Material (SRM) | 75 to 125% |
| MS Tune Check | Daily | Not Applicable |
| Initial Calibration Levels Frequency | Multipoint calibration daily, at least 4 calibration points | Correlation coefficient, 0.995 |
| Initial Calibration Verification (ICV) | Immediately after initial calibration | 90 to 110% of the actual concentration |
| Initial Calibration Blank (ICB) | Immediately after high standard verification | < 0.046 $ng/m^3$ |
| High Standard Verification | Following the initial calibration blank analysis | 95 to 105% of the actual concentration |
| Interference Check Standard (ICS) | Following the initial calibration verification, every 8 hours, and at the end of a run | 80 to 120% of the actual concentration |
| Continuing Calibration Check | Analyzed before the first sample, after every 10 samples, and at the end of the run | 90 to 110% of the actual concentration |
| Continuing Clarification Blanks | Analyzed following each continuing calibration verification | < 0.046 $ng/m^3$ |
| Blanks<br>Field Blank<br>Laboratory Reagent Blank<br>Laboratory Calibration Blank | <br>1 per month (for 1-in-6 day sampling)<br>1 per sample batch<br>Daily | <br>< MDL<br>< MDL<br>< MDL |
| Laboratory Control Sample (NIST SRM) Frequency | Daily or 1 per sample batch | 80% to 120% recovery |
| Matrix Spike (MS) | 1 per sample batch | Recovery 75 to 125% |
| Serial Dilution | 1 per sample batch | 90 to 110% of undiluted sample |

**Table 3.2-8. Technical Specifications/Criteria for Hexavalent Chromium**

| Parameter | Requirement | Acceptance Criteria |
|---|---|---|
| ***Field Sampling*** | | |
| Collection Rotameter Calibration | Prior to system deployment and annually thereafter. | Correlation coefficient ≥ 0.9995 |
| Filter Preparation | Purity of reagents is critical | 99.99% purity or better |
| Filter Background | Checked one filter per batch cleaned | Not Applicable |
| Filter Shipment | Ship cold, over Blue Ice | Not Applicable |
| Sampling Period | 24 hours | ± 1 hour |
| Filter Storage | Store in freezer (-18 °C) | Not Applicable |
| ***Analysis*** | | |
| Holding Time (Days) | Extraction: Within 21 days of sampling<br>Analysis: Within 24 hours of extraction | Not Applicable |
| Initial Calibration Levels<br>Frequency | Multipoint calibration daily, with at least 5 calibration points from 0.1 to 2 ng/mL | Correlation coefficient ≥ 0.995<br>Relative standard deviation < 10% |
| Initial Calibration Check Standard | Second source standard following the initial calibration | Recovery 90-110% |
| Continuing Calibration Check<br>Frequency | After every $10^{th}$ sample and at the end of sample analysis. | Recovery 90-110% |
| Blanks<br>Field Blank<br><br>Laboratory Reagent Blank | <br>1 per month (for 1-in-6 day sampling).<br>Every batch. | <br>< MDL<br><br>< MDL |
| Performance Standards<br>Frequency | Quarterly | ≥ 85% recovery |
| LCS<br>Frequency | Second source standard.<br>Every batch of filters extracted. | ± 10% of theoretical value |
| Method Spike | Every batch | ± 20% of theoretical |
| Duplicate Laboratory Analyses | One for every collocated sample | ± 20% for all values > 5 × MDL |
| Field Sample Recovery | If the ambient temperature is predicted to be greater than 50 °F, the sample must be recovered the day after a collection event ends. If the ambient temperature is predicted to be less than 50 °F, the sample can be recovered within 72 hours after a collection event. | Recovered in accordance with the specifications of the requirement. |

## Table 3.2-9. Technical Specifications/Criteria for Carbonyl Compounds

| Parameter | Requirement | Acceptance Criteria |
|---|---|---|
| ***Field Sampling*** | | |
| Sampling Period | 24 hours | ± 1 hour |
| Sampler Certification<br>Zero | Humidified Zero air or Nitrogen<br>Performed prior to field deployment and after any major component repair/replacement | < 0.2 ppbv for each analyte |
| Cartridge Lot Blank Check | Minimum of 3 cartridges for each new lot | Formaldehyde <0.15 µg/cartridge<br>Acetaldehyde < 0.10 µg/cartridge<br>< 0.30 µg/cartridge Acetone<br>< 0.10 µg/cartridge all others |
| Field Blank | Frequency = 1 per calendar month | <0.30 µg/cartridge Formaldehyde<br><0.4 µg/cartridge Acetaldehyde<br>< 0.75 µg/cartridge Acetone<br>< 7.0 µg/cartridge sum of all others |
| ***Analysis*** | | |
| Holding Time (Days) | Preparation: 14 days from sample collection (tube at 4 °C).<br>Analysis: 30 days from preparation (extract at 4 °C). | Not Applicable |
| HPLC Column Efficiency | Determined at instrument setup and once per sample batch | Resolution between Acetone hydrazone and Propionaldehyde hydrazone ≥ 1.0<br>Column efficiency > 5,000 plate counts |
| HPLC Linearity Check | Performed at instrument setup and when calibration check fails to meet acceptance criteria.<br>Analyze a 5-point calibration curve and a second source QC sample in triplicate. | Correlation coefficient ≥ 0.999, relative error for each level against calibration curve ≤ 20% relative error<br>Intercept acceptance must be <25 milli Amp unit (mAu) area counts per compound |
| Retention Time Check | Once every 12 hours or less | Acetaldehyde, Benzaldehyde, Hexaldehyde within retention time window established by determining 3σ or ± 2% of the mean calibration and midpoint standards, whichever is greater |
| Initial Calibration Levels<br>Frequency | Multipoint calibration:<br>6-point curve from 0.01 µg/mL to 3.0 µg/mL.<br>Every six months or after major instrument change. | Correlation coefficient ≥ 0.999<br>Relative error for each level against calibration curve ≤ 20% |
| Continuing Calibration Check | Once every 12 hours | 85 to 115% recovery |
| Calibration Accuracy | Second source standard, analyzed once after multipoint calibration, in triplicate | 85 to 115% recovery |
| Laboratory Reagent Blank Frequency | Bracket sample batch | Measured concentration $\underline{<}$ 5 x MDL |

**Table 3.2-9. Technical Specifications/Criteria for Carbonyl Compounds (Continued)**

| Parameter | Requirement | Acceptance Criteria |
|---|---|---|
| Performance Standards Frequency | 2 per calendar year. | No specific acceptance criteria; evaluation of performance is goal |
| LCS Frequency | Second source standard Once every 12 hours after calibration check | 85 to 115% recovery |
| Laboratory Duplicates Frequency | Replicate analyses of every duplicate field sample. 12 replicate analyses for 1-in-6 day sampling. | ± 20% RPD |
| Method Spike/Method Spike Duplicate (MS/MSD)[4] | One MS/MSD per batch of 20 samples | 80 to 120% recovery for Formaldehyde and Acetaldehyde and 70-30% for all other compounds |

**Table 3.2-10. Technical Specifications/Criteria for PAH Measurements**

| Parameter | Requirement | Acceptance Criteria Detail and Flag |
|---|---|---|
| ***Field Sampling*** | | |
| Sampling Period | 24 hours | ± 1 hour |
| High Volume Sampler Calibration | Prior to system deployment and annually thereafter | ± 10% from the indicated flow rate or ± 10% from the design flow rate |
| Field Blank | 1 per month | Not Applicable |
| ***Analysis*** | | |
| Holding Time (Days) | Preparation: 14 days from sample collection (at 4 °C). Analysis: 45 days from preparation (4 °C). | Not Applicable |
| Decafluorotriphenylphosphine (DFTPP) instrument tune check | Daily prior to calibration check and sample analysis; every 12 hours if instrument is operated 24 hours/day | Evaluation criteria in Table 3 of EPA Compendium Method |
| Five-point calibration | Following any major change, repair, or maintenance if daily quality control check is not acceptable. Minimum frequency every six weeks, more frequently if required. | ± 30% Difference for each compound |
| Continuing calibration certification (CCC) Standard | Daily (or every 12 hours) | ± 30% Difference for each compound relative to the mean of the calibration curve. |
| Method Blank | With every extraction batch | All analytes < 5 x MDL |
| Surrogate compound recoveries: Laboratory surrogates fluorene-$d_{10}$ pyrene-$d_{10}$ Field Surrogates fluoranthene-$d_{10}$ benzo(a)pyrene-$d_{12}$ | Every sample/blank and laboratory control standard | 60-120% Recovery |
| LCS | Every 20 samples | To be determined by control charting recovery in laboratory. |

**Table 3.2-10. Technical Specifications/Criteria for PAH Measurements (Continued)**

| Parameter | Requirement | Acceptance Criteria Detail and Flag |
|---|---|---|
| Internal Standard Response:<br>naphthalene-$d_8$<br>acenaphthylene-$d_{10}$<br>chrysene-$d_{12}$<br>perylene-$d_{12}$ | Every sample/blank/LCS | -50 to 100% from the midpoint standard level of the most recent initial calibration |
| Duplicate and/or Replicate Analyses | Duplicate and/or Replicate samples only | 10% RPD for concentrations greater than 0.5 µg/mL |

# SECTION 4
# MEASUREMENT METHODS FOR THE NATTS PROGRAM

## 4.0 INTRODUCTION

Section 4 presents information and specifications pertaining to the sample collection and analysis methods that are required for the measurement of the MQO Core Analytes for the NATTS Program. To accomplish consistency in the data generated across the entire nation, use of these methods and adherence to the MQOs presented in Section 3 of this document is mandatory. The information presented for each individual method below represents the approach, configurations and procedures that EPA offers as their desired standardized mode of sampling and analysis across the NATTS Program. The approaches as presented are those conducted by the EPA National Monitoring Programs (NMP) Contract Laboratory and are all EPA reviewed and approved annually through a comprehensive Level 1 QAPP. EPA does realize that State and Local Agencies conducting sampling and analysis outside of the EPA NMP Contract Laboratory may deviate from the information/specifications presented. However, as it would be impractical to attempt to identify and describe in this document any/all of the deviations that are possible, only the EPA approved NMP Contract Laboratory approaches, configurations and procedures are presented. NATTS participants using these methods but wishing to apply alternate approaches, configurations, and procedures (i.e., deviations) other than those specified in this TAD may do so with Regional EPA approval (provided that the alternate approaches, configurations, and procedures meet the MQOs). In this case, the NATTS participant must demonstrate equivalent performance to the methodology specified in this TAD prior to the initiation of sampling and analysis. 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:

4.3 Method IO-3.5 (Trace Metals)

4.4 Hexavalent Chromium Method (Hexavalent Chromium)

4.5 Method TO-13A (PAH)

4.6 Methods for Meteorological Monitoring

## Missed Sample Make-up Policy

In the event of a missed sample, the affected NATTS monitoring agency will endeavor to make up the missed sample at some point between the missed scheduled sampling date and the subsequent scheduled sampling date, preferably as close to the missed sample date as is reasonably possible. If it is not feasible to perform the make-up prior to the subsequent scheduled sampling date, the sample must be made up within the same Calendar Quarter averaging period that the sample was missed within. Calendar Quarters are defined as:

- Winter Quarter – January 1 through March 31.
- Spring Quarter – April 1 through June 30.
- Summer Quarter – July 1 through September 30.
- Fall Quarter – October 1 through December 31.

An annual averaging period will begin with each Winter Quarter (i.e., January 1$^{st}$) and run through the next Fall Quarter (i.e., December 31$^{st}$).

## Data Report Conditions

NATTS Data must be reported and up-loaded into AQS under the conditions as follows:

- Volatile Organic Compounds (Method TO-15) – Standard Conditions;
- Carbonyl Compounds (Method TO-11A) – Standard Conditions;
- Trace Metals (Method IO-3.5) – Local Conditions, or both Local and Standard Conditions;
- Hexavalent Chromium (EPA Method) – Standard Conditions; and
- Polycyclic Aromatic Hydrocarbons (Method TO-13A) – Standard Conditions.

Standard conditions are defined in section 5.3.1.4.

## 4.1 OVERVIEW OF EPA COMPENDIUM METHOD TO-15 (Volatile Organic Compounds)

EPA Compendium Method TO-15[1] 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 CAA Amendments of 1990. 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. This method, as described below, will be used to report VOCs for the NATTS Program.

### *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 low resolution GC/MS/SIM. 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 must 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 must 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:

$$RPD = \frac{|X_1 - X_2|}{\overline{X}} \times 100 \qquad (4.1\text{-}1)$$

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;

$\overline{X}$ = 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-15[1] addresses 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). In EPA Method TO-15, the primary approach to sample collection is based on integrating the sample over the collection duration so that the final sample pressure achieved in the canister is negative or subambient (typically 2-5”Hg). However, the method does make provisions for positive pressure sampling, (i.e., collecting samples that have a final pressure that is greater than atmospheric), with associated cautions presented regarding moisture condensation with increasing pressure and loss of polar VOC. For the NATTS Program, the preferred configuration and approach to sampling using EPA Compendium Method TO-15 entails collecting integrated negative pressure (i.e., subambient final pressure) whole air samples[2] in precleaned, evacuated passivated stainless steel canisters.

#### 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 inch (in.) outer diameter (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 must be constructed of 1/8- in. or 1/4- 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 must 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 must 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 must be in the breathing zone at a height of approximately 2 to 4 meters (m) above ground level. In addition, the inlet funnel must be positioned more than 1 m, both vertically and horizontally, away from the housing structure. The inlet funnel must be positioned away from nearby obstructions such as a forest canopy or building. The vertical distance between the inlet funnel and any obstacle must be at least two times the height difference between the obstacle and the inlet funnel. The unrestricted airflow across the inlet funnel will 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 must 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.

With continuous use, the sample inlet and manifold can accumulate deposits of particulate material and other potential contaminants. The sample inlet and manifold must be cleaned to remove these materials at a recommended quarterly frequency. To clean the assembly, the sample lines and blower must 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 must 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 must then be rinsed with the distilled water and allowed to dry completely before reassembling.

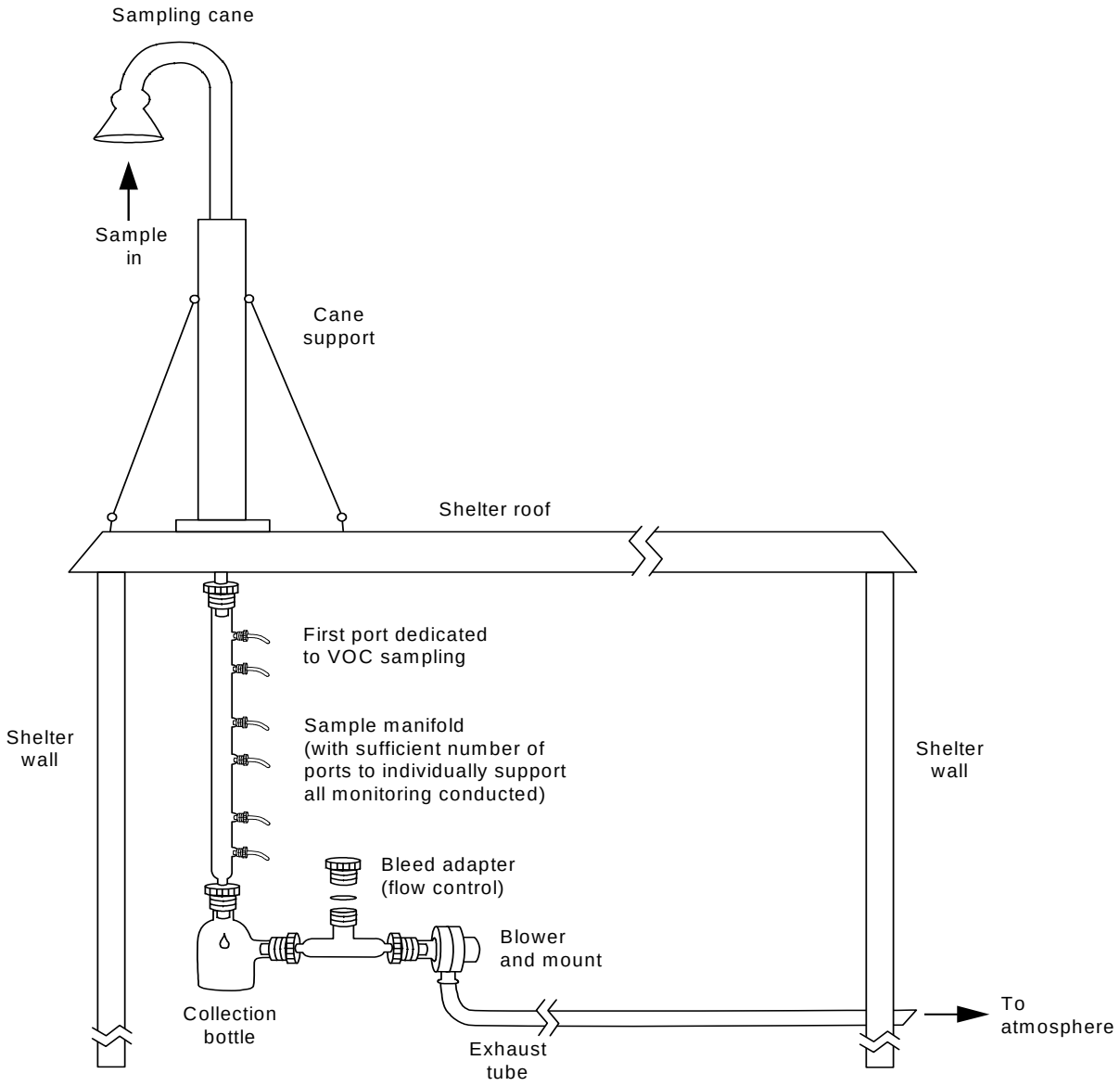


**Figure 4.1-1. Vertical Configuration**

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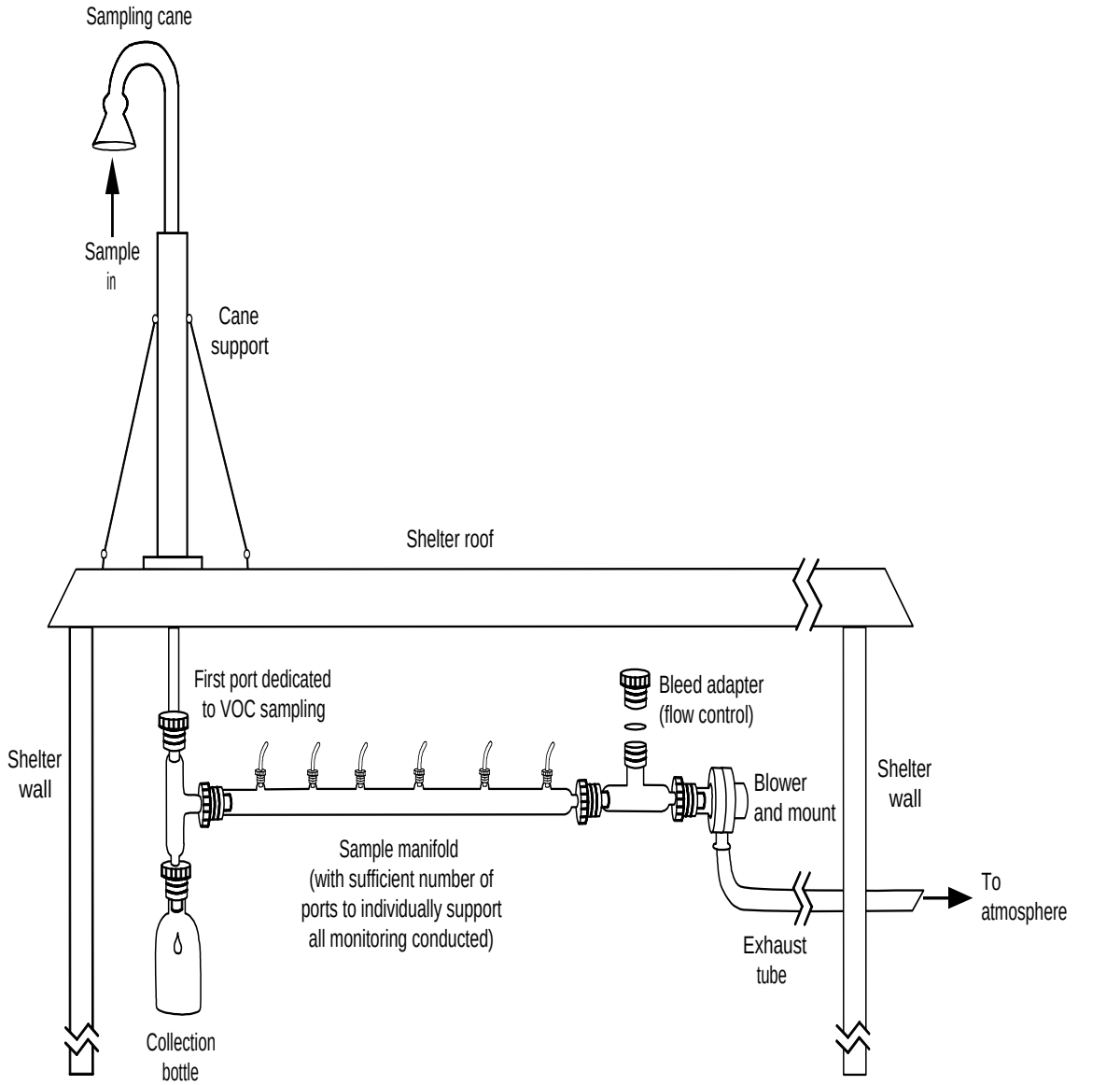


**Figure 4.1-2. Horizontal Configuration**

### 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.

Although EPA Compendium Method TO-15 makes provision for the collection of either negative or positive final pressure samples because consistency of data is a paramount consideration for the NATTS Program, standardization on one approach is strongly recommended. Canister sampling systems used to collect samples for the NATTS Program must meet the following specifications:

- The sampling system will yield a **subambient final sample pressure** (i.e., approximately 2 to 10 in. Hg).
- 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 percent 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.

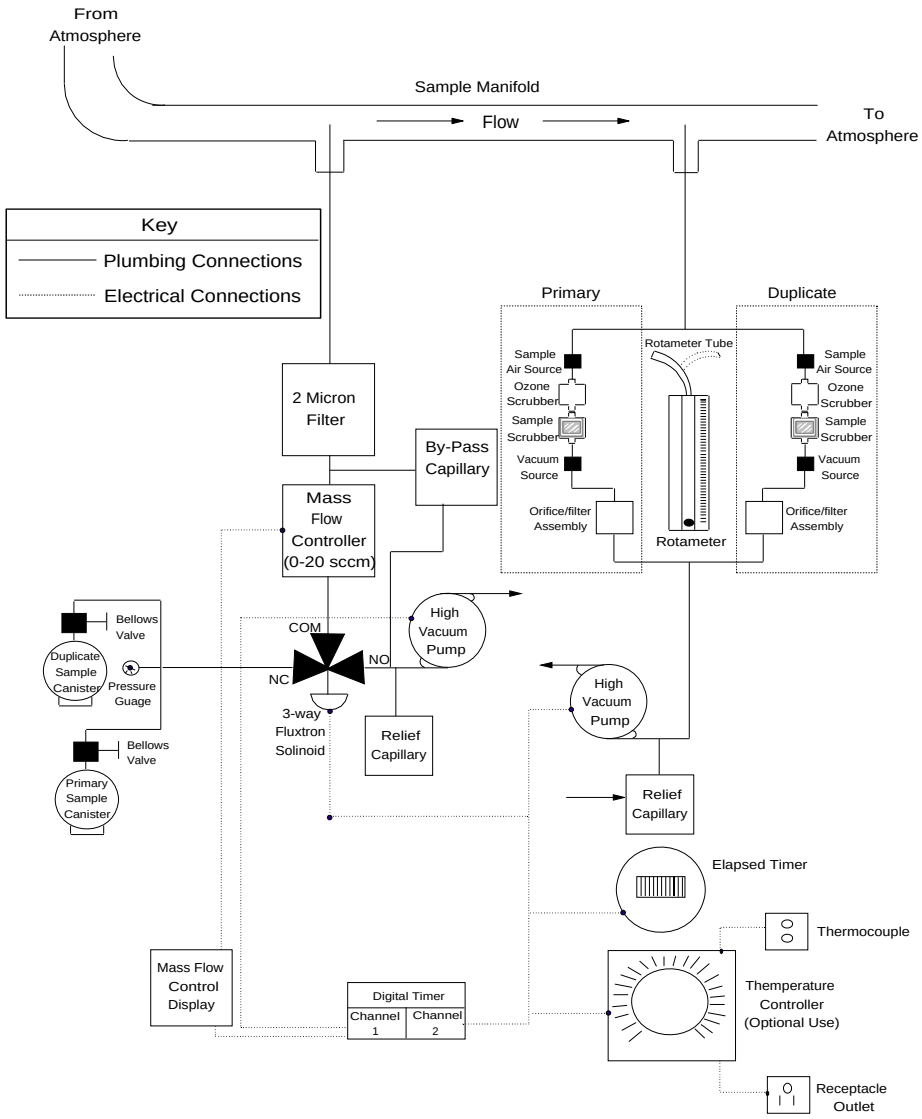


**Figure. 4.1-3. A Typical NATTS Sample Collection System**

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 (±10 percent) over a specific sampling period under conditions of changing temperature (20 to 40 °C) and humidity (0 to 100 percent 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 must be chromatographic-grade stainless steel, and all fittings must 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 certification process, to the largest extent possible, should follow the standard collection procedures used in the field for regular sample collection. The following procedure is required to certify canister sampling systems.

A challenge sample, consisting of a certified standard blend of VOCs that span the analytical chromatographic range at a known concentration in clean, humidified zero air or nitrogen, is collected through the sampling system into a canister. This certification collection is typically performed over a 24-hour duration (like typical field sample collections). However, shorter durations can be applied if required to reduce the volume of standard gas used, or because of gas generation system limitations. The zero air must be humidified to approximately 70 percent relative humidity (RH). Typical challenge gas concentrations are approximately 5-7 ppbv per compound. A reference sample is concurrently collected using a dedicated flow control device that has been characterized prior to each use. The samples are then analyzed using a gas chromatograph/mass spectrometer (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 are required to be in the range of 85 to 115 percent of the concentrations determined for the reference sample. A system-specific overall recovery must also be calculated. The overall recovery is the average of the individual compound recoveries. Each sampling system is required to have an overall recovery of 85 to 115 percent. 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 must 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 must be hydrocarbon-free and humidified to approximately 70 percent 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.

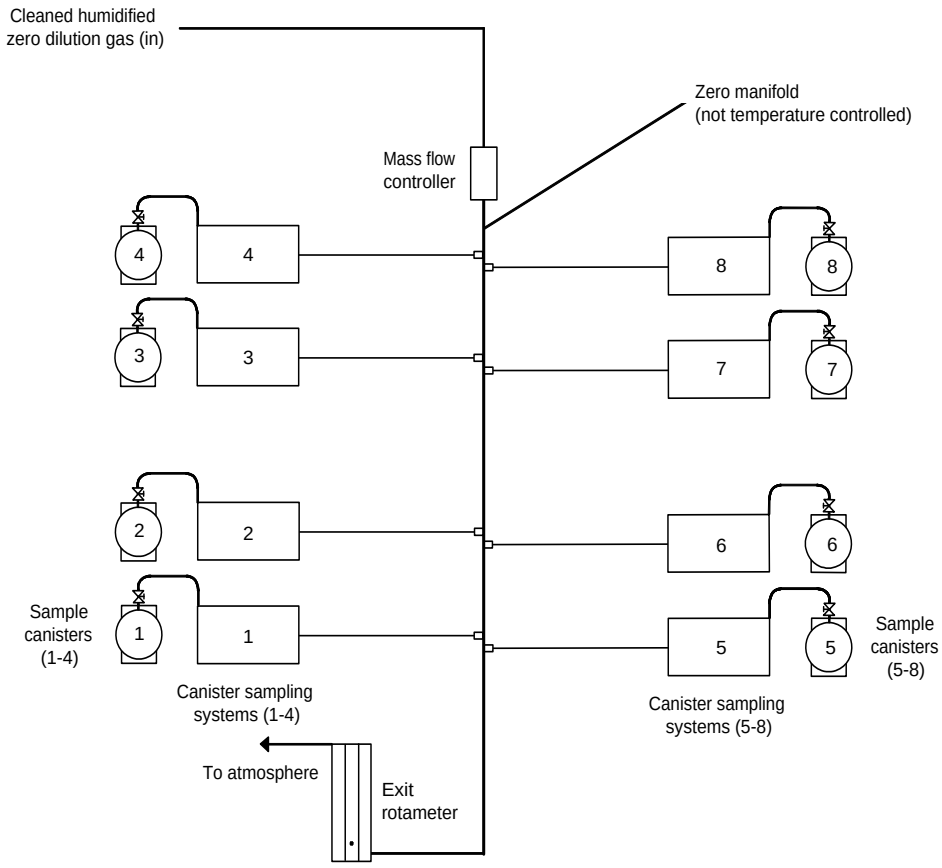


**Figure 4.1-4. Dedicated Manifold for Zero Gas Certification**

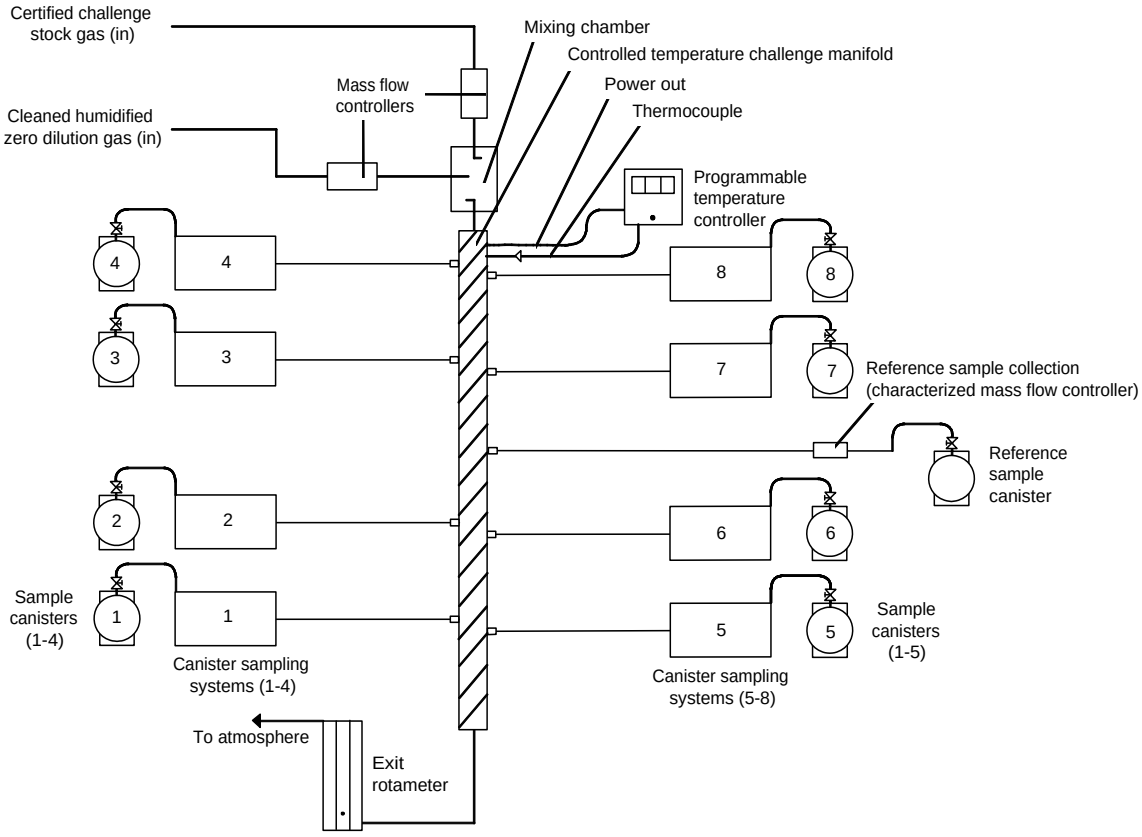


**Figure 4.1-5. Dedicated Manifold for Challenge Gas Certification**

### 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.

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 one hour to remove accumulated moisture. During the dry purge, determine the certification flow requirements using the following equation:

$$Q_t = \left[(Q_s \times N_1) + (Q_R \times N_2)\right] \times F_1 \qquad (4.1\text{-}2)$$

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:

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

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)

$$Q_P = F_2 \times Q_T \qquad (4.1\text{-}4)$$

where:

$Q_P$ = Pollutant flow rate (mL/min)

$Q_T$ = Total required flow rate

$$Q_D = Q_T - Q_P \qquad (4.1\text{-}5)$$

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 percent RH, for 48 hours. Dry the manifold and samplers with dry zero air for one hour. Adjust the zero air stream to 70 percent 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 must 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 VOCs[3]. 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 29.5" 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 29.5" 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 percent of the flow rate can be directed to the humidifier (to bubble through the water to become saturated) while the other 20 percent bypasses the humidifier. This procedure allows the humidification apparatus to supply cleaned, dried air that has been humidified to an RH of approximately 80 percent.

- 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.

- 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 29.5” Hg absolute. High moisture content will impede the performance of the high vacuum pump.

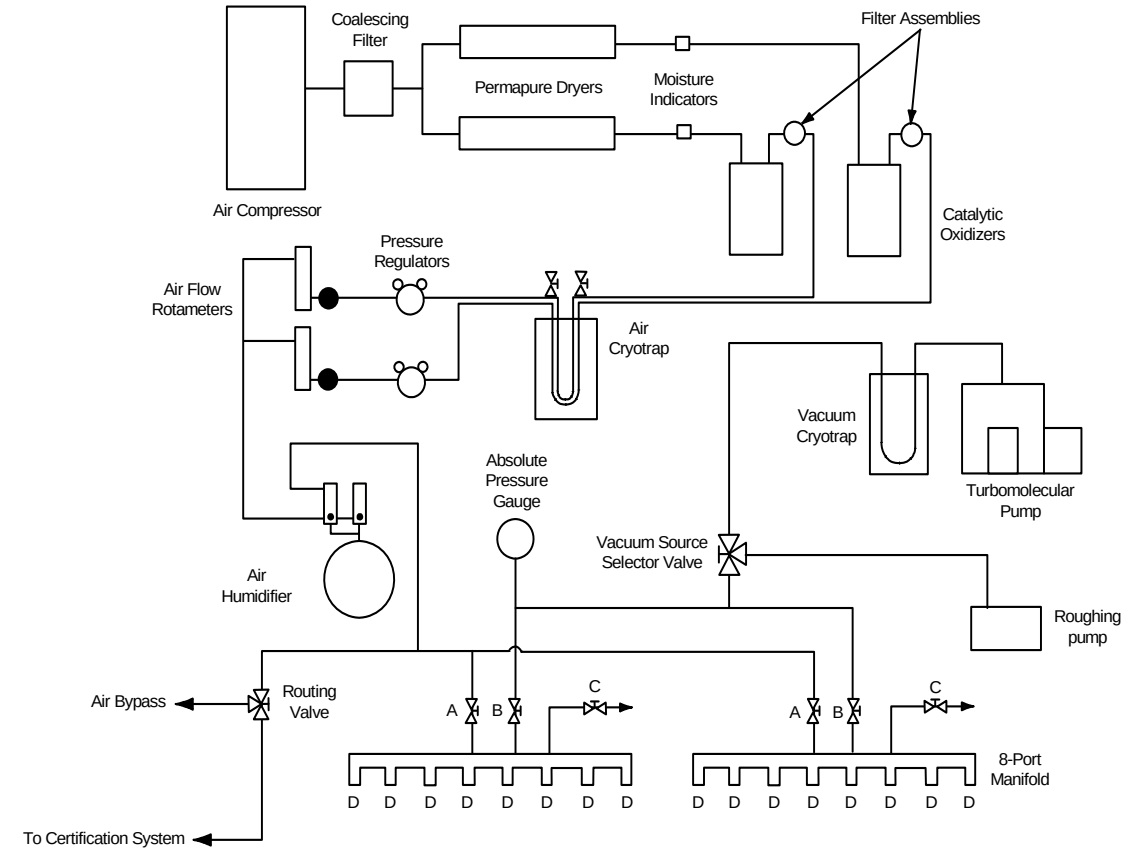


**Figure 4.1-6. Schematic of a Canister Cleanup System**

- 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 29.5" Hg absolute.

- Air bypass valve. The air bypass valve is used to allow a 1.0-liters per min (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 cryotraps 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 cryotraps do 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 29.5” 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 cryotraps (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. Route 100 percent of the air flow through the humidifier to achieve approximately 80 percent RH.

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-15[1] 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 29.5” 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 and/or after any major component repair. 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 two minutes.

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 percent 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 must be constructed of glass, stainless steel, or Viton®. The use of Teflon® or other plastics or polymers must 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-15[1], 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 gas chromatograph (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. A flame ionization detector (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-15[1], 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 | | Primary Ion | Secondary Ion |
|---|---|---|---|
| Acetonitrile | 75-05-8 | 41 | 40 |
| Acetylene | 74-86-2 | 26 | 25 |
| **Acrolein** | **107-02-8** | **56** | **26, 27, 29, 55** |
| Acrylonitrile | 107-13-1 | 53 | 52 |
| *tert*-Amyl Methyl Ether | 994-05-8 | 73 | 87 |
| **Benzene** | **71-43-2** | **78** | **77** |
| Bromochloromethane | 74-97-5 | 128 | 130, 49 |
| Bromodichloromethane | 75-27-4 | 83 | 85, 129 |
| Bromoform | 75-25-2 | 173 | 171, 175, 252 |
| Bromomethane | 74-83-9 | 94 | 96 |
| **1,3-Butadiene** | **106-99-0** | **54** | **53, 39** |
| Carbon Disulfide | 75-15-0 | 76 | 44, 78 |
| **Carbon Tetrachloride** | 56-23-5 | 117 | 119 |
| Chlorobenzene | 108-90-7 | 112 | 77, 114 |
| Chloroethane | 75-00-3 | 64 | 66 |
| **Chloroform** | 67-66-3 | 83 | 85 |
| Chloromethane | 74-87-3 | 50 | 52 |
| Chloromethylbenzene | 100-44-7 | 91 | 126 |
| Chloroprene | 126-99-8 | 53 | 88, 90 |
| Dibromochloromethane | 124-48-1 | 129 | 127, 131 |
| 1,2-Dibromoethane | 106-93-4 | 107 | 109 |
| *m*-Dichlorobenzene | 541-73-1 | 146 | 148, 111 |
| *o*-Dichlorobenzene | 95-50-1 | 146 | 148, 111 |
| *p*-Dichlorobenzene | 106-46-7 | 146 | 148, 111 |
| Dichlorodifluoromethane | 75-71-8 | 85 | 87, 101 |
| 1,1-Dichloroethane | 75-34-3 | 63 | 65 |
| 1,2-Dichloroethane | 107-06-2 | 62 | 64 |

**Bold** indicates required MQO Core Analytes.
Shading indicates other Analytes of Primary Interest to the NATTS Program.

**Table 4.1-1. Characteristic Masses Used for Quantitation of VOCs (Continued)**

| Compound | | Primary Ion | Secondary Ion |
|---|---|---|---|
| 1,1-Dichloroethene | 75-35-4 | 96 | 98, 61 |
| *cis*-1,2-Dichloroethylene | 56-60-5 | 96 | 61, 98 |
| *trans*-1,2-Dichloroethylene | 56-60-5 | 96 | 98, 61 |
| 1,2-Dichloropropane | 78-87-5 | 63 | 62, 41 |
| *cis*-1,3-Dichloropropene | 10061-01-5 | 75 | 39, 77 |
| *trans*-1,3-Dichloropropene | 10061-02-6 | 75 | 39, 77 |
| Dichlorotetrafluoroethane | 1320-37-2 | 85 | 135, 87 |
| Ethyl Acrylate | 140-88-5 | 55 | 99 |
| Ethyl *tert*-Butyl Ether | 637-92-3 | 59 | 87, 57 |
| Ethylbenzene | 100-41-4 | 91 | 106 |
| Hexachloro-1,3-Butadiene | 87-68-3 | 225 | 227, 223 |
| Methyl Ethyl Ketone | 78-93-3 | 43 | 72 |
| Methyl Isobutyl Ketone | 108-10-1 | 43 | 58, 100 |
| Methyl Methacrylate | 80-62-6 | 41 | 69, 100 |
| Methyl *tert*-Butyl Ether | 1634-04-1 | 73 | 57 |
| Methylene Chloride | 75-09-2 | 84 | 49 |
| *n*-Octane | 111-65-9 | 85 | 57, 71 |
| Propylene | 115-07-1 | 41 | 39, 42 |
| Styrene | 100-42-5 | 104 | 78, 103 |
| 1,1,2,2-Tetrachloroethane | 79-34-5 | 83 | 85 |
| **Tetrachloroethylene** | 127-18-4 | 166 | 164, 131 |
| Toluene | 108-88-3 | 91 | 92 |
| 1,2,4-Trichlorobenzene | 120-82-1 | 180 | 182, 184 |
| 1,1,1-Trichloroethane | 71-55-6 | 97 | 99, 61 |
| 1,1,2-Trichloroethane | 79-00–5 | 97 | 83, 61 |
| **Trichloroethylene** | 79-01-6 | 130 | 132, 95 |
| Trichlorofluoromethane | 75-69-4 | 101 | 103, 105 |

**Bold** indicates required MQO Core Analytes.
Shading indicates other Analytes of Primary Interest to the NATTS Program.

**Table 4.1-1. Characteristic Masses Used for Quantitation of VOCs (Continued)**

| Compound | | Primary Ion | Secondary Ion |
|---|---|---|---|
| Trichlorotrifluoroethane | 26523-64-8 | 101 | 151, 103 |
| 1,2,4-Trimethylbenzene | 95-63-6 | 105 | 1220 |
| 1,3,5-Trimethylbenzene | 108-67-8 | 105 | 120 |
| *m*-, *p*-Xylene | 108-38-3/106-42-3 | 91 | 106 |
| *o*-Xylene | 95-47-6 | 91 | 106 |
| **Vinyl Chloride** | 75-01-4 | 62 | 64 |

**Bold** indicates required MQO Core Analytes.
Shading indicates other Analytes of Primary Interest to the NATTS Program.

#### 4.1.8.3 Humidity

Humidity in canister samples can present some chromatography problems ranging from poor reproducibility to column degradation[7]. 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 Volatile Organic Compound 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-micrometer (μm) 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 4-bromofluorobenzene(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 (SIM 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) must be traceable to an NIST SRM and include the VOCs of interest in one or more cylinders.

- Laboratory control standard. The calibration stock(s) must 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 $d_{14}$-hexane, 1,4-difluorobenzene, and $d_5$-dichlorobenzene at a nominal concentration of 30 ppbv. The internal standard (IS) must 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 IS gas mixture. Tuning criteria are shown in Table 4.1-2.

- Sample canisters. These canisters are stainless steel (typically 6 liters (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 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 in the range of 500 ppbv – 1 ppmv 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. 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 must be prepared for each of the six calibration concentrations, 0.25 ppbv, 0.50 ppbv, 1.0 ppbv, 2.5 ppbv, 5.0 ppbv, and 10.0 ppbv. Each standard must be assigned a unique standard identification number, and the preparation of each standard must be documented in a standards logbook. The prepared standards must stabilize at equilibrium for at least 24 hours prior to analysis. A diagram of a dynamic flow dilution system is included in Section 9.2 of EPA Compendium Method TO-15[1]. The mass flow controllers of the dilution system must be recalibrated annually, and the calibration must be documented in the standards logbook.

To calculate the final diluted compound concentration:

Diluted Conc. = (Original Conc.)(Stock gas flow rate)/(Airflow rate + 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/IS gas mixture in a cylinder is loaded through the preconcentrator system along with the sample to introduce the ISs and BFB to the sample analysis. The same amount of the BFB/IS gas mixture is loaded with each analysis, whether sample, blank, or standard. Table 4.1-3 shows the IS compounds and their characteristic masses.

**Table 4.1-3. Internal Standards and 4-Bromofluorobenzene: 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: | 5.00 min |
| EMV Mode: | Absolute |
| Resulting EM Voltage: | 1282 (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: | 7.20 |
| Plot 1 Ion: | 39.00 |
| Ions In Group: | 39.00, 41.00, 42.00 |

GROUP 3

| | |
|---|---|
| Group ID: | 3 |
| Resolution: | Low |
| Group Start Time: | 8.20 |
| 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: | 11.20 |
| 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: | 13.40 |
| Plot 1 Ion: | 41.00 |
| Ions In Group: | 25.00, 26.00, 27.00, 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: | 17.80 |
| 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: | 20.90 |
| 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: | 23.00 |
| 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: | 25.10 |
| 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: | 27.50 |
| 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: | 29.60 |
| 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: | 32.50 |
| 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: | 34.40 |
| 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: | 39.80 |
| Plot 1 Ion: | 180.00 |
| Ions In Group: | 128.00, 180.00, 182.00, 184.00, 223.00, 225.00 |

*Timed MS Detector Entries*

| | |
|---|---|
| Time (min): | 43.00 |
| State (MS on/off): | Off |

*GC Temperature Information*

| | |
|---|---|
| Column: | Restek Rxi-lms, 60 m, 0.32 i.d., 1-µm 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 |

| Level | Rate (°C/min) | Final Temp (°C) | Final Time (min) |
|---|---|---|---|
| 1 | 15.00 | 0 | 0.00 |
| 2 | 5.00 | 150 | 0.00 |
| 3 | 25.00 | 250 | 1.00 |
| 4 | 50.00 | 150 | 9.00 |

Next Run Time: 54.33 min

*Preconcentrator Interface Conditions*

| | Initial Temperature | DesorptionTemperature |
|---|---|---|
| Trap 1: Glass Bead/Tenax® Trap | -155 °C | 10 °C |
| Trap 2: Tenax® Trap | -55 °C | 200 °C |
| Cryofocuser | -185 °C | 100 °C |

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

### 4.1.8.6 Preparation of the Gas Chromatograph/Mass Spectrometer 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, IS retention times, and MDLs must 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 IS from the target compounds must be achieved prior to analysis. The use of ISs 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 psig @ 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 IS gas mixture is attached to the preconcentrator system with stainless steel tubing to allow the BFB and the ISs to be concentrated with the sample prior to injection. Any changes or maintenance to the system must 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, 2.5, 5, and 10 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 ±30 percent with up to two compounds allowed to be within ±40 percent. 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 must record the expected due date (three months from the date of calibration) for the next calibration in the analysis logbook.

The relative response factor (RRF) is calculated as follows:

$$RRF = \left(A_t\right)\left(C_{is}\right) / \left(A_{is}\right)\left(C_t\right) \qquad (4.1\text{-}6)$$

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 IS

$C_t$ = concentration of the target compound (ppbv)

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

The RRTs are calculated as follows:

(4.1-7)

$$\boldsymbol{RRT} = \frac{\boldsymbol{RT_t}}{\boldsymbol{RT_{is}}} \qquad (4.1\text{-}7)$$

where:

$RT_t$ = retention time for the target compound (seconds)

$RT_{is}$ = retention time for the IS (seconds).

The MRRTs are calculated as follows:

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

where:

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

A second source calibration check must be analyzed immediately following the initial calibration as an 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. If it is at a high concentration, a lower concentration standard can be prepared using the dynamic flow dilution system. The recoveries

for the LCS should be from 70 to 130 percent of expected concentration. If the LCS does not meet criteria, it is reanalyzed. If acceptance criteria are still not achieved, recalibration is required.

$$\text{Percent Recovery} = \frac{\text{observed value}}{\text{expected value}} \times 100 \qquad (4.1\text{-}9)$$

### 4.1.8.8 Analytical Sequence

Sample analysis can begin after the daily system performance check, continuing calibration (or initial calibration), LCS, and daily system blank criteria have met acceptance criteria. Daily QC criteria are presented in Section 4.1.8.10.

- 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 must 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 ±30 percent 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 must be repeated. If still not valid, system maintenance and/or recalibration with new standards is required.

$$RPD = \frac{RRF_t - MRRF_i}{MRRF_i} \times 100 \qquad (4.1\text{-}10)$$

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.

- 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 three 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 laboratory information management system (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 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 must 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 °C, the autosampler preconcentrator collects the specified volume of a single sample out of a canister along with the specified volume of the BFB/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 ± 40 percent 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 ± 40 percent 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.

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

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 must be diluted either by reducing the 400 milliliters (mL) sample volume or (in the canister) by adding clean, pressurized nitrogen or air. Samples diluted with nitrogen or air must 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 Volatile Organic Compound Analysis*

Three measurements of method acceptability are presented below.

#### 4.1.9.1 Determination of Method Detection Limits

Method Detection Limits for the ambient air analysis are experimentally determined in accordance with 40 CFR, Part 136, Appendix B, with 99 percent 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-15[1].

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

| Compound | Target MDL ($ug/m^3$) | Compound | Target MDL ($ug/m^3$) |
|---|---|---|---|
| Acetonitrile | 0.1 | 1,2-Dichloropropane | 0.050* |
| Acetylene | 0.010* | *cis*-1,3-Dichloropropene | 0.3 |
| **Acrolein** | **0.1** | *trans*-1,3-Dichloropropene | 0.3 |
| Acrylonitrile | 0.1 | Dichlorotetrafluoroethane | 0.020* |
| *tert*-Amyl Methyl Ether | 0.050* | Ethyl Acrylate | 0.071 |
| **Benzene** | **0.13** | Ethyl *tert*-Butyl Ether | 0.020* |
| Bromochloromethane | 0.030* | Ethylbenzene | 0.5 |
| Bromodichloromethane | 0.050* | Hexachloro-1,3-Butadiene | 0.5 |
| Bromoform | 0.91 | Methyl Ethyl Ketone | 0.5 |
| Bromomethane | 0.010* | Methyl Isobutyl Ketone | 0.5 |
| **1,3-Butadiene** | **0.1** | Methyl Methacrylate | 0.5 |
| Carbon Disulfide | 0.5 | Methyl *tert*-Butyl Ether | 0.5 |
| Carbon Tetrachloride | 0.1 | Methylene Chloride | 0.5 |
| Chlorobenzene | 0.5 | Octane | 0.030* |
| Chloroethane | 0.010* | Propylene | 0.040* |
| **Chloroform** | **0.5** | Styrene | 0.5 |
| Chloromethane | 0.020* | 1,1,2,2-Tetrachloroethane | 0.2 |
| Chloromethylbenzene | 0.050* | **Tetrachloroethylene** | **0.17** |
| Chloroprene | 0.5 | Toluene | 0.5 |
| Dibromochloromethane | 0.040* | 1,2,4-Trichlorobenzene | 0.5 |
| 1,2-Dibromoethane | 0.060* | 1,1,1-Trichloroethane | 0.030* |
| *m*-Dichlorobenzene | 0.090* | 1,1,2-Trichloroethane | 0.15 |
| *o*-Dichlorobenzene | 0.090* | **Trichloroethylene** | **0.5** |
| *p*-Dichlorobenzene | 0.091 | Trichlorofluoromethane | 0.020* |
| Dichlorodifluoromethane | 0.030* | Trichlorotrifluoroethane | 0.050* |
| 1,1-Dichloroethane | 0.030* | 1,2,4-Trimethylbenzene | 0.080* |
| 1,2-Dichloroethane | 0.040* | 1,3,5-Trimethylbenzene | 0.080* |
| 1,1-Dichloroethene | 0.020* | **Vinyl Chloride** | **0.11** |
| *cis*-1,2-Dichloroethylene | 0.030* | *m*-,*p*-Xylene | 0.5 |
| *trans*-1,2-Dichloroethylene | 0.020* | *o*-Xylene | 0.5 |

**Bold** indicates required MQO Core Analytes.
Shading indicates other Analytes of Primary Interest to the NATTS Program.
*Risk values are not determined for these compounds. Concentrations are determined following Method TO-15 and STM-D5466.

At least seven (usually seven to10) VOC standards are prepared at the same concentration in separate and individual canisters. A concentration that is one to five times the expected detection limit must 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 must be prepared at a concentration of 0.25 ppbv or lower. Each standard will be analyzed once with an injected volume equivalent to the sample volume analyzed, however, one-half of the standard injected amount can be used to obtain the lower MDL concentrations. The standard deviation for each compound must be calculated for all of the analyses and must 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 must be flagged when the data are reported. All calculated values must be reported.

**Table 4.1-5. Student's t Values at the 99 Percent 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 percent of the total sample number). The RPD between the replicate analyses must be within 25 percent, except with compound concentrations less than five times the MDL for each compound. A replicate

analysis that does not meet the criteria must be reanalyzed. The equation for percent difference is:

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

where:

$X_1$ = first measurement

$X_2$ = second measurement

$X_{avg}$ = average of two measurements.

### 4.1.9.3 Performance Evaluation 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:

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

### 4.1.10 *Quality Control Specifications*

Quality control 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<br>2) Clean ion source and/or quadrupoles |
| Multipoint (at least five) calibration bracketing the expected sample concentrations. | Multipoint calibration: 5 or 6 points, ranging from 0.25 to 15 ppbv At least quarterly or after failure to meet acceptance criteria or after major change in instrumentation. | 1) RSD of response factors ≤± 30%<br>2) RRT for target peaks ± 0.06 RRT units from mean RRT | 1) Repeat an individual standard analysis<br>2) Repeat calibration curve<br>3) Prepare new calibration standards and repeat analysis |

**Table 4.1-6. Summary of Air Toxics TO-15 Quality Control Procedures (Continued)**

| QC Check | Frequency | Acceptance Criteria | Corrective Action |
|---|---|---|---|
| LCS (Second Source Standard) | Following the initial calibration | ± 30% bias from mean response factor from multipoint calibration | 1) Repeat analysis<br>2) Repeat calibration |
| Continuing Calibration Check Frequency | Daily[1] on the days of sample analysis | ± 30% bias from mean response factor from multipoint calibration | 1) Repeat calibration check<br>2) Repeat calibration curve |
| System Blank Analysis | Daily[1] following BFB and calibration check; prior to sample analysis | 1) <0.2 ppbv per analyte<br>2) IS area response ± 40% and IS retention time ± 0.33 min of most recent calibration check | 1) Repeat analysis with new blank canister<br>2) Check system for leaks, contamination<br>3) Reanalyze blank |
| Duplicate and Replicate Analysis | All duplicate field samples | <25% 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 |

[1]Every 24 hours frequency

## 4.2 OVERVIEW OF COMPENDIUM METHOD TO-11A (Carbonyl Compounds)

EPA Compendium Method TO-11A[8] will be applied to the determination of formaldehyde and other carbonyl compounds (aldehydes and ketones) in ambient air. EPA Compendium Method TO-11A[8] utilizes a coated solid adsorbent for collection of carbonyl compounds from ambient air followed by HPLC analysis with ultraviolet (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 percent 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-11A[8] ( http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-11ar.pdf). EPA Compendium Method TO-11A[8] 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.

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 must be less than 0.15 micrograms (μg)/cartridge. For the NATTS Program 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. (See Section 4.2.3.5 for details).

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-11A[8] is used. To eliminate this interference, removal or scrubbing of Ozone ($O_3$) from the sample air stream 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 $O_3$ and the carbonyl compounds and

the duration of sampling. Significant negative interference from $O_3$ has been observed at concentrations of formaldehyde and $O_3$ typical of clean ambient air. Because of these issues, it is required that the $O_3$ interference be removed before the ambient air sample stream reaches the coated cartridge. This removal process entails constructing or purchasing an $O_3$ 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-11A[8] for NATTS Program carbonyl measurements are presented below.

#### 4.2.1.1 Ozone Scrubbers

The EPA has determined through laboratory tests that $O_3$ present in ambient air interferes with the measurement of carbonyl compounds when using EPA Compendium Method TO-11A[8]. Ozone can interfere with carbonyl analyses in three ways:

- The $O_3$ reacts with the DNPH on the cartridge and makes the DNPH unavailable for derivatizing carbonyl compounds;
- The $O_3$ 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 $O_3$ and the carbonyl compounds and the duration of sampling. Carbonyl compound losses have been estimated to be as great as 48 percent on days when the ambient $O_3$ concentration reaches 120 ppbv. Eliminating this measurement interference by removing or scrubbing $O_3$ 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 $O_3$ scrubbers, the denuder $O_3$ scrubber and the cartridge $O_3$ scrubber, have been developed. Both the denuder and cartridge $O_3$ scrubbers use KI as the scrubbing agent. Scrubbing is based on the reaction of $O_3$ with KI, specifically:

$$O_3 + 2I^- + H_2O \rightarrow I_2 + O_2 + 2OH^- \qquad (4.2\text{-}1)$$

where:

$O_3$ = ozone (ambient)

$H_2O$ = 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 Ozone 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. Ozone 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 is recoated with a saturated solution of KI annually, typically consistent with annual re-certification of the sampling system.

The denuder $O_3$ scrubber prepared as described in EPA Compendium Method TO-11A[8] has been found to effectively remove $O_3$ from the air stream for up to 100,000 ppb-hours. Thus, the scrubber is expected to last for 12 months of 24-hour sampling on every sixth day when sampling air with an average $O_3$ concentration of 120 ppbv and considering that $O_3$ is typically not an issue for all sampling events. If sampling frequency is increased, the usable period for the $O_3$ scrubber is proportionately decreased.

The $O_3$ scrubber must be recoated with a saturated solution of KI, or be replaced with a new $O_3$ scrubber annually. To recoat the denuder, the copper tube is filled with a saturated solution of KI in water. The solution will remain in contact with the tube for a few minutes, and then the tube is drained. The tube must 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™ $O_3$ 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 $O_3$ 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 must be followed carefully to ensure timely recoating or replacement.

Denuder Ozone Scrubber Equipment

Figure 4.2-1 presents a cross-sectional view of the denuder $O_3$ scrubber. The scrubber is comprised of the following components:

- Copper tubing. 0.250 in. copper tubing at least 36 in. length, coiled into a spiral approximately 2 to 4 in. diameter; used as the body of the $O_3$ 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 $O_3$ 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. A 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. A Type K active temperature controller is used to maintain the $O_3$ scrubber at 66 °C as referenced by the Type K thermocouple.
- Fittings. Bulkhead unions attached to the entrance and exit of the copper coil are used to allow connection to other components of the sampling system.
- Chassis box. An aluminum box enclosure is used to contain the fittings, coated copper tube, heater, and thermocouple.

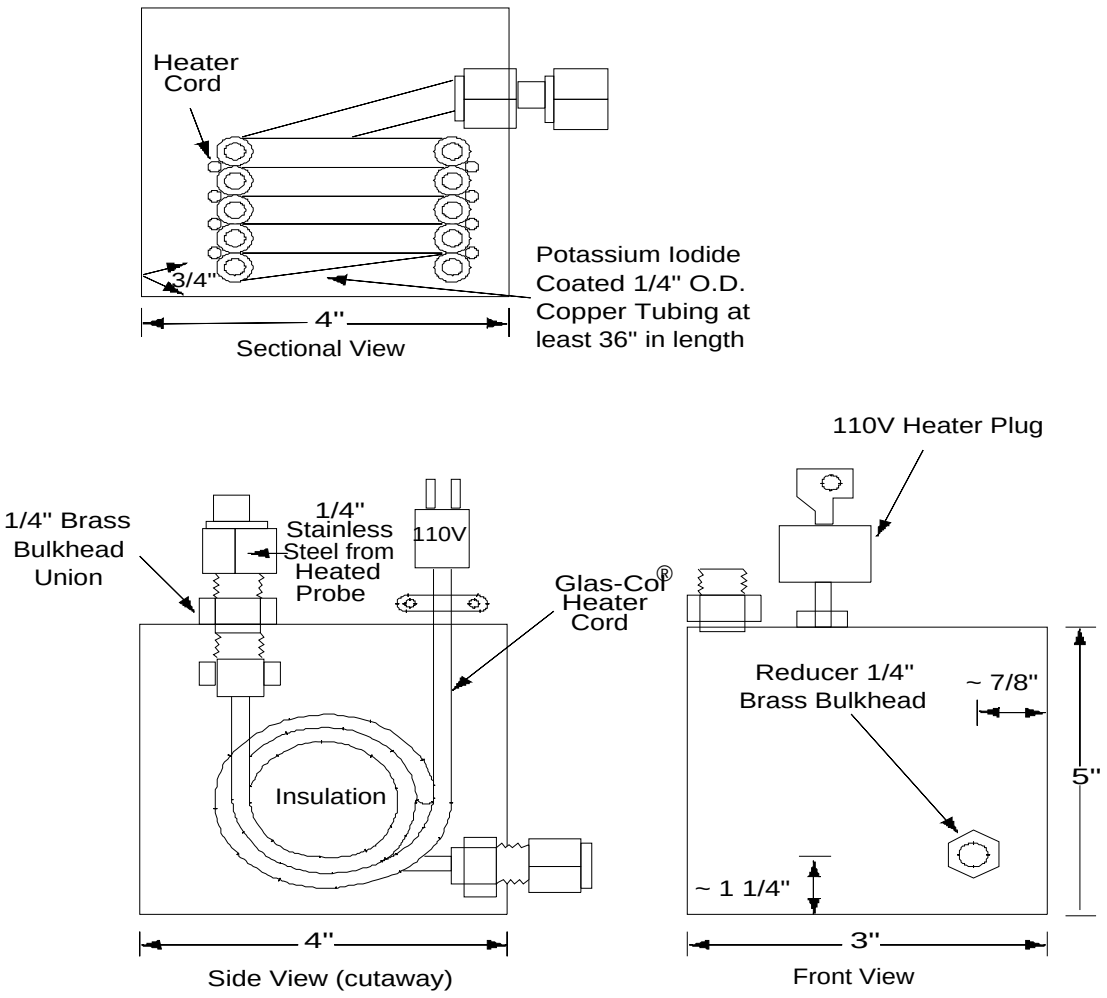


**Figure 4.2-1. Cross-Sectional View of the Denuder Ozone Scrubber**

#### 4.2.1.3 Cartridge Ozone Scrubber

Although allowable under EPA Compendium Method TO-11A[8], use of cartridge $O_3$ scrubbers is not allowed for NATTS.

### *4.2.2 Sample Collection Systems*

Sample collection systems must 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 must be kept as short as possible.

- Ozone scrubber. This is a temperature-controlled denuder scrubber used to remove ambient $O_3$ 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 (±30 percent) over a specific sampling period under conditions of changing temperature (20 to 40 °C) and humidity (0 to 100 percent 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 must be chromatographic-grade stainless steel, and all fittings must be 316-grade stainless steel. Note that if the manifold is heated, stainless steel tubing must 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 annually 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 or nitrogen. Consistent with normal procedures used to collect field samples, a humidified zero air or nitrogen blank is collected through the sampling system to gauge the potential for additive bias. 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). If possible, the zero certification should be completed directly after the annual $O_3$ scrubber recharge or replacement.

#### 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 milliliters (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 must 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 must 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 (or other appropriate) 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 must 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 percent 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 must 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 must 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 will be detailed in a supplied user's manual.

- The overall configuration and components comprising that configuration will allow for simple operation, maintenance, and service of the sample collection system. Materials used in the construction of components of the sample collection system must exhibit nonbiasing characteristics. The components themselves must generally conform to the descriptions presented above. All surfaces that come in direct contact with sampled air must be constructed of glass, stainless steel, Teflon®, or Viton®.

- The sampling system must incorporate or provide for removal of $O_3$ consistently with the denuder $O_3$ scrubber design detailed above.

- The sampling system must incorporate a digital timer or microprocessor event control device. At a minimum this event control device will 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 must incorporate a battery backup system to address power failure situations. Incorporation of a battery backup system will result in fewer invalidated sample collections and a higher sample collection completion rate. The battery backup system will 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 will 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 will 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 will 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-11A[8] 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. Acetonitrile 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 |
| *o*-Tolualdehyde | 529-20-4 |
| *m*-Tolualdehyde | 620-23-5 |
| *p*-Tolualdehyde | 104-87-0 |
| Hexaldehyde | 66-25-1 |
| 2,5-Dimethylbenzaldehyde | 5779-94-2 |

**Bold** indicates required MQO Core Analytes.
[1]Analytical problems similar to those of acrolein are encountered with crotonaldehyde.

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 must be examined closely before extracting. Cartridges that are leaking silica gel must be voided. Cartridges that are dark orange or reddish contain moisture and must 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 must 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-11A[8] is presently unsuitable 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.

#### 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 a LIMS, given an ID number, placed in a sealable bag with the COC and stored in a refrigerator at <4°C until extraction. Extraction must 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 will be HPLC grade, and each must be sonicated or degassed with helium prior to use or run through a comparable system. The HPLC grade water is filtered through a 0.2-μm nylon membrane filter to eliminate microbial growth. Solvent will pump at the desired flow rate of 1 to 2-mL/min for 30 min. Prior to the first injection, system pressure must 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 3.0 μg/mL of each target analyte purchased as a DNPH derivative of the carbonyl compound. These solutions are stable up to six 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 Secondary Source Quality Control (SSQC) standard is also analyzed three times to evaluate precision and to validate each new curve. An SSQC is a standard 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. 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 six 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 must be within 20 percent of the theoretical concentration.

$$\text{Relative Percent Error} = \frac{\text{TLC - OLC}}{\text{TLC}} * 100$$

where:

TLC = theoretical level of concentration

OLC = observed level of concentration

- The SSQC standard must be within 15 percent of target concentrations.
- The intercept must be less than 25mAu 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 is to 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 extracted 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" (COA) accompanies each lot of DNPH-coated, prepacked cartridges. This COA is used as a metric to show that the cartridges were tested and found to be acceptable by the vendor prior to shipment to the laboratory. Independent of the concentrations presented on each COA, three cartridges from each lot are analyzed as laboratory certification blanks to assess whether they meet the acceptance criteria presented below. If the laboratory certification blanks do not meet the specified blank acceptance criteria, the carbonyl tubes must be shipped back to the manufacturer and a new lot requested. For laboratory certification blanks to be acceptable, the following criteria must be met:

- Formaldehyde: < 0.15 micrograms (μg)/cartridge
- Acetaldehyde: < 0.10 μg/cartridge
- Acetone: < 0.30 μg/cartridge
- Others: < 0.10 μg/cartridge.

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

- Formaldehyde: < 0.3 μg/cartridge
- Acetaldehyde: < 0.4 μg/cartridge
- Acetone: < 0.75 μg/cartridge
- Sum of others: < 7.0 μg/cartridge.

If a field blank does not meet the criteria the sampling site is notified so that another field blank can be scheduled. Field blank sampling will continue until the sample meets the acceptance criteria. Field blank data is collected and submitted to AQS. This data is used to assess the potential for field contamination. It is not used to correct regular sampling data in any way.

The following criteria must be met for method blanks:

- Formaldehyde: < 0.15 μg/cartridge
- Acetaldehyde: < 0.10 μg/cartridge
- Acetone: < 0.30 μg/cartridge
- Others: < 0.1 μg/cartridge.

If the method blank fails to meet acceptance criteria, that method blank will be reanalyzed and the laboratory checked for signs of possible contamination.

#### 4.2.3.6 Precision and Accuracy

For 10 percent 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 must agree to within 10 percent for concentrations > 0.5 μg/cartridge and the means of the replicate analyses for the duplicate samples must agree to within 20 percent. If the means of the duplicate samples do not agree to within 20 percent and the replicate analyses are within 10 percent, 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:

$$RPD = \frac{|X1 - X2|}{\bar{x}} \times 100 \qquad (4.2\text{-}3)$$

where:

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

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

$\bar{x}$ = 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 MDL. Seven to 10 separate and individual commercially prepared DNPH-coated, prepacked cartridges are spiked with the standard. All seven to 10 spiked tubes are extracted as explained in Section 4.2.3.3. The measured concentrations are calculated using the calibration curve. The concentration of derivatized aldehyde/ketone in the sample is calculated below:

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

where:

$C$ = concentration of derivatized compound (μg/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. Method detection limits must be calculated in units of ppbv and $\mu g/m^3$ reflecting different collection volumes across the range of 100 L through 2000 L. Table 4.2-3 shows Target MDLs for Carbonyl Compounds.

**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 Method Detection Limits for Carbonyl Compounds for the NATTS Program**

| Analyte | Target Method Detection Limit ($\mu g/m^3$) | MDL* ($\mu g/m^3$) |
|---|---|---|
| **Formaldehyde** | **0.10000** | **0.010** |
| **Acetaldehyde** | **0.10000** | **0.009** |
| Acetone | NA | 0.01** |
| Propionaldehyde | NA | 0.007** |
| Crotonaldehyde | NA | 0.005** |
| Butyr/Isobutyraldehyde | NA | 0.006** |
| Benzaldehyde | NA | 0.005** |
| Isovaleraldehyde | NA | 0.004** |
| Valeraldehyde | NA | 0.005** |
| Tolualdehydes | NA | 0.02** |
| Hexaldehyde | NA | 0.004** |
| 2,5-Dimethylbenzaldehyde | NA | 0.003** |

**Bold** indicates required MQO Core Analytes.
*Can be obtained using a volume of 1000 liters. **Risk values are not determined for these compounds. Concentrations are determined following Method TO-11A.

### 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, the method blanks and the method spikes 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 MDLs. Carbonyl QC procedures are presented in Table 4.2-4.

#### 4.2.3.9 Method Spikes

A MS and MSD, 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 must be within ±20 percent 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.

## 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<br>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 ±20% or less relative error | Check integration, reintegrate or recalibrate |
| | | | Intercept acceptance must be <25 mAu area counts per compound. | 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 ±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 and at least one per batch of 20 samples. | Compounds must be less than values listed:<br>Formaldehyde <0.15 µg/cartridge<br>Acetaldehyde <0.10 µg/cartridge<br>Acetone <0.30 µg/cartridge<br>Others <0.10 µg/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 (Continued)**

| 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:<br>Formaldehyde<br><0.4 µg/mL derivatized<br><0.3 µg/cartridge underivatized<br>Acetaldehyde<br><0.4 µg/mL derivatized<br><0.4 µg/cartridge underivatized<br>Acetone<br><0.6 µg/mL derivatized<br><0.75 µg/cartridge underivatized<br>Others<br><0.10 µg/mL derivatized<br><7.0 µg/cartridge underivatized | If field blank fails, notify site coordinator and schedule another field blank. If no reason for failure is identified, and corresponding sample has high concentration values, field blank subtract that sample only and flag data in report. If sample does not have high values, do NOT blank subtract, but flag data. Additional Field Blanks are collected until the problem is resolved and data is acceptable. |
| 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 |
| MS/MSD | Analyze MS/MSD, using calibration standard | One MS/MSD per batch of 20 samples | 80 to 120% recovery for Formaldehyde and Acetaldehyde and 70 to 130% for all other 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 method, 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 to determine whether reintegration is needed on any peak. If the concentration of an analyte exceeds the linear range of the instrument, the sample may be diluted with ACN, reanalyzed and flagged as diluted, or the sample may be flagged as

out of calibration range. Quantitation is based on raw amounts of analyte in $\mu$g/mL calculated by the data system from the curve. Results in $\mu g/m^3$ are then calculated as described below.

$$\mu g/m^3 = \frac{\text{raw amount } (\mu g/mL) * 5 \text{ (mL)}}{V \text{ (liters)} * 1000 \text{ (liters/m}^3\text{)}} \quad (4.2\text{-}5)$$

where:

5 = extraction volume in mL
V = volume of air collected in liters (local 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 (Trace Metals)

EPA Compendium Method IO-3.5[9] (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. The method involves collection on filters and detection by ICP/MS. The 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. However, only 20 compounds are listed in Method IO3.5[9]. The method, as described below, will be used to report metals for the NATTS Program.

### *4.3.1 General Description of Sampling Method and Analytical Method Requirements/Capabilities*

EPA Compendium Method IO-3.5[9] describes the multielement determination of trace elements by ICP/MS. Ambient air is pulled through filter media using a high or low volume sampler. Particulate phase samples are collected on an 8 in. x 10 in. quartz fiber filter for high

volume sampling, or a 47 mm Teflon® filter for low volume sampling. 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 MS having a minimum resolution capability of 1 amu peak width at 5 percent 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 quartz fiber or Teflon® filter over a 24-hour collection period.

#### 4.3.2.1 Sample Collection Procedure

The metals sample collection is performed using a commercially available high volume sampling system with a 10 µm size-selective inlet [Particulate matter with an aerodynamic diameter ≤ 10 microns ($PM_{10}$) Sample Collection]. The High and Low Volume sampler specifications for a 24 hour sampling period are presented in Table 4.3-1.

**Table 4.3-1. $PM_{10}$ Sample Collection Method Comparison**

| Collection Method | Filter Media | Flow Rate | Total Sample Volume |
|---|---|---|---|
| Low Volume | 47 mm Teflon | 16.7 L/min (Lpm) | 24 $m^3$ |
| High volume | 8 in. x 10 in. Quartz fiber | .13 to 1.70 $m^3$/min (40 to 60 $ft^3$/min) | 1,600 – 2,400 $m^3$ (57,000 – 86,000 $ft^3$) |

The quartz filter is 8 in. x 10 in. and is constructed of spectro-quality grade quartz material with a pH of approximately 7.5. The filters must have a collection efficiency of 99 percent for particles of 0.3 μm in diameter or larger. Each 8 in. x 10 in. filter must have a unique ID number that is a permanent part of the filter. The Teflon® filter is 46.2 mm with a pore size of 2 microns and a filter deposit area of 11.86 $cm^2$. They do not have an associated unique ID number on the filter.

The sampler must be located in an unobstructed area at least 2 meters from any obstacle to airflow. The inlet of the high volume sampler must be positioned in the breathing zone, 1.2 to 3 meters (4 to 10 feet) above ground level. The sampler must be greater than 20 meters from trees or obstructions and must have unrestricted airflow 270 degrees around the sampler inlet. The sampler inlet must be at least 2 meters, but not greater than 4 meters, from a collocated $PM_{10}$ sampler inlet.

Similar to monitoring for other pollutants, optimal placement of the sampler inlet for $PM_{10}$ monitoring must be at breathing height level. However, practical factors such as prevention of vandalism, security, and safety precautions must also be considered when siting a $PM_{10}$ monitor. Given these considerations, the sampler inlet for microscale $PM_{10}$ monitors must be 2 to 7 meters (6.5 to 23 feet) 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 $PM_{10}$ 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 $PM_{10}$ stations must also be 2 to 7 meters above ground level. For middle or larger spatial scales, increased diffusion results in vertical concentration gradients that are not as great as the microscale. Thus, the required height of the air intake for middle or larger scales is 2 to 15 meters (6.5 to 50 feet).

If the sampler is located on a roof or other structure, there must be a minimum of a 2 meter 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 must be placed at least 5 meters 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 must be considered for sampling. Trees provide surfaces for particulate deposition and also restrict airflow. Therefore, the sampler must be placed at least 20 meters from the drip line and must be 10 meters 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 must 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 low and high volume sampler are calibrated using a calibrated orifice transfer standard in accordance with the specifications of EPA Reference Method, *Appendix J to Part 50—Reference Method for the Determination of Particulate Matter as $PM_{10}$ the Atmosphere (Low Volume Method)*. Choose a minimum of three flow rates, spaced over the acceptable flow rate range specified for the method (low volume or high volume) that can be obtained by suitable adjustment of the samplers flow rate. In accordance with the sampler manufacturer's instruction manual, obtain or verify the calibration relationship between the flow rate as indicated by the transfer standard and the sampler's flow indicator response. The differential pressure readings are used to create a curve that establishes the flow characteristics of the sampler.

Following calibration, verify that the sampler is operating at its design flow rate with a clean filter in place. 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 the manufacturer's instruction manual, 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 five 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 five 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.

10. For high volume filters, fold the filter in two onto itself (particulate-sampled sides facing) so that none of the particulate mass is lost. Place the folded filter in an appropriately sized envelope for transport to the laboratory.

11. For low volume filters, place it immediately into its uniquely numbered Petri dish.

### *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 4.3-2.

**Table 4.3-2. 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** |
| Chromium and compounds | 7440-47-3 |
| Cobalt and compounds | 7440-48-4 |
| **Lead and compounds** | **7439-92-1** |
| **Manganese and compounds** | **7439-96-5** |
| Mercury and compounds | 7439-97-6 |
| **Nickel and compounds** | **7440-02-0** |
| Selenium and compounds | 7780-49-2 |

**Bold** indicates required MQO Core Analytes.

#### 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 must 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 must 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 must 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 MS 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 must 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. Internal Standards 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 must 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 $^{40}Ar^{16}O$ on the determination of $^{56}Fe$; $^{38}ArH$ on the determination of $^{39}K$; $^{40}Ar$ on the determination of $^{40}Ca$; $^{40}Ar^{2+}$ on the determination of $^{80}Se$; $^{40}Ar^{35}Cl$ on the determination of $^{75}As$; and $^{40}Ar^{12}C$ 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 $^{40}Ar^{16}O$, 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 nanograms (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. If the filters are only extracted with diluted nitric acid, it would impose fewer mass interferences on the measurement. Certain elements such as antimony, however, will not be stable in a solution containing only nitric acid. In order to recover antimony more efficiently, 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

High Volume ambient air quartz fiber filters (8 in. x 10 in.) should be received folded in half lengthwise with the particulate material inward and with the entire filter enclosed in a protective envelope. Low volume ambient air Teflon® filters (47 mm) should be stored in individual Petri dishes. These filters are stored at approximately 15 to 30 °C until analysis. The maximum sample holding time is usually 180 days.

Cutting Procedure for High Volume Filters

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.

The filters can be extracted using one of three separate techniques: microwave, hot acid digestion, or sonication. After cooling, the digestate is mixed and filtered to remove any insoluble material before analysis.

Digestion Procedure: Microwave Digestion for Ambient Filters

**Note: Nitric and hydrochloric acid fumes are toxic**. Samples must be prepared in a well-ventilated fume hood. Mixing of the acids results in an exothermic reaction; acids should be stirred slowly.

The filter strip is retrieved and placed on its edge in a labeled centrifuge tube with vinyl gloves or plastic forceps. Accordion-fold or tightly roll the filter and place into the lower portion of the centrifuge tube to ensure that the acid volume will cover the entire strip. A laboratory microwave is used to extract the metals with a hydrochloric/nitric acid solution. The samples are cooled, filtered, and water is added to produce a final volume of 20 mL.

Duplicate sample and MS sample frequency is normally one per 20 field samples or a minimum of one per extraction set. Blank filter samples should be digested and analyzed, and extraction blanks should be prepared to ensure low levels of metals in the reagents used.

Digestion Procedure: Hot Acid Digestion for Ambient Filters

The hot acid procedure is used as an alternate when microwave technology is not available. With vinyl gloves or plastic forceps, the filter strip is placed in a 150-mL Griffin beaker; the filter is placed in the lower portion of the beaker to ensure that the acid volume will cover the entire filter. A mixture of diluted nitric and hydrochloric acid is added and the beaker is placed on a hot plate in a fume hood and refluxed for 30 min. Water is added to the cooled sample, and the extract in the beaker is filtered into a 20-mL volumetric flask.

Duplicate sample and MS sample frequency is normally one per 20 field samples or a minimum of one per extraction set. Blank filter samples should be digested and analyzed, and extraction blanks should be prepared to ensure low levels of metals in the reagents used.

Digestion Procedure: Sonication for Ambient Filters

The sonication method is used as an alternative to digesting with both nitric and hydrochloric acid. With vinyl gloves or plastic forceps, the filter (strip for high volume and whole filter for low volume) is placed into the lower portion of a 50 mL centrifuge tube to ensure that the acid volume with cover the entire filter. Diluted nitric acid is added and the tube is placed in a sonicator and extracted for up to two hours. The digestate is filtered and brought to a final volume of 50 mL in a volumetric flask.

Duplicate sample and MS sample frequency is normally one per 20 field samples or a minimum of one per extraction set. Blank filter samples should be digested and analyzed, and extraction blanks should be prepared to ensure low levels of metals in the reagents used.

#### 4.3.3.3 Standard and Quality Control Sample Preparation

Standard stock solutions may be purchased from a commercial source or prepared from ultrahigh-purity grade chemicals or metals (99.99 percent 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.

Internal Standards

Internal Standards 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 one percent volume per volume (v/v) nitric acid. These internal standards are normally added using a peristaltic pump. Concentrations of 200 µg/L are suggested.

Blanks

Four types of blanks are required for this method. A calibration blank establishes the analytical calibration curve and is prepared in the same acid concentration as the samples being analyzed. The method blank (MB) assesses possible contamination from the sample preparation procedure and spectral background. The MB 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 two percent (v/v) nitric acid in deionized water.

Continuing calibration blanks (CCB) are analyzed following each of the continuing calibration verification (CCV) samples.

Tuning Solution

A tuning solution is used to determine instrument performance and verify that the instrument has reached thermal stability. The solution is prepared by mixing beryllium, magnesium, cobalt, indium and lead stock solutions in one percent (v/v) nitric acid to produce a concentration of 100 μg/L of each element. Internal Standards are not added to this solution.

QC Sample

A QC sample is obtained by diluting an appropriate aliquot of a second source standard in one percent (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 five percent 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 five percent.

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. The average of the three integrations should be used for instrument calibration and data reporting.

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 or a minimum of one min. To establish equilibrium, solutions should be aspirated for at least 30 seconds 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. Internal standards 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 it with the solution prior to nebulization using a second channel of the peristaltic pump and a mixing coil. The concentration of the ISs 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 IS 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 measurements of the QC sample exceed ±10 percent 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 percent, analysis of the standard is repeated. If the analyte is again outside the 10 percent limit, the instrument must be recalibrated and the previous 10 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 Quality Control*

Each laboratory analyzing filters following EPA Compendium Method IO-3.5[9] 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 Lot Blank Correction

Quartz filters typically have relatively high background concentrations for some target metals, especially compared to typical ambient concentrations at rural sites. To address this matter, the NATTS Program sanctions lot blank corrections for $PM_{10}$ high-volume sampler, 8 in. x 10 in. quartz filters with the following stipulations:

- Only applies to quartz filters (no blank correction for Teflon®);

- Not required, but acceptable (more of an issue for rural site than urban site).

The procedure for lot blank correction is to analyze five percent (i.e., three of 60 filters per box, taken near the top, middle, and bottom). The average mass (ng) for each target analyte then constitutes that analyte's lot blank value to be subtracted from the corresponding sample values when using filters from that box. The lot blank corrected data must be flagged as such in AQS; the appropriate flag is "CB". Lot blank values (ng) and the blank category ("Lot") must be loaded into AQS.

As the principle purpose of the NATTS network is long-term trends, consistency at each site is paramount. Each site must adopt an all or none approach to $PM_{10}$ quartz filter lot blank correction (i.e., if any year of data is corrected, all other years must likewise be corrected).

#### 4.3.4.2 Precision

For 10 percent 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 ±10 percent, and the means of the replicate analyses for the collocated sample pairs should agree to within ±20 percent. If the collocated sample pairs do not agree to within ±20 percent and the replicate analyses are within ±10 percent, 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:

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

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 $X2$.

#### 4.3.4.3 Method Detection Limits

Method detection limits are determined according to the procedures of 40 CFR Part 136 Appendix B. However, for metals that are measured in the filter blanks at concentrations greater than three times the estimated MDL, seven to 10 replicate blank filter strips should be analyzed to determine the MDL values (from FACA on 40 CFR Part 136, Appendix B found at: http://www.epa.gov/waterscience/methods/det/). If concentrations in the blank filter strips are below the estimated MDL, the filter strips should be spiked and digested filters should be fortified at a concentration of two to five times the estimated MDL. Both procedures should be prepared following the entire analytical method. The minimum MDLs that must be achieved are shown in Table 4.3-3.

**Table 4.3-3. Target Method Detection Limits for EPA Compendium Method IO-3.5**

| Compound | Target MDLs ($\mu g/m^3$) | Hi Vol MDLs* ($\mu g/m^3$) | Low Vol MDLs* ($\mu g/m^3$) |
|---|---|---|---|
| Antimony | NA | 0.00001 | 0.00008 |
| **Arsenic** | **0.0010** | **0.00001** | **0.00002** |
| **Beryllium** | **0.00042** | **0.000002** | **0.00004** |
| **Cadmium** | **0.00056** | **0.00003** | **0.00026** |
| Chromium | NA | 0.00034 | 0.00085 |
| Cobalt | NA | 0.00001 | 0.00002 |
| **Lead** | **0.0010** | **0.00006** | **0.00008** |
| **Manganese** | **0.0010** | **0.00006** | **0.00005** |
| Mercury | NA | 0.00002 | 0.00013 |
| **Nickel** | **0.0021** | **0.00013** | **0.00006** |
| Selenium | NA | 0.00001 | 0.00014 |

**Bold** indicates required MQO Core Analytes.
Shading indicates other Analytes of Primary Interest to the NATTS Program.
*Risk values are not determined for these compounds. Concentrations are determined following Method IO3-5.

Because of the varying concentrations for some compounds in the blank filters (i.e., chromium and lead), it is likely that both of these techniques will be used. The MDL is calculated as follows:

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

where:

$t$ = Student's t value for a 99 percent 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.

All MDL results should be verified using a low level calibration check standard. Method detection limits 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).

#### 4.3.4.4 Quality Control Specifications

Quality Control specifications (QCS) for ICP/MS analysis are summarized in Table 4.3-4.

**Table 4.3-4. Quality Control Specifications for ICP/MS Analysis**

| QC Procedure | Typical Frequency | Criteria |
|---|---|---|
| Initial calibration (IC) | Multipoint calibration daily, with at least 5 calibration points from 0.1 to 2 ng/mL | Correlation coefficient ≥ 0.995 |
| ICV using the QCS | Second source standard following the initial calibration | Recovery 90-110% |
| ICB | Immediately after initial calibration verification | Must be less than MDLs per element |
| ICS | Following the high standard verification every 8 hours and at the end of a run | Recovery from 80 to 120% |
| CCV | Analyzed before the first sample, after every 10 samples and at the end of the run | Recovery 90-110% |
| CCBs | Analyzed following each continuing calibration verification | Must be less than MDLs per element |
| Reagent blank (RB) or MB | 1 per 20 samples, a minimum of 1 per batch | Must be less than MDLs per element |
| 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 |
| MS/MSD | 1 per 20 samples per sample batch | Percent recovery of 75 to125% |
| 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.

| *Instrument* | *VG PlasmaQuad Type I* |
|---|---|
| Plasma forward power | 1.35 kW |
| Coolant flow rate | 13.5 Lpm |
| Auxiliary flow rate | 0.6 Lpm |
| Nebulizer flow rate | 0.86 Lpm |
| Solution uptake rate | 0.6 mL/min |
| Spray chamber temperature | 15 °C |
| | |
| *Data Acquisition* | |
| Detector mode | Pulse counting |
| Replicate integrations | 3 |
| Mass range | 8 to 240 amu |
| Dwell time | 50 microseconds |

| | |
|---|---|
| Number of MCA channels | 1 |
| Number of scan sweeps | 60 |
| Total acquisition time | 5.5 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 integration considered to be a statistical outlier is 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 seconds 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, flagging concentrations reported below the determined MDL. Reported values should be calibration and method 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 when 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 OVERVIEW OF EPA METHOD FOR HEXAVALENT CHROMIUM

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 $Cr^{6+}$, speciation of chromium must be performed to identify the presence of the hexavalent state. The analysis of $Cr^{6+}$ 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 has been modified and approved for use by the EPA in a Standard Operating Procedure for the Determination of Hexavalent Chromium In Ambient Air Analyzed By Ion Chromatography (IC)[11].

The method determines $Cr^{6+}$ 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 IC using a system comprised of a guard column, an analytical column, a post-column deriviatization module, and a ultraviolet-visible (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. This method, as described below, will be used to report Hexavalent Chromium for the NATTS Program.

### *4.4.1 Hexavalent Chromium Sample Collection*

A $Cr^{6+}$ 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 samples can be collected using two types of sampling system configurations. The first configuration uses a pre-loaded filter head. The second configuration has the filter prepared and sent to the field in a Petri dish for loading. 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 (DI) 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 4.4.1.3) 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, including funnel, or filter provided in the Petri dish (used in the second sampling methodology), and field data sheet are placed in a plastic shipping container. The shipping container is placed in a cooler with Blue Ice and driven to the field, or shipped 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 a flow control device 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 must be kept as short as possible to minimize the system residence time. If a rotameter is used, it must be calibrated in the field to determine true readings. Figure 4.4-1 presents the $Cr^{6+}$ sampling system configuration using a flow rotameter.

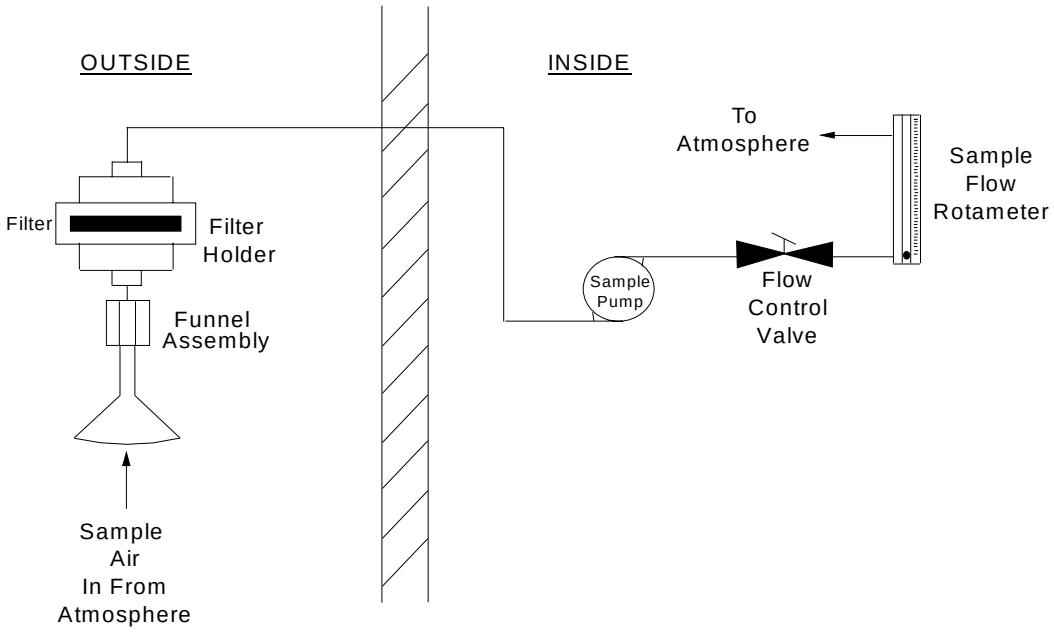


**Figure 4.4-1. A Typical Hexavalent Chromium Sampling System**

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. After sampling has ended if the ambient temperature is predicted to be greater than 50 °F, the sample must be recovered the day after a collection event ends. If the ambient temperature is predicted to be less than 50 °F, the sample can be recovered within 72 hours after a collection event ends. Use vinyl gloves to remove each sample filter (i.e., one at a time), and cap both ends. Sample event

number, sample type, location, sample flow rate or total flow, and collection date must 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 either driven or through the use of an overnight service.

6. Upon receipt at the laboratory, the sample is logged into a laboratory tracking system, and the plastic shipping container is placed in a freezer until it is ready for sample preparation and analysis.

It is imperative that the sample recovery is performed the day after an event if the ambient temperature is greater than 60° F, regardless of weekends or holidays. If the ambient temperatures are less than 60° F, the filters can stay in the sampler for up to four days after collection has ended.

#### 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 percent Nitric acid bath for a minimum of 18 hours and a maximum of 24 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 must be discarded. The filters are then removed to Teflon® coated or a plastic net in the glove box and nitrogen-purged for seven hours until dried. The filters are then soaked in the Sodium Bicarbonate impregnating solution [0.12 molar (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 10 percent Nitric and 0.12 M Sodium Bicarbonate solutions used to prepare the filters must be prepared fresh before use.

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 for seven hours until dried. The

filters will curl when completely dried. Prepared filters are placed in separate petri dishes labeled with preparation date, initials of the preparer, and given a unique lot number. The filters, in individual petri dishes, can be stored in the freezer until ready for field deployment for up to three 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 available.

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 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 $Cr^{6+}$.

- 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 millimolar (mM) Ammonium hydroxide - In a 2 L volumetric flask, dissolve 66 grams (g) of Ammonium sulfate in approximately 1 L DI water. Add 7 mL of Ammonium hydroxide and dilute to 2 L with DI water.

- Post-column Derivatizing Reagent (PDR). In a 1 L volumetric flask, dissolve 0.5 g of 1,5-Diphenylcarbazide in 100 mL of HPLC-grade Methanol. Sonicate until DPC goes into solution. Add approximately 500 mL of DI water. Add 28 mL of 98 percent 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, add 5.0 g of Sodium Bicarbonate. Dilute to 500 mL with DI water. Sonicate for approximately 20 min, or until dissolved.

- 20 mM Sodium Bicarbonate Solution. In a 1 L volumetric flask, dissolve 1.68 g of Sodium Bicarbonate in approximately 500 mL DI water. Sonicate for approximately 20 min, or until dissolved. Dilute to 1 L with DI water.

- Primary Stock Solutions. A primary stock solution 1000 µg/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 separate source primary stock solutions should be prepared and/or obtained. One is to be used exclusively for the calibration standards and the other for 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 LCS/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.

  - 0.1 ng/mL $Cr^{6+}$ - Dilute 10 µL of the working stock solution to 100 mL using the 20 mM Sodium Bicarbonate in DI water solution.

  - 0.2 ng/mL $Cr^{6+}$ - Dilute 20 µL of the working stock solution to 100 mL using the 20 mM Sodium Bicarbonate in DI water solution.

  - 0.5 ng/mL $Cr^{6+}$ - Dilute 50 µL of the working stock solution to 100 mL using the 20 mM Sodium Bicarbonate in DI water solution.

  - 1.0 ng/mL $Cr^{6+}$ - Dilute 100 µL of the working stock solution to 100 mL using the 20 mM Sodium Bicarbonate in DI water solution.

  - 2.0 ng/mL $Cr^{6+}$ - 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 ICV is run immediately following the calibration standards and a 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 IC is equilibrated, calibrated and ready to perform the analysis when extraction of the filters is finished.

Sample Preparation

The glassware is washed and rinsed with distilled DI water 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.

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. Extracts are stable for up to 24 hours in the refrigerator, however the samples should be analyzed immediately after preparation.

Typical Analytical System Operating Conditions

To perform analysis of exposed filters for $Cr^{6+}$, an IC consisting of the following modular units is required:

*Instrument Information*

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

The analysis is performed by IC with postcolumn deriviatization using DPC. In the analysis, $Cr^{6+}$ exists as chromate due to the near-neutral pH of the eluent. After separation through the column, $Cr^{6+}$ 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 should be NIST certified, when available.

#### 4.4.2.5 Preparation of the Ion Chromatography Analytical System

The analytical system must be characterized and optimized prior to operation. Parameters as retention times, identification of coeluting peaks, and MDLs 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 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 five min.
- 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 $Cr^{6+}$. An acceptable coefficient of correlation is $\geq 0.995$. 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 instrument's 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).

The Coefficient of Correlation, R, is the square root of R² 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 ±10 percent 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, ICV and ICB samples have met acceptance criteria. 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 ICV after the calibration. Analyze a CCV after every 10 samples and at the end of the sequence to verify instrument calibration. If the calibration check response is not within ±15 percent of expected response, determine the cause (85-115 percent recovery). The instrument may be malfunctioning, the check standard may not be prepared correctly, or the instrument may need to be recalibrated. The ICV and CCV percent recovery is calculated below:

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

- Initial Calibration Blank/Continuing Calibration Blank. Analyze an ICB after the ICV. Analyze a 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. 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 90-110 percent 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 ±10 percent.

- 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 nine 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 percent methanol and 1 N Sulfuric acid).
- Detection Wavelength – 530 nm.
- Sample Volume – 830 µL.

The $Cr^{6+}$ 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. $Cr^{6+}$ concentration in units of ng/mL are calculated below:

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

To calculate the concentration of $Cr^{6+}$ in the air sampled, the volume of air sampled must be known.

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

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 analytical results to reflect

actual sample concentrations. 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

Method detection limits must be determined annually according to the procedures from 40 CFR Part 136 Appendix B, with 99 percent confidence level and a standard deviation estimate having n-1 degrees of freedom. **The target MDL for $Cr^{6+}$ is 0. 08 ng/$m^3$, however concentrations have been determined below 0.0043 ng/$m^3$ following this method**. Comparability of data reported is essential at the low levels of hexavalent chromium detected in the ambient air.

At least seven (usually seven to 10) separate and individual filters are prepared and spiked at the same concentration. Filters are spiked at a level of two to five times the estimated MDL. All seven to 10 filters are then extracted and analyzed. 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 Percent 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 |

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 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 percent of the total sample number per year).

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

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

Where:

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

### 4.4.2.12 Quality Control Specifications

Quality control 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 | Multipoint calibration daily with at least 5 calibration points from 0.1 to 2 ng/mL | Correlation coefficient >0.995 | 1) Repeat analysis of calibration standards.<br>2) Reprepare calibration standards and reanalyze. |
| ICV | Second source standard, following the initial calibration | Recovery 90-110% | 1) Repeat analysis of calibration check standard<br>2) Repeat analysis of calibration standards<br>3) Reprepare calibration standards and reanalyze |
| ICB | One per Batch, following the ICV | Below MDL | 1) Reprepare blank and reanalyze.<br>2) Correct contamination and reanalyze blank.<br>3) Flag data of all samples in the batch. |
| CCV | Every 10 samples | Recovery 90-110% | 1) Repeat analysis of CCV.<br>2) Reprepare CCV.<br>3) Flag data bracketed by unacceptable CCV. |
| Laboratory Control Sample | One per 10 samples | Recovery 90-110% | 1) Reanalyze.<br>2) Reprepare spike and reanalyze.<br>3) Flag data of all samples since the last acceptable spike. |
| Collocate Sample and Replicate Analysis | Collocate and/or Replicate samples analyses | RPD < 20% for concentrations greater than 5 x the MDL. | 1) Check integration<br>2) Check instrument function<br>3) Flag samples |
| CCB | After every CCV and at the end of the sequence | Below MDL | 1) Reanalyze.<br>2) Reprepare blank and reanalyze.<br>3) Correct contamination and reanalyze blank.<br>4) Flag data of all samples in the batch. |

## 4.5 OVERVIEW OF EPA COMPENDIUM METHOD TO-13A

EPA Compendium Method TO-13A[12] (http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-13ar.pdf)[13] and ASTM 6209-98 sample collection procedures will be used to collect samples and analyze samples for PAHs in ambient

air as required for the NATTS Program. Although the ASTM Method adds three extra PAHs to the TO-13A compound list, the overall procedures do not differ. Method TO-13A[12] and ASTM D 6209-98 are used to prepare and analyze ambient air samples collected on a filter and polyurethane foam (PUF)/XAD-2® sorbent. During sample preparation, the filter and the sorbent are extracted together because of the postcollection volatilization distributes PAHs between the particulate phase (collected on the filter) and the gaseous phase (collected on the PUF/XAD-2®). This method, as described below, will be used to report PAHs for the NATTS Program.

### *4.5.1 Polycyclic Aromatic Hydrocarbons Sample Collection*

Within the category of SVOCs, 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. Polycyclic aromatic hydrocarbons 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. Polycyclic aromatic hydrocarbons generally occur as complex mixtures rather than 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 GC/MS SIM mode. EPA Compendium Method TO-13A,[12] "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 available on-line at www.epa.gov/ttn/amtic/airtox.html; the specific location of Compendium Method TO-13A[12] is www.epa.gov/ttn/amtic/files/ambient/airtox/to-13arr.pdf. The ASTM D 6209-98, "Standard Test Method for Determination of Gaseous and Particulate Polycyclic Aromatic Hydrocarbons in Ambient Air (Collection on Sorbent-Backed Filters with Gas Chromatographic/Mass

Spectrometric Analysis)", is included in the Atmospheric Analysis ASTM Standards on-line at http://www.astm.org/Standards/atmospheric-analysis-standards.html.

Polycyclic aromatic hydrocarbons 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-13A[12] and ASTM D 6209-98 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 sorbent[14-19]. 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-13A[12] and ASTM D 6209-98 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 $m^3$/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 XAD-2® cartridge, which provides for efficient collection of most PAHs involving three aromatic rings or higher.

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-13A[12] and ASTM D 6209-98 are 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 using SIM detection. The use of GC/MS (SIM) 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[19,20] 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. Polyurethane foam cartridges, however, are easier to handle in the field and maintain better flow characteristics during sampling. A PUF/XAD-2® combination allows the best combined collection efficiency.

Filters and PUF/XAD-2® cartridges are cleaned in solvents and vacuum dried; however, PUF and XAD-2® can also be purchased precleaned. The filters and PUF/XAD-2® cartridges are stored in screw-capped jars wrapped in aluminum foil (or otherwise protected from light) before careful installation on the sampler. Approximately 200 to 300 $m^3$ of air is drawn through the filter and PUF/XAD-2® cartridge using a high volume flow rate air sampler or equivalent. The amount of air sampled through the filter and PUF/XAD-2® cartridge is recorded, and the filter and cartridge are placed in an appropriately labeled container and shipped along with COC forms to the analytical laboratory for analysis.

The filters and PUF/XAD-2® cartridges are extracted with the appropriate solvent and prepared 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 the Accelerated Solvent Extraction (ASE) System may be used if performance equivalent to standard extraction procedures is demonstrated. The ASE allows automated extraction using a specialized oven design that ensures uniform heating and control of temperature, which ensures uniform extraction from cell to cell and batch to batch.

#### 4.5.1.1 Sampling Equipment and Materials

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 200 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.

- PUF plugs. The PUF plug is constructed of 3-inch thick sheet polyethane with a density of 0.022 g/cm$^3$. The PUF plug has an outside diameter of approximately 2 3/8 inches, or is approximately 1/8-in. larger in diameter than the opening in the glass sample cartridge.

- XAD-2® Resin. XAD-2® resin is a styrene-divinylbenzene polymer. Fifteen grams of XAD-2® is used for each sampling episode.

- 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/XAD-2® plug. The extra course glass frits should be used to increase the pore size and overall flow allowed through the cartridge during sampling.

#### 4.5.1.2 Sample Collection Procedures

The sampler must 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 must stretch 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 must be done in a controlled environment to minimize contamination.

Solvent must be allowed to evaporate before the PUF/XAD-2® 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.[12] and ASTM D 6209-98. 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/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 PUF/XAD-2®. The PUF/XAD-2® cartridge is then removed from the high volume sampler and transported to the laboratory.

### *4.5.2 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[12] and ASTM D 6209-98.

#### 4.5.2.1 Interferences

Method interferences may arise from contaminants in solvents, reagents, glassware, and other sample processing hardware that result in discrete artifacts and/or elevated baselines in the ion profiles. All of these materials must routinely demonstrate that it is free from contaminants under the conditions of the analysis by analysis of laboratory reagent blanks (i.e., Method Blanks).

Matrix interferences may be caused by contaminants that are co-extracted from the sample. Additional cleanup of sample extracts by column chromatography may be required.

During sample transport and analysis, heat, $O_3$, $NO_2$, and UV light may cause sample degradation. Incandescent or UV-shielded light must be used in the laboratory during analysis. During transport, field samples must be shipped back to the laboratory chilled (~4°C) using blue ice.

#### 4.5.2.2 Preparation of Reagents and Materials

- Glassware – All glassware must be carefully cleaned before use. Glassware must 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 must be washed carefully using laboratory detergent and hot water, rinsed with tap water, then rinsed with reagent water. The glassware must then be drained dry and heated in a muffle furnace at 400°C for four hours. After drying and rinsing, glassware must be sealed and stored in a clean environment to prevent contamination. Glassware must be stored inverted or capped with solvent-rinsed aluminum foil. **Note: Volumetric glassware must not be heated in a muffle furnace.** Volumetric glassware must be rinsed with chromatographic-grade methylene chloride.

- Solvent and materials - All chemicals, reagents and standards purchased for analysis will be inspected by the requestor to verify the material is received as ordered and meets the method requirements.

- Quartz filters – The quartz filters are baked at 400°C for five hours before use and stored in a clean container prior to shipment to the field.

#### 4.5.2.3 Preparation of a Sampling Cartridge

The PUF plugs are 6.0 cm in diameter, cylindrical plugs cut from 3 in. sheet stock. The PUF plugs are purchased pre-cleaned. They are cut in half equally and half of the PUF plug is fit, with slight compression, in the glass sampling module supported by the glass frit. The module containing half of the PUF plug is then placed on a balance and tared. Then 15g of XAD-2® is added to the module and the other half of the PUF plug is placed on top such that it compresses the XAD-2® resin between the two halves of the PUF plug. The compression of the PUF is enough force to hold the XAD-2® in place during sampling.

The sampling module containing the pre-cleaned PUF and XAD-2® resin is wrapped in aluminum foil, placed in a cleaned labeled glass or plastic shipping container, and sealed with Teflon tape.

Immediately prior to field deployment, the field surrogate compounds (fluoranthene-$d_{10}$ and benzo(a)pyrene-$d_{12}$) are spiked in the center of the PUF cartridge using a microsyringe. The spike consists of 100 microliters (µL) of a 10 µg/mL solution of the surrogate compounds to yield a final amount of 1 µg of each compound.

#### 4.5.2.4 Reagents

Reagent and Standard containers used to store prepared solutions will be labeled with expiration date and preparation staff initials.

- Sodium sulfate - anhydrous (ACS) - Granular (purified by washing with hexane followed by heating at 400 °C for 4 hours in a shallow tray).
- Nitrogen - High purity grade, best source
- Toluene - High purity, best source
- Helium - Ultra high purity, best source
- Native and Isotopically-Labeled PAH Isomers for Calibration and Spiking Standards

Isotopically labeled standards are available from Cambridge Isotopes; native compounds, best source. Prior to sampling, the cartridges are spiked with field surrogate compounds.

- Decafluorotriphenylphosphine

  A standard solution containing 25 ng/µL of DFTPP in methylene chloride must be purchased or prepared. This standard will verify the mass spectrometer tune.

#### 4.5.2.5 Stock Solutions

Stock solutions of most of the native PAH can be purchased as concentrated combined solutions, best source. Stock PAH standard solutions must be replaced after one year or sooner if comparison with quality control check samples indicates a problem.

- Secondary dilution standards

  Using stock standard solutions, prepare secondary dilution standards in either singly or as a composite. Secondary dilution standards must be stored with minimal head space and should be checked frequently for signs of degradation or evaporation.

- Surrogate Standards

  The field surrogate standards used for Method TO-13A[12] and ASTM D 6209-98 are fluoranthene-$d_{10}$ and benzo(a)pyrene-$d_{12}$, and the laboratory surrogate standards are fluorene-$d_{10}$ and pyrene-$d_{10}$. The field surrogate standards are spiked onto the sorbent sampling medium prior to shipment to the field. The laboratory surrogate standards are spiked onto the sorbent immediately prior to extraction.

- Internal Standards

  The ISs used for Method TO-13A[12] and ASTM D 6209-98 are naphthalene-$d_{10}$, acenaphthene-$d_{10}$, phenanthrene-$d_{10}$, chrysene-$d_{10}$, and perylene-$d_{12}$.

- Calibration Standards

  Calibration PAH standards can be generated from the stock PAH standard using serial dilution utilizing the following equation:

$$C_1V_1 = C_2V_2$$

where:

$C_1$ = Concentration of stock PAH standards, ng/µL
$V_1$ = Volume of stock PAH standard solution taken to make PAH calibration standards, µL
$C_2$ = Final concentration of PAH calibration standards, ng/µL
$V_2$ = Final volume diluted to generate PAH calibration standards, µL.

Using the above equation, a series of PAH calibration standards can be prepared over the range 0.10 ng/µL to 2.00 ng/µL (0.10, 0.20, 0.50, 1.5, and 2.0 ng/µL).

- Calibration Verification Standards

  The calibration verification standards must be prepared at a concentration near the mid-point of the initial calibration range from the secondary dilution of stock standards or from a pre-mixed certified solution from a second source.

  NOTE: All target analytes for a particular analysis will be included in the initial calibration and calibration verification standard(s). No quantitative result will be reported for a target analyte that was not included in the calibration standard(s).

- Laboratory Control Sample

  The LCS consists of an Analytical Comparison Exchange Standard spiked into the PUF matrix prior to extraction.

Great care must be taken to maintain the integrity of all standard solutions. All standards in hexane must be stored at -10°C or less, in amber bottles with PTFE-lined screw caps.

### 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 column (30-m × 0.32-mm i.d.) cross-linked 5% phenyl methyl silicone, 1.0-µm film thickness (or equivalent) may be used (i.e., J&W DB-5). The GC is coupled directly to the ion source of the MS. The MS 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 MS must be capable of producing a mass spectrum for DFTPP that meets the criteria in Table 4.5-2 when 1 µL of the GC/MS tuning standard (50 ng DFTPP on-column) is injected through the GC.

**Table 4.5-1. Decafluorotriphenylphosphine: 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 |
| 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 |

### *4.5.3 Sample Extraction, Concentration and Cleanup*

Field samples must be stored and shipped in coolers using Blue Ice chilled (<4 °C) until the samples are received at the analytical laboratory. After receipt, the samples must be refrigerated at 4 °C. Samples must be extracted within 14 days after sampling and analyzed within 40 days after extraction.

Sample can be extracted using Soxhlet extraction procedure of using an Automatic Solvent Extracting procedure.

#### 4.5.3.1 Soxhlet Extraction Procedure

A Soxhlet extraction is performed using approximately 700 mL of 10 percent diethyl ether in hexane, with the sorbent and filter extracted together in the Soxhlet extractor; the extractor must 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 must range from 60 to 120 percent. The extractor is allowed to cool and is then disassembled. The extract is dried by passing it through a drying column containing approximately 10 g of cleaned ACS 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 MS 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[12] and ASTM D 6209-98. 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.

#### 4.5.3.2 Automatic Solvent Extraction Procedure

Sample extraction can be performed using a Dionex ASE 300 extractor. The extraction cell is assembled, and the filter, sorbent and a filler layer of Ottawa Sand are placed into the extraction cell where they will be extracted together using 25 percent toluene in hexane. Prior to extraction, laboratory surrogate standards (fluorene-$d_{10}$ and pyrene-$d_{10}$) are added to each sample, blank, and MS sample to monitor for unusual matrix effects and sample processing errors. The solvent bottles in the Solvent Controller should be filled with the appropriate solvents. The same extraction method can be used for all TO-13A[12] and ASTM D 6209-98 extractions on the Dionex ASE 300. At the end of the extraction, the extracted samples in the 250mL sample collection bottles must be capped and placed into a refrigerator until sample

concentration. Sample concentration can be performed using a RapidVap®. The RapidVap® concentrates sample extracts using nitrogen blowdown in a heated water bath. During concentration, the sample tubes are gently swirled to prevent loss of target compounds on the tube walls. The RapidVap® can be programmed for use with many different solvents to reach various final volumes dictated by the analysis method.

#### 4.5.3.3 Sample Cleanup

If the extract is cloudy, impurities may be removed by solid phase extraction using activated silica gel according to the procedures in EPA Compendium Method TO-13A[12] and ASTM D 6209-98. For most ambient air matrices, cleanup procedures are not required.

### *4.5.4 Initial Calibration*

Prior to the analysis of blanks, LCSs, and samples and after tuning criteria have been met, the GC/MS system will be calibrated at a minimum of five concentrations to determine instrument sensitivity and the linearity of the GC/MS response for the compounds of interest and surrogate compounds. A multipoint calibration must be performed when the analysis is set up, when the laboratory takes corrective action, or if the continuing calibration acceptance criteria have not been met. Ion source cleaning or repair or column replacement may also require repeating the multipoint calibration.

The following procedure is performed to calibrate the GC/MS system:

- Set up the GC/MS system according to the parameters listed above;
- Allow all spiking solutions, sample extracts, calibration standards (CALs), and blanks to come to ambient temperature (~ 1 hr) before analysis.
- Verify that tuning criteria have been met;
- Prepare five calibration standards containing the compounds of interest, internal standards, and surrogate compounds according to the following concentrations:
    - CAL1, 0.10 ng/µL;
    - CAL2, 0.20 ng/µL;
    - CAL3, 0.50 ng/µL;

- CAL4, 1.00 ng/µL;
- CAL5, 2.00 ng/µL.
- Surrogate compounds, 0.10, 0.20, 0.50, 1.00, and 2.00 ng/µL;
- Internal standards, 0.50 ng/µL. Internal standards are added immediately before analysis.

Calibrate the GC/MS by injecting 1.0 µL of each calibration standard. Calibrate the GC/MS system in the SIM mode, using the quantitation ions presented in Table 4.5-3 for each compound.

**Table 4.5-2. Initial Calibration Criteria**

| Compound | Primary Quantitation Ion | Secondary Quantitation Ions |
|---|---|---|
| **Internal Standards** | | |
| Naphthalene-$d_8$ | 136 | 68, 137 |
| Acenaphthene-$d_{10}$ | 164 | 162, 165 |
| Phenanthrene-$d_{10}$ | 188 | 94, 189 |
| Chrysene-$d_{12}$ | 240 | 120, 241 |
| Perylene-$d_{12}$ | 264 | 260, 265 |
| **Laboratory Surrogate Compounds** | | |
| Fluorene-$d_{10}$ | 176 | 88, 177 |
| Pyrene-$d_{10}$ | 212 | 106, 213 |
| **Field Surrogate Compounds** | | |
| Fluoranthene-$d_{10}$ | 212 | 106, 213 |
| Benzo(a)pyrene-$d_{12}$ | 264 | 132, 265 |
| **Analytes** | | |
| Acenaphthene | 154 | 153, 152 |
| Acenaphthylene | 152 | 151, 153 |
| Anthracene | 178 | 89, 179 |
| Benz(a)anthracene | 228 | 114, 229 |
| Benzo(a)pyrene | 252 | 253, 126 |
| Benzo(e)pyrene | 252 | 253, 126 |
| Benzo(b)fluoranthene | 252 | 253, 126 |
| Benzo(g,h,i)perylene | 276 | 138, 277 |
| Benzo(k)fluoranthene | 252 | 253, 126 |
| Chrysene | 228 | 114, 229 |
| Coronene | 300 | 150, 301 |
| Cyclopental[cd]pyrene | 226 | 113, 227 |
| Dibenz(a,h)anthracene | 278 | 139, 279 |
| Fluoranthene | 202 | 101, 203 |
| Fluorene | 166 | 165, 167 |

**Table 4.5-2. Initial Calibration Criteria (Continued)**

| Compound | Primary Quantitation Ion | Secondary Quantitation Ions |
|---|---|---|
| 9-Fluorenone | 180 | 152, 181 |
| Indeno(1,2,3-cd)pyrene | 276 | 138, 227 |
| Naphthalene | 128 | 129, 127 |
| Perylene | 252 | 253, 126 |
| Phenanthrene | 178 | 179, 89 |
| Pyrene | 202 | 101, 203 |
| Retene | 219 | 234, 205 |

Secondary ion(s) are to be used for quantitation only in the event of matrix interferences with the primary ions. If secondary ion quantitation is used, calculate a RRF using the area response for the most intense secondary ion that is free of interferences and document the reasons for the use of the secondary ion.

Calculate relative response factors for each compound of interest using the equation below. The RRF is calculated as follows:

$$RRF = [A_s \times C_{is}]/[A_{is} \times C_s]$$

where:

$A_s$ = Peak area for the characteristic ion of the analyte or surrogate

$A_{is}$ = Peak area for the characteristic ion of the internal standard

$C_s$ = Concentration of the analyte or surrogate

$C_{is}$ = Concentration of the internal standard.

Using the relative response factors from the initial calibration, the data system calculates the percent relative standard deviation for all compounds of interest. The following criteria presented in Table 4.5-4 must be achieved for an acceptable calibration curve. The ASTM method includes no minimum RRF criteria, therefore none are listed for the ASTM compounds.

**Table 4.5-3. Relative Response Factors and Acceptance Criteria**

| Compounds of Interest | Minimum RRF | Maximum % RSD | Maximum % Difference |
|---|---|---|---|
| Naphthalene | 0.700 | 30 | 30 |
| Acenaphthylene | 1.300 | 30 | 30 |
| Acenaphthene | 0.800 | 30 | 30 |
| Fluorene | 0.900 | 30 | 30 |
| Phenanthrene | 0.700 | 30 | 30 |
| Anthracene | 0.700 | 30 | 30 |
| Fluoranthene | 0.600 | 30 | 30 |
| Pyrene | 0.600 | 30 | 30 |
| Benz(*a*)anthracene | 0.800 | 30 | 30 |
| Chrysene | 0.700 | 30 | 30 |
| Benzo(*b*)fluoranthene | 0.700 | 30 | 30 |
| Benzo(*k*)fluoranthene | 0.700 | 30 | 30 |
| Benzo(*a*)pyrene | 0.700 | 30 | 30 |
| Indeno(1,2,3-*cd*)pyrene | 0.500 | 30 | 30 |
| Dibenz(*a,h*)anthracene | 0.400 | 30 | 30 |
| Benzo(*g,h,i*)perylene | 0.500 | 30 | 30 |
| Perylene | 0.500 | 30 | 30 |
| Coronene | 0.700 | 30 | 30 |

The relative retention times for each of the compounds of interest and surrogates at each calibration level must be within ± 0.06 relative retention time units of the mean relative retention time for that compound.

Calibration Verification

Prior to the analysis of samples and blanks and after tuning criteria have been met, the initial calibration of the GC/MS system must be checked by analyzing a continuing calibration standard (CAL3) to ensure that the GC/MS system continues to meet sensitivity and linearity requirements of Method TO-13A[12] and ASTM D 6209-98. The RRF for each compound of interest and surrogate compound must be ≥ the minimum acceptable response factor and the percent difference between the measured RRF and the mean RRF from the calibration curve must be within 30 percent. If the criteria for percent difference are not met for the compounds of interest or the surrogate compounds, remedial action must be taken and re-calibration may be

necessary. The only exclusion from the RRF criteria are the ASTM only compounds. There is no minimum RRF criteria listed in the ASTM method and no research has been done to determine the appropriate minimum RRF.

### *4.5.5 Analysis of Samples*

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 SIM to monitor the compounds of interest at the highest possible level of sensitivity. Selected ion monitoring monitors only the specified ions; the ability to characterize other compounds is precluded. The GC/MS is tuned using a 5-ng/µL 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 MS must be tuned to maximize the signal for the DFTPP ions above mass 150. The MS must 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 must be established with the highest possible sensitivity for the high masses. The stability of this tune must 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 (approximately 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 GC, 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 ≥ 20 percent 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 must 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:

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

where:

*Concentration* = concentration of the compound of interest, ng/std $m^3$

$A_x$ = 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

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

$V_i$ = volume of air sampled, std $m^3$

$V_t$ = 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 Determination of Method Detection Limits*

As with PAH 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)/µL, the analyst can make some estimate of MDLs from this standard.

— Determine a spiking level for the sorbent matrix. Seven to 10 separate and individual sorbent media must 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/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 100 to 250 pg/µL. Surrogate compounds and internal standards 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 percent confidence level with n - 1 degrees of freedom. The Student's t values at the 99 percent confidence level are shown in Table 4.5-5.

**Table 4.5-4. Student's t Values at the 99 Percent 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-13A[12] PAH analytes is shown in Table 4.5-6. Target detection limits are set using the screening approach from "A Preliminary Risk-Based Screening Approach for Air Toxics Monitoring Data Sets" (EPA-904-B-06-001, Feb 2006, V1.2).

**Table 4.5-5. Target Method Detection Limits for EPA Compendium Method TO-13A Analytes: Extraction from Spiked PUF**

| Analyte | Target MDL ($\mu g/m^3$) | MDL* ($\mu g/m^3$) |
|---|---|---|
| Acenaphthene | 0.00010 | 0.00004 |
| Acenaphthylene | 0.00010 | 0.00005 |
| Anthracene | 0.00010 | 0.00005 |
| Benz(a)anthracene | 0.00910 | 0.00006 |
| **Benzo(a)pyrene** | **0.00091** | **0.00006** |
| Benzo(e)pyrene | 0.00010 | 0.00005 |
| Dibenzo(g,h,i)perylene | NA | 0.00003** |
| Benzo(b)fluoranthene | 0.00910 | 0.00006 |
| Benzo(k)fluoranthene | 0.00910 | 0.00006 |
| Chrysene | 0.00910 | 0.00004 |
| Coronene | NA | 0.00004** |
| Cyclopenta(c,d)pyrene | NA | 0.00006** |
| Dibenz(a,h)anthracene | 0.00910 | 0.00005 |
| Fluoranthene | 0.00010 | 0.00005 |
| Fluorene | 0.00010 | 0.00004 |
| 9-Fluorenone | NA | 0.00005** |
| Indeno(1,2,3-cd)pyrene | 0.00910 | 0.00004 |
| **Naphthalene** | **0.0290** | **0.00024** |
| Perylene | NA | 0.00003** |
| Phenanthrene | 0.00010 | 0.00006 |
| Pyrene | 0.00010 | 0.00006 |
| Retene | NA | 0.00006** |

**Bold** indicates required MQO Core Analytes.
Shading indicates other Analytes of Primary interest to the NATTS Program
******Risk values are not determined for these compounds. Concentrations are determined following Method TO-13A and ASTM-D6209. *Can be obtained using a volume of 300 $m^3$.

### *4.5.7 Quality Control*

The quality control procedures necessary to evaluate the GC/MS system include evaluation of retention time windows, calibration verification, and stability of internal standard signal levels.

- The GC/MS system must be tuned to meet DFTPP acceptance criteria.
- The initial calibration of the GC/MS system must meet EPA Compendium Method TO-13A and ASTM D 6209 – 98$^{e1}$ (for ASTM only compounds) acceptance criteria.
- The GC/MS system must meet LCS acceptance criteria every 12 hours of operation.
- For each batch of field samples (up to 20 samples) a laboratory RB and LCS must be analyzed and must meet acceptance criteria.
- A field blank must be analyzed at a frequency dependent upon the sampling frequency. For a 6-day sampling frequency, one field blank per month 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.
- Internal standard signal areas must meet project specifications, and surrogate compound recoveries must be within a 60 to 120 percent recovery window. If significant changes are made to the analytical system (i.e., chromatographic column changed, ion source cleaned, quadrupoles cleaned, etc.), the calibration must be repeated.

Quality control specifications for the NATTS PAH program are presented in Table 4.5-7. Overall MQOs for PAH sampling and analysis are shown in Section 3 (Table 3.3-1).

**Table 4.5-6. Summary of PAH TO-13A Quality Control Procedures**

| Parameter | Requirement | Acceptance Criteria Detail and Flag |
|---|---|---|
| Holding Time (Days) | Preparation: 14 days from sample collection (at 4 °C).<br>Analysis: 45 days from preparation (4 °C). | |
| DFTPP instrument tune check | Daily prior to calibration check and sample analysis; every 12 hours if instrument is operated 24 hours/day | Evaluation criteria in Table 3 of EPA Compendium Method |

**Table 4.5-6. Summary of PAH TO-13A Quality Control Procedures (Continued)**

| Parameter | Requirement | Acceptance Criteria Detail and Flag |
|---|---|---|
| Five-point calibration | Following any major change, repair, or maintenance if daily quality control check is not acceptable. Minimum frequency every six weeks, more frequently if required. | ± 30% Difference for each compound |
| CCC Standard | Daily (or every 12 hours) | ± 30% Difference for each compound relative to the mean of the calibration curve. |
| Method Blank | With every extraction batch | All analytes < 5 x MDL |
| Surrogate compound recoveries:<br>Laboratory surrogates<br>fluorene-$d_{10}$<br>pyrene-$d_{10}$<br>Field Surrogates<br>fluoranthene-$d_{10}$<br>benzo(a)pyrene-$d_{12}$ | Every sample/blank and laboratory control standard | 60-120% Recovery |
| LCS | Every 20 samples | To be determined by control charting recovery in laboratory. |
| Internal Standard Response:<br>naphthalene-$d_8$<br>acenaphthylene-$d_{10}$<br>chrysene-$d_{12}$<br>perylene-$d_{12}$ | Every sample/blank/LCS | -50 to 100% from the midpoint standard level of the most recent initial calibration |
| Duplicate and/or Replicate Analyses | Duplicate and/or Replicate samples only | 10% RPD for concentrations greater than 0.5 µg/mL |
| Field Blank | Monthly | Not Applicable |

## 4.6 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. Measurement of site specific meteorological parameters is not a requirement of the NATTS Program but is highly desirable if it can be accomplished. If site specific meteorological monitoring is conducted at a NATTS Site, the specifications presented in Table 4.8-1 should be considered.

**Table 4.6-1. Overview of Meteorological Monitoring Requirements**

| Question | Answer |
|---|---|
| How to monitor? | Measurements are to be in situ and continuous. |
| What parameters? | 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. |

If site specific meteorological monitoring is not conducted, it is a requirement of the NATTS Program that each site provide location information and details on the closest off-site meteorological monitoring station (i.e., National Weather Service (NWS), etc.). Detailed guidance for the required meteorological monitoring parameters is available through the EPA document, "Meteorological Monitoring Guidance for Regulatory Modeling Applications."[21] 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).*[22]

### *4.6.1 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-second 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 4.6-2. 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/$m^2$ |

**Table 4.6-2. System Specifications for Surface Meteorological Measurements (Continued)**

| Parameter | Method | Reporting Units | Operating Range | Resolution |
|---|---|---|---|---|
| Barometric Pressure | Aneroid Barometer | mb | 600 – 1100 mb | 0.5 hPa |
| Precipitation | Tipping Bucket | mm/hour | 0 – 250 mm/hour | 0.25 mm |

#### 4.6.1.1 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.[23] 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."[24] 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 10 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.[21]

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.

#### 4.6.1.2 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 AGL.[22] The location of the site for wind measurements should ensure that the horizontal distance to obstructions (e.g., buildings, trees, etc.) is at least 10 times the height of the obstruction. In urban areas (where the "10 times" criterion may not be met), a protocol should be provided to invalidate the measurements for the problem directions. Evans et al.[23] 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 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 five degrees of the true wind direction from an initial displacement of 10 degrees) should be $\leq$0.5 m $s^{-1}$. Overshoot must be $\leq$ 25 percent and the damping ratio should lie between 0.4 and 0.7.

#### 4.6.1.3 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.[23,24] 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 percent) should be ≤ 60 seconds. 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 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).

#### 4.6.1.4 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 centimeters AGL 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.

#### 4.6.1.5 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-infrared (IR) (0.73 to 4.0 μm) radiation. About 97 percent of the solar radiation reaching the outer atmosphere of earth lies between 0.29 and 3.0 μm.[25] 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.[26] 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 4.6-3), especially if the measurements are to be used for estimating heat flux.[25] 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 4.6-3. 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 |
| Temperature Response | % | ±1 | ±2 | ±5 |
| Nonlinearity | %FS | ±0.5 | ±2 | ±5 |
| Spectral Sensitivity | % | ±2 | ±5 | ±10 |
| Response Time (99%) | seconds | < 25 | < 60 | < 240 |

### 4.6.1.6 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 AGL. The height of the station above mean sea level and the height of the pressure sensor AGL 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

### *4.6.2 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 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 $O_3$ 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 4.6-4. 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 AGL)** | | | | | | |
| 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 AGL)** | | | | | | |
| 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 |

NM = Not measured; no capability for this variable.
[1]Typically meteorological towers do not exceed 100 m. However, radio and TV towers may exceed 600 m.
[2]The standard deviation of horizontal and vertical wind components.
[3]The sodar system antenna must be properly oriented with respect to true north, and 10 m wind direction must have proper alignment and integrity.

**Table 4.6-4. Capabilities and Limitations of Meteorological Measurement Systems for Vertical Profiling of the Lower Atmosphere (Continued)**

| Variable | Tower | Sodar[3] | Mini-sodar | Radar | Radar with RASS | Radiosonde | Tethersonde |
|---|---|---|---|---|---|---|---|
| | 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.
[1]Typically meteorological towers do not exceed 100 m. However, radio and TV towers may exceed 600 m.
[2]The standard deviation of horizontal and vertical wind components.
[3]The 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.

### 4.6.2.1 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.

#### 4.6.2.2 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.

#### 4.6.2.3 Balloon Systems

Balloon-based systems include rawinsonde (sometimes called radiosonde) and tethersonde 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 4.6-5.

**Table 4.6-5. 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 atmosphere[27]. The functional precision of NWS radiosonde measurements is shown in Table 4.6-6.

**Table 4.6-6. 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 [≤ 3.1 m/s]<br>±14 degrees [5.1 m/s]<br>±9 degrees [10.3 m/s]<br>±6 degrees [15.4 m/s]<br>±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. Tethersondes 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.

#### 4.6.2.4 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 three-component wind velocity profiles: radar and sodar. Radars (also called wind profilers) transmit an electromagnetic signal (approximately 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 (approximately 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 three-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 to10 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 $\alpha$ 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.

#### 4.6.2.5 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.[28,29] 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 4.6-7.

**Table 4.6-7. 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 backscatter | For continuous monitoring of boundary layer conditions. Range, however, is limited for sodar; estimates of the mixing height are 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.

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# SECTION 5
# DATA VALIDATION AND MANAGEMENT

## 5.0 INTRODUCTION

After air toxics data have been collected using the required sampling and analytical techniques described in earlier sections, the management of this information is key to the success of the NATTS mission. The integrity of the data collected and compiled in an acceptable management system is critical, as the data will be used to address human exposure to air toxics. Three elements concerning data management are discussed:

- data validation and reporting;
- data archiving; and
- data preparation for entry into EPA's AQS[1] data base.

## 5.1 DATA VALIDATION

The purpose of data validation is to detect and then verify or remove any data values that may not represent actual air quality conditions at the sampling station[2]. Validation of data is a key component of ensuring data quality. To help ensure data consistency, the techniques for validating data should be the same across all sites in the NATTS Program. In general, the data collected according to the specifications of advocated methodology are not automatically considered valid. To be validated, the data must be reviewed to confirm that sampling, analysis, and OA/QC were performed according to the specifications as presented in this TAD. Use of data validation techniques greatly reduces the risk of inconsistent/unacceptable data entering the EPA AQS data management system. Examples of validating field data include checks of monitoring equipment flow rates, sampling times, sample storage conditions, and hold times. If data have potentially been biased by "catastrophic releases" (such as a gasoline spill nearby), those data may be invalidated from the data set as they may artificially affect the data assessment and trend recognition. If a NATTS site is located in close proximity to a chemical manufacturing plant and a benzene leak occurs at the plant on a sampling day, the sample may

show a very high ambient concentration of benzene. The resulting monitoring data should be flagged for later evaluation during the review process. The site logbook should also be reviewed for any unusual circumstances recorded during a sample collection period.

Laboratory data must be validated to confirm that the QC requirements for blanks, calibration curves, and regular calibration checks meet the method requirements as presented in this TAD.

The objectives for data validation should include the following:

- To produce a database with values that are of known quality;
- To evaluate the internal, spatial, temporal, and physical consistency of the data and accept, correct, flag, and/or invalidate as appropriate; and
- To intercompare data to identify errors, biases, or outliers and accept, flag, correct, and/or invalidate as appropriate.

Typical elements of data validation include the following:

- Sample receipt. As soon as samples are received at the laboratory from the field, the COC documentation is checked to verify the sample identity and to invalidate samples with sampling anomalies;
- Sample analysis. The analyst preparing the sample verifies that all samples are prepared following individual method specifications;
- Post-Sample Analysis. After sample analysis, a reviewer verifies that all samples were prepared and analyzed within method-specified hold times;
- Preliminary data review. The instrumental analyst reviews the compound ID information obtained by the analytical instrumentation (GC/MS, HPLC, IC, ICP/MS);
- Second level review. A second reviewer verifies the analyst's determinations and prepares a quarterly report; and

- Third level review. The third reviewer reviews the quarterly report for a sample set, from sampling to analytical detection and quantitative analysis and final report.

Data validation should include the use of statistical analysis to determine invalid data. All statistical terms used in this section can be found in *Introduction to Probability and Statistics*[3]. As data are collected over a period of time, the statistics derived below can be compared against the historical data set. Preparation of a scatterplot and/or boxplot of NATTS Program site data is an effective way to visually determine potential outliers from the main body of data. Potential outlier data should be rigorously reviewed to determine whether contamination or operational errors occurred, which would invalidate the data.

Another statistical procedure for data evaluation includes determining the central tendency of the data set. There are four different ways to describe this central tendency:

- Arithmetic mean. The sum of the measured concentrations divided by the number of samples;
- Geometric mean. The result of multiplying the concentrations of samples with each other and taking the $n^{th}$ root of the number (n) of samples (e.g., for a data set with 20 concentrations, the $20^{th}$ root of the product would be taken);
- Median. The concentration value that represents the midpoint of the data set when arranged in order of magnitude (e.g., 50 percent of the data is greater than the median and 50 percent of the data is less than the median); and
- Mode. The concentration that has the highest frequency.

Data analysts calculate these values to identify outliers for data validation. It is very important to proceed from the "big picture" to a closer view, proceeding from a month of data to a week and then to a day. This strategy is important in forming an overall understanding of the data. Another important factor is to inspect every species that is reported, even when low concentrations are expected. Data validation is critical because serious errors in data analysis, modeling results, and trends analysis can be caused by erroneous individual data values.

The three types of plots useful in data evaluation are discussed in more detail below.

— Time series plots. To take full advantage of time series plots, the time series of every species and species group should be plotted and inspected to identify outliers, calibration spikes, abrupt changes in concentrations, possible misidentification of peaks, and extended periods of unusually high or low concentrations. It is useful to plot species together which are primarily emitted by the same type of source (e.g., benzene and acetylene are both present in automobile exhaust), or to plot species together which are emitted from different sources.

— Scatter plots. In preparing scatter plots, several pairs of species or species groups such as benzene and toluene, benzene and acetylene, benzene and ethane, and other pairs should be plotted and inspected. Scatter plots are useful for comparing the relationship between species at one site or at a pair of sites.

— Fingerprint plots. Fingerprint plots show the concentration of each species in a sample (in chromatographic order) and help to identify unique characteristics of the samples. Fingerprint plots should be inspected quickly and fingerprints of samples that have been flagged (i.e., identified as suspect or invalid) should be inspected in time series or scatter plot analyses. Checking fingerprint plots one-by-one allows an analyst to observe diurnal changes in species or species groups quickly. The analyst should then inspect hours or days surrounding suspect and invalid data to see if there is any carryover effect.

Final data validation will be performed by EPA in the process of calculating trends in NATTS compounds concentrations. For each NATTS Program site, and on a national basis, final data validation techniques include calculating and assessing the following statistical parameters:

— The variance (or dispersion). The average of the square of the deviations of the measurements about their mean;

— The standard deviation. Equal to the positive square root of the variance; and

— The confidence interval. Uses the standard deviation (SD) and size of the sample population, along with a t-value, to determine the statistical range in which the arithmetic mean may reside under a *normal* distribution.

Individual confidence intervals and coefficients of variation will be compared to the DQO coefficient of variation (i.e., ± 15 percent) as final validation for use of the data in trends analysis.

AQS reporting provides a regular summary of the results and observations made during NATTS Program monitoring. All the data must be submitted to EPA's AQS data base within 120 days following the end of each calendar quarter.

## 5.2 DATA ARCHIVING

Data archiving is the backing up and storage of data that must be retained but not regularly accessed[4]. After data have been validated and reported to AQS, all records used to generate the data must be archived by the participating agency in a manner that is easily accessible and retrievable. These archived records should be stored for a period of no less than six years in a separate physical location from the laboratory or field site to minimize the potential for data loss.

## 5.3 EPA'S AIR QUALITY SYSTEM

EPA's AQS is a computer-based system for handling storage and retrieval of information pertaining to airborne pollutants. The AQS is administered by the EPA, OAQPS, in Research Triangle Park, NC. AQS contains data from state and local agencies, tribes, and federal organizations, including descriptions of air monitoring sites and monitoring equipment, measured concentrations of air pollutants and related parameters, and calculated summary and statistical information. Reporting agencies submit air quality data as formatted transactions using EPA Central Data Exchange (CDX).

Twenty types of transactions are used to provide data and control information for updating the AQS data base, with detailed instructions available for coding individual transactions[5]. Four general types of values are used to code air quality transactions: codes,

dates, numeric data, and alphanumeric data. Each of these values must be entered on transactions exactly as they are stored in the AQS tables. The 20 AQS transaction formats contain certain fields in common, as well as unique fields:

- The transaction type specifies which batch transaction is being processed by the batch load software and determines which tables and columns will be updated with the data in the delimited fields;
- The action code indicates the data manipulation action to be performed by the transaction;
- The state code identifies one of the 50 states, U.S. territories, Washington, DC, or foreign countries;
- The county code identifies a county or equivalent geopolitical entity such as parish, independent city, or Tribal entity. For foreign countries, the county code identifies the geopolitical equivalent to U.S. states, such as Mexican states or Canadian provinces;
- The site ID is a numeric code that uniquely identifies each air monitoring site within a county. Site numbers are not assigned continuously or in any particular order. Local organizations are free to allocate site numbers in any way they choose as long as there is no duplication within a county;
- A set of three site transactions is used to update site information:
  - Type AA (Basic Site Information)
  - Type AB (Site Street Information)
  - Type AC (Site Open Path Information).
- A set of 11 transactions is used to update monitor information in the site file:
  - Type MA (Basic Monitor Information)
  - Type MB (Monitor Sampling Periods)
  - Type MC (Monitor Type Information)
  - Type MD (Monitor Agency Role)
  - Type ME (Monitoring Objective Information)
  - Type MF (Monitor Sampling Schedule)
  - Type MG (Monitor Street Description)
  - Type MH (Monitor Obstruction Information)
  - Type MI (Monitor Regulatory Compliance)
  - Type MJ (Monitor Collocation Period)
  - Type MK (Monitor Protocol).

- Raw Data Transactions
  - Type RC (Composite Raw Data)
  - Type RD (Hourly, Daily, and Subhourly Raw Data).
  - Type RB (Field or Trip Blank Data).

- Accuracy/Precision Transactions
  - Type RA (Accuracy Data)
  - Type RP (Precision Data)

- Annual Summary Data (Transaction Type RS).

### 5.3.1 *Air Toxics Flagging and Reporting for EPA's Air Quality System Database*

The guidance presented in this section explains and outlines how to report and flag air toxics data collected by Regional, State, Local and Tribal agencies that report their data to EPA's AQS database**.**

#### 5.3.1.1 Clarification of Terminology

There are a plethora of scientific terms and acronyms that are used for defining the lowest level that can be detected by a given piece of instrumentation. Some (*not all*) of the terms and acronyms that are related to the quantification and detection of instrument sensitivity and reporting of data are presented below. After careful review of all terms available, it was decided to simplify the schema. It is realized that some laboratory and data analysts will wonder why terms they are most comfortable with are not included. The explanation given here is that, in most instances, these terms define the same concept, but have different monikers. Therefore, terms that are utilized most often are included in this document. Generally, two distinct classes of terms exist: quantitation limits (QL) and detection limits (DL). The definitions associated with these two classes are presented below:

**Quantitation Limits—**The lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the

concentration of the lowest calibration standard, assuming that all method-specific sample weights, volumes, and cleanup procedures have been employed.

**Detection Limits —**Minimum concentration of an analyte that can be measured above instrument background. The DL is an estimate of concentrations at which one can be fairly certain that the compound is present. Concentrations below this limit may not be detected. Concentrations above this limit are almost certainly detected.

**Sample Quantitation Limit —**Also known as a Practical Quantitation Limit (PQL), Sample Quantitation Limit (SQL) is the lowest concentration of an analyte that can be reliably measured within specified limits of precision and accuracy during routine laboratory operating conditions. The Agency has used the SQL to estimate or evaluate the minimum concentration at which most laboratories can be expected to reliably measure a specific chemical contaminant during day-to-day analyses of drinking water samples. Normally, the SQL is determined as a multiplier of the method detection limit (eg., 3.18 times) and is considered the lowest concentration that can be accurately measured, as opposed to just detected. *Report the values at or between the SQL and MDL using the "SQ" QA flag.*

**Method Detection Limit—**EPA definition: the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte (Part 136, App. B). Determined by taking a minimum of seven aliquots of the sample (in case of air sample analysis we are using individual canister samples) to be used to calculate the MDL and process each through the entire analytical method. Make all computations according to the defined method with the final results in the method reporting units ($\mu g/m^3$). The EPA Compendium Methods state that MDLs must be determined and reported. **EPA policy dictates that all data*, to include values <u>below</u> MDL,* shall be reported to AQS.** *Data values at or below the MDL must be flagged with an "MD" flag. <u>Do not report 1/2 MDL or any integer of the MDL, only report the actual measured value and the "MD" QA flag.</u>*

**Non-Detected Compounds—**If a reporting agency cannot reliably detect a compound, then report 0 and the "ND" flag.

A summary of flags associated with QLs and DLs is presented in Table 5.3-1.

**Table 5.3-1. Summary of Quantitation Limit/Detection Limit Flags and their Application**

| If Concentration is | Value to Report | Flag Applied |
|---|---|---|
| > SQL | Value | None |
| > MDL ≤ SQL | Value | SQ |
| ≤ MDL | Value | MD |
| Not Detected | 0 | ND |

### 5.3.1.2 Data Flagging

There are clear and established situations when flags should be applied to ambient air toxics data for the NATTS program. The flags fall into four categories: quantification and detection flags, laboratory flags, chain-of-custody flags, and field maintenance and operation flags. There are also flags that must be used when an agency submits collocated or duplicate data for the calculation of precision. Most of these flags currently exist in EPA's AQS database. Those flags that are new to AQS, and detailed in this document, are scripted in **bold.** (Note: AQS can accommodate up to 10 flags per record.)

### 5.3.1.3 Types of Flags and Hierarchy

For air toxics data submittals there are two qualifier flag types: Null and QA.

- **Null** flag**—**This type of flag should be assigned when a scheduled sample is not usable (e.g., canister leaked, canister damaged in shipment, etc.).
- **QA Qualifier** flag**—**These flags are used to denote there was a procedural or quality assurance issue that happened that could possibly affect the uncertainty or concentration of the value. (Note: the flags for the QL and DL are QA qualified flags.)

Air Quality System flags can be used in combination if they are non-Null flags. If a Null flag is used, no other flag is necessary, nor should another flag be used since no data are reported.

Among the new flags are blank issue identifier flags (as noted in Table 5.3-3). These should be used if reported blank values are above those set by the individual laboratories SOPs or QAPP. If high blank values are associated with samples, it is important that the values be reported but appropriately flagged. Do not invalidate values due to high blank values. Also, a field sample hold time flag has been added for $Cr^{6+}$.

**Table 5.3-2. Quantitation and Detection Flags**

| Qualifier Type | Qualifier Type Description | Qualifier Code | Qualifier Description |
|---|---|---|---|
| QA | Quality Assurance Qualifier | **SQ** | Values greater than MDL and less-than-or-equal-to SQL |
| QA | Quality Assurance Qualifier | **MD** | Values less-than-or-equal-to MDL |
| QA | Quality Assurance Qualifier | **ND** | No value detected |

**Table 5.3-3. Laboratory Generated Flags**

| Qualifier Type | Qualifier Type Desc | Qualifier Code | Qualifier Description |
|---|---|---|---|
| NULL | Null Data Qualifier | AR | General lab error |
| NULL | Null Data Qualifier | AS | Poor quality assurance results |
| NULL | Null Data Qualifier | BH | Interference / co-elution |
| QA | Quality Assurance Qualifier | **FB** | Field blank value above acceptable limit |
| QA | Quality Assurance Qualifier | **TB** | Trip blank value above acceptable limit |
| QA | Quality Assurance Qualifier | **LB** | Lab blank value above acceptable limit |
| QA | Quality Assurance Qualifier | **LJ** | Analyte identified; reported value estimated |
| QA | Quality Assurance Qualifier | **LK** | Analyte identified; reported value may be biased high |
| QA | Quality Assurance Qualifier | **LL** | Analyte identified; reported value may be biased low |
| QA | Quality Assurance Qualifier | **EH** | Estimated; exceeds upper range |
| QA | Quality Assurance Qualifier | **CC** | Clean canister residue |
| QA | Quality Assurance Qualifier | 7 | Below lowest calibration level |
| QA | Quality Assurance Qualifier | CB | Lot Blank corrected; $PM_{10}$ Metals data |
| QA | Quality Assurance Qualifier | HT | $CR^{6+}$ Sample pick-up hold time specifications exceeded; data questionable. |

## Table 5.3-4. Chain-of-Custody Flags

| Qualifier Type | Qualifier Type Desc | Qualifier Code | Qualifier Desc |
|---|---|---|---|
| NULL | Null Data Qualifier | **MC** | Module end cap missing |
| NULL | Null Data Qualifier | **TS** | Holding time or transport temperature out of spec |
| NULL | Null Data Qualifier | AF | Scheduled but not collected |
| NULL | Null Data Qualifier | AG | Sample time out of limits |
| NULL | Null Data Qualifier | AJ | Filter damage |
| NULL | Null Data Qualifier | AK | Filter or sample leak |
| NULL | Null Data Qualifier | AL | Voided by operator |
| NULL | Null Data Qualifier | AM | Miscellaneous void |
| NULL | Null Data Qualifier | AQ | Collection error |
| NULL | Null Data Qualifier | **FI** | Filter Inspection flag |

## Table 5.3-5. Field Operations and Maintenance Flags

| Qualifier Type | Qualifier Type Desc | Qualifier Code | Qualifier Desc |
|---|---|---|---|
| NULL | Null Data Qualifier | AA | Sample pressure out of limits |
| NULL | Null Data Qualifier | AB | Technician unavailable |
| NULL | Null Data Qualifier | AC | Construction repairs in the area |
| NULL | Null Data Qualifier | AD | Shelter storm damage |
| NULL | Null Data Qualifier | AE | Shelter temperature out of specification |
| NULL | Null Data Qualifier | AH | Sample flow rate out of limits |
| NULL | Null Data Qualifier | AI | Insufficient data to make calculation |
| NULL | Null Data Qualifier | AN | Machine malfunction |
| NULL | Null Data Qualifier | AO | Bad weather |
| NULL | Null Data Qualifier | AP | Vandalism |
| NULL | Null Data Qualifier | AT | Calibration |
| NULL | Null Data Qualifier | AU | Monitoring waived |
| NULL | Null Data Qualifier | AV | Power failure |
| NULL | Null Data Qualifier | AW | Wildfire damage |
| NULL | Null Data Qualifier | AX | Precision check performed |
| NULL | Null Data Qualifier | AY | QC Control points (Zero /Span) |
| NULL | Null Data Qualifier | AZ | QC audit |
| NULL | Null Data Qualifier | BA | Maintenance / routine repairs |
| NULL | Null Data Qualifier | BB | Unable to reach site |
| NULL | Null Data Qualifier | BC | Multipoint calibration |
| NULL | Null Data Qualifier | BD | Auto calibration |
| NULL | Null Data Qualifier | BE | Building site repair |
| NULL | Null Data Qualifier | BF | Precision, zero or span performed |
| NULL | Null Data Qualifier | BI | Lost or damaged in transit |
| NULL | Null Data Qualifier | BJ | Operator Error |
| NULL | Null Data Qualifier | BK | Site computer/data logger down |

**Table 5.3-5. Field Operations and Maintenance Flags (Continued)**

| Qualifier Type | Qualifier Type Desc | Qualifier Code | Qualifier Desc |
|---|---|---|---|
| QA | Quality Assurance Qualifier | 2 | Operational Deviation |
| QA | Quality Assurance Qualifier | 3 | Field Issue |
| QA | Quality Assurance Qualifier | V | Validated value |
| QA | Quality Assurance Qualifier | W | Flow rate average out of specs. |
| QA | Quality Assurance Qualifier | X | Filter temperature difference out of spec. |
| QA | Quality Assurance Qualifier | **HT** | Sample pick-up hold time exceeded; data questionable |

### 5.3.1.4 Reporting Units

For the NATTS program, air toxics data may be reported to AQS in valid units (e.g., ppbv, parts per billion as carbon, $\mu g/m^3$, $ng/m^3$) specific to each target pollutant. With the exception of $PM_{10}$ metals, all data will be reported in standard conditions which, for ambient air monitoring, are defined as a pressure of 760 mm Hg or one atmosphere, and a temperature of $25^o$ Celsius or $298.15^o$ Kelvin. $PM_{10}$ metals data will be reported in local conditions, but may also be reported in both standard and local conditions at the discretion of the monitoring agency.

### 5.3.1.5 Flagging for Collocated, Duplicate and Replicate Data

The addition of duplicate/collocated replicate split samples is new and noted in **bold.** Additional information on reporting precision data can be found in EPA's AQS Data Coding Manual.

**Precision Information—**Method precision is determined by qualifying the variability associated with sample collection, and the variability associated with sample analysis. Collection precision determination is addressed through collection and analysis of collocated samples or duplicates samples. Analytical precision is addressed through the replicate analyses of these collocated or duplicate samples. The definitions of these terms are:

- Collocated Sample Collection – Collocated samples are samples collected simultaneously using two completely separate sampling systems, and then analyzing

the samples and comparing the results obtained. This approach provides information on "Inter-system" variability.

- Duplicate Sample Collection – Duplicate samples are samples collected simultaneously using one collection system (i.e., two separate samples through the same sampling system at the same time), and then analyzing the samples and comparing the results obtained. This simultaneous collection is typically accomplished by teeing the line from the flow control device to the canisters, and then doubling the collection flow rate. This approach provides information on "Intra-system" variability.

- Replicate Analysis – Replicate analyses is the analysis of one discrete sample multiple times. These are also known as "split" sample analyses. This approach provides information on "Analytical" variability.

Precision ID will differentiate the duplicates, replicates, and primary-replicate duplicate / collocated-replicates as follows:

1) Use Precision ID = '1' for the duplicate or collocated;
2) Use Precision ID = '2' for the primary replicate;
3) Use Precision ID = '**31**' for the duplicate/collocated-replicate sample #1;
4) Use Precision ID = '**32**' for the duplicate/collocated-replicate sample #2.

The duplicate, replicate, and duplicate-replicate values will be reported in the 'Indicated Value' field of the Raw Precision (RP) transactions (on three separate rows) and the corresponding method code in the 'Indicated Method' field. The primary sampler values, which also are submitted with Raw Hourly, Daily and Sub-Hourly (RD) transactions, will be repeated in the 'Test Value' field (on all 3 rows) along with the corresponding method code ('Test Method'). Below is an example scenario that outlines the coding required.

Example: Adding duplicate/collocated, replicate, and duplicate-replicate information

Duplicate/collocated information reported with Precision ID = 1

```
RP|I|10|003|1011|45201|6|1|7|001|110|20000101|1.35|110|1.25||
                          ^       ^            ^     ^    ^
```

Precision ID Prim. Meth. Prim. Value Dup. Meth (l) & Value(r)

Primary replicate information reported with Precision ID = 2

```
RP|I|10|003|1011|45201|6|2|7|001|110|20000101|1.35|110|1.36|||
                        ^       ^              ^   ^    ^
```

Precision ID Prim. Meth. Prim. Value Rep. Meth (l) & Value (r)

Duplicate/collocated-replicate #1 information reported with Precision ID = **31**

```
RP|I|10|003|1011|45201|6|31|7|001|110|20000101|1.35|110|1.33|||
                        ^       ^              ^   ^    ^
```

Precision ID Prim. Meth. Prim. Value Dup-Rep. Meth (l) & Value (r)

Duplicate/collocated-replicate #2 information reported with Precision ID = **32**

```
RP|I|10|003|1011|45201|6|32|7|001|110|20000101|1.35|110|1.33|||
                        ^       ^              ^   ^    ^
```

Precision ID Prim. Meth. Prim. Value Dup-Rep. Meth (l) & Value (r)

### *5.3.2 Data Entry into Air Quality System*

EPA's AQS[1] contains ambient air pollution data collected by EPA, state, local, and tribal air pollution control agencies from thousands of monitoring stations. AQS also contains meteorological data, descriptive information about each monitoring station (including its geographic location and its operator), and data QA/QC information. AQS users rely upon the system data to assess air quality, assist in attainment/nonattainment designations, perform modeling for permit review analysis, and other air quality management functions. With quarterly reporting of data to AQS, the NATTS Program will use data gathered in AQS to assess trends in air quality data.

The AQS database is EPA's data management repository for NATTS Program network data, which contains validated measurements of ambient concentrations of air pollutants and associated meteorological data. As with other types of EPA ambient air monitoring programs (i.e., criteria pollutants, Photochemical Assessment Monitoring Stations (PAMS), etc.), NATTS Program data must be prepared and entered into AQS. Data preparation and entry is the responsibility of each participating agency.

To enter data into AQS, the user must connect to the AQS website and also to the CDX website using a web browser to facilitate transferring input files. The user must be registered

and have a valid password (i.e., which are the same for both AQS and CDX). Specific details of these procedures are available at: http://www.epa.gov/tn/airs/airsaqs/manuals/manuals.htm.
If required, additional assistance is available by calling the AQS help line at (866) 411-4372.

## Section 5
## References and Resources

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4. *White Paper: Storage—Are You Backed Up?*; Sun Microsystems; 2002. Available at: http://www.sun.com/storage/white-papers/backup-article.html.

5. *AQS Data Coding Manual (AQ2)*, Version 1.1; U.S. Environmental Protection Agency: Office of Air Quality Planning and Standards, Information Transfer and Program Integration Division, Information Management Group, Research Triangle Park, NC, August 9, 2002.