TECHNICAL ASSISTANCE DOCUMENT
FOR THE
NATIONAL AIR TOXICS TRENDS STATIONS PROGRAM

Revision 3

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ACRONYMS AND ABBREVIATIONS

ACN	acetonitrile
ADQ	audit of data quality
AIRS	Aerometric Information Retrieval System
amu	atomic mass unit
ANP	annual network plan
ANSI	American National Standards Institute
AQS	Air Quality System
ASE	accelerated solvent extraction
ASQ	American Society for Quality
BFB	bromofluorobenzene
CAA	Clean Air Act
CAL	calibration
CAR	corrective action report
CARB	California Air Resources Board
CAS	Chemical Abstracts Service
CCB	continuing calibration blank
CCV	continuing calibration verification
CDCF	canister dilution correction factor
CDS	chromatography data system
CFR	Code of Federal Regulations
COA	certificate of analysis
COC	chain of custody
Cr6+	hexavalent chromium
CV	coefficient of variation
DART	Data Analysis and Reporting Tool
DB	dilution blank
DFTPP	decafluorotriphenylphosphine
DL	detection limit
DNPH	2,4-dinitrophenylhydrazine
DOC	demonstration of capability
DQI	data quality indicator
DQ FAC	Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs
DQO	data quality objective
ECTD	extended cold trap dehydration
EPA	United States Environmental Protection Agency
ESMB	extraction solvent method blank
eV	electron volt

FAA	flame atomic absorption
FAEM	flexible approaches to environmental measurement
FID	flame ionization detector
FRM	federal reference method
g	gram(s)
GC	gas chromatograph
GC/MS	gas chromatograph/mass spectrometry
GFAA	graphite furnace atomic absorption spectrometry
GPRA	Government Performance Results Act
HAP	hazardous air pollutant
HCF	hydrocarbon-free
Hg	mercury
HPLC	high performance liquid chromatograph
HQ	hazard quotient
IB	instrument blank
IC	ion chromatograph
ICAL	initial calibration
ICB	initial calibration blank
ICP/AES	inductively coupled plasma/atomic emission spectroscopy
ICP/MS	inductively coupled plasma/mass spectrometer
ICS	interference check standard
ICV	initial calibration verification
ID	identifier
IDCF	instrument dilution correction factor
in.	inch(es)
IS	internal standard
K-D	Kuderna-Danish
KI	potassium iodide
L	liter(s)
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
LFB	laboratory fortified blank
LIMS	laboratory information management system
LPM	liter(s) per minute
M	molar
m	meter(s)
m^3	cubic meter(s)
m/z	mass to charge
MB	method blank
MDL	method detection limit

MFC	mass flow controller
mg	milligram(s)
min	minute(s)
mL	milliliter(s)
mm	millimeter(s)
mM	millimolar
MPT	microscale purge and trap
MQO	measurement quality objective
MS	mass spectrometer or matrix spike
MUR	method update rule
µg	microgram(s)
µL	microliter(s)
µm	micrometer(s)
n	number
NAAQS	national ambient air quality standards
NATTS	National Air Toxics Trends Station
ng	nanograms(s)
nm	nanometer(s)
O_2	oxygen molecule
O_3	ozone molecule
OAQPS	Office of Air Quality Planning and Standards (EPA)
OH^-	hydroxide ion
PAH	polycyclic aromatic hydrocarbon
PM	particulate matter
$PM_{2.5}$	particulate matter with aerodynamic diameter $\leq$ 2.5 microns
PM_{10}	particulate matter with aerodynamic diameter $\leq$ 10 microns
POC	parameter occurrence code
ppb	part(s) per billion
ppbv	part(s) per billion by volume
ppm	part(s) per million
ppmv	part(s) per million by volume
psi	pound(s) per square inch
psia	pound(s) per square inch absolute
psig	pound(s) per square inch gauge
PT	proficiency test
PTFE	polytetrafluoroethylene
PUF	polyurethane foam
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
QFF	quartz fiber filter
QL	quantitation limit

QMP	quality management plan
QSA	quality systems audit
RB	reagent blank
RBS	reagent blank spike
RH	relative humidity
RPD	relative percent difference
RRF	relative response factor
RRT	relative retention time
RSD	relative standard deviation
RT	retention time
SB	solvent blank
SIM	selective ion monitoring
SLT	state, local, or tribal agency
SMB	solvent method blank
SOP	standard operating procedure
SQL	sample quantitation limit
SSCV	second source calibration verification
STP	temperature and pressure
SVOC	semi-volatile organic compound
TAD	technical assistance document
TOF	time of flight
TSA	technical systems audit
TTP	through the probe
UATS	urban air toxics strategy
UV	ultraviolet
VOC	volatile organic compound
v/v	volume per volume

1.0: INTRODUCTION

1.1 Background

Hazardous air pollutants (HAPs), or air toxics, are regulated under the Clean Air Act (CAA) as amended in 1990 and include a list of 189 toxic pollutants associated with adverse health effects. Such HAPs are emitted by numerous stationary and mobile sources. The U.S. Environmental Protection Agency (EPA) Government Performance Results Act (GPRA) commitments specify a goal of reducing air toxics emissions by 75% from 1993 levels to significantly reduce the potential for human health risk.

The National Air Toxics Trends Station (NATTS) Program was developed to fulfill the need for long-term ambient air toxics monitoring data required to assess attainment of GPRA commitments. The NATTS network was designed to generate data of a known, consistent, and standardized quality sufficient to enable the identification of spatial, and, more importantly, long-term temporal trends in the concentrations of air toxics. This technical assistance document (TAD) presents best practices and sets forth requirements for the collection and reporting of NATTS network air toxics data and is intended as an aid to the agencies responsible for implementing the NATTS Program. EPA recognizes that the partnership between the EPA and state and local air monitoring agencies is intrinsic to attaining the goal of the NATTS Program to generate high quality data needed to accomplish the end goal of trends detection. This TAD includes information on the implementation and maintenance of the necessary quality system, on the collection and analysis of air samples, and on the reporting of results to EPA's Air Quality System (AQS) database.

1.2 Target Analytes: Analytes of Critical Concern/Risk Drivers

While it is impractical to measure all HAPs at all monitoring sites, HAPs have been assigned by analyte class to a tiered system according to their relative toxicity. The 1990 CAA amendments required EPA to develop a subset of the 189 toxic pollutants identified in Section 112 that have the greatest impact on the public and the environment in urban areas. The resulting subset of air toxics consisted of 33 HAPs which are identified in the Integrated Urban Air Toxics Strategy (UATS)[1], commonly referred to as the Urban HAP List. This subset of 33 HAPs covers a variety of inhalation exposure periods (acute/chronic), exposure pathways (inhalation, dermal, ingestion), and associated adverse health effects (cancer/non-cancer). However, the NATTS Program is primarily concerned with traditional inhalation pathway exposures of more ubiquitous HAPs, and is focused on measuring HAPs which have available and cost-effective measurement methods. As such, 18 of the 33 UATS HAPs were selected as core HAPs for the NATTS Program. HAPs omitted from the UATS list include those for which analysis methods are less cost-efficient or less reliable and those HAPs deemed to have a lesser impact on inhalation exposure but a greater impact on the welfare of watersheds and water bodies through airborne deposition. Also omitted from the NATTS program were those HAPs which are categorized as persistent bio-accumulative compounds (PBTs) such as pesticides, mercury, polychlorinated biphenyls (PCBs), and dioxins.[2]

Hexavalent chromium was removed from the list of NATTS core HAPs due to it being a local source-driven pollutant (and not ubiquitous) and due to the preponderance of non-detect results on a national scale which provided little useful data. Sites are not required to, but may elect to, collect and report hexavalent chromium data. With the removal of hexavalent chromium, the 17 remaining UATS HAPs included polycyclic organic matter (POM), which was added later (in 2007) as speciated polycyclic aromatic hydrocarbons (PAHs). The replacement of POM with naphthalene and benzo(a)pyrene brought the list of required NATTS core HAPs to 18.

Sixty of the 189 HAPs have been selected as "Analytes of Principle Interest" for the NATTS Program; these 60 belong to one of four different analyte classes according to the method by which they are typically measured, i.e. volatile organic compounds (VOCs), carbonyls, metals, and (PAHs). These 60 "Analytes of Principle Interest" include 17 (18 when replacing POM with naphthalene and benzo(a)pyrene) of the UATS HAPs (mentioned previously) and are listed in Table 1.2-1 along with their analyte classes and concentrations corresponding to a 10^{-6} cancer risk and a noncancer risk at a hazard quotient (HQ) of 0.1. Of these 60 HAPs, 18 have been identified as major risk drivers based on a relative ranking performed by EPA and have been designated NATTS Core, or Tier I, analytes; these compounds must be measured at all NATTS sites. The remaining 42 Tier II HAPs are highly desired and should be measured and reported. EPA recognizes that additional resources are required to provide quality-assured data for the additional Tier II analytes; however, given that these methods are already conducted to measure the Tier I Core analytes, data for many of Tier II analytes can be reported with modest additional resource input.

Table 1.2-1. Analytes of Principle Interest for the NATTS Program

HAP	Analyte Class and Collection and Analysis Method	Tier	10^{-6} Cancer Risk Concentration ($\mu g/m^3$)	Noncancer Risk [Hazard Quotient = 0.1] Concentration ($\mu g/m^3$)
acrolein	VOC by TO-15	I (UATS)	-	0.002
tetrachloroethylene		I (UATS)	3.8 [a]	4 [a]
benzene		I (UATS)	0.13	3
carbon tetrachloride		I (UATS)	0.17	19
chloroform		I (UATS)	-	9.8
trichloroethylene		I (UATS)	0.21 [a]	0.2 [a]
1,3-butadiene		I (UATS)	0.03	0.2
vinyl chloride		I (UATS)	0.11	10
acetonitrile		II	-	6
acrylonitrile		II (UATS)	0.015	2
bromoform		II	0.91	-
carbon disulfide		II	-	70
chlorobenzene		II	100	-
chloroprene		II	-	0.7
p-dichlorobenzene		II	0.091	80
cis-1,3-dichloropropene		II (UATS)	0.3	2
trans-1,3-dichloropropene		II (UATS)	0.3	2
ethyl acrylate		II	0.071	-
ethyl benzene		II	-	100
hexachloro-1,3-butadiene		II	0.0022	9
methyl ethyl ketone		II	-	500
methyl isobutyl ketone		II	-	300
methyl methacrylate		II	-	70
methyl tert-butyl ether		II	3.8	300
methylene chloride		II (UATS)	2.1	100
styrene		II	-	100
1,1,2,2-tetrachloroethane		II (UATS)	0.017	-
toluene		II	-	40
1,1,2-trichloroethane		II	0.063	40
1,2,4-trichlorobenzene		II	-	20
m&p-xylenes		II	-	10
o-xylene		II	-	10
formaldehyde	carbonyl by TO-11A	I (UATS)	0.08 [a]	0.08 [a]
acetaldehyde		I (UATS)	0.45	0.9

Table 1.2-1. Analytes of Principle Interest for the NATTS Program (Continued)

HAP	Analyte Class and Collection and Analysis Method	Tier	10^{-6} Cancer Risk Concentration ($\mu g/m^3$)	Noncancer Risk [Hazard Quotient = 0.1] Concentration ($\mu g/m^3$)
nickel	metal by IO-3.1 and IO-3.5	I (UATS)	0.0021	0.009
arsenic		I (UATS)	0.00023	0.003
cadmium		I (UATS)	0.00056	0.002
manganese		I (UATS)	-	0.005
beryllium		I (UATS)	0.00042	0.002
lead		I (UATS)	-	0.015
antimony		II	-	0.02
chromium		II (UATS)	0.00008	0.01
cobalt		II	-	0.01
selenium		II	-	2
naphthalene	PAH by TO-13A	I (UATS [b])	0.029	0.029
benzo(a)pyrene		I (UATS [b])	0.00091	0.3
acenaphthene		II (UATS [b])	-	0.3
acenaphthylene		II (UATS [b])	-	0.3
anthracene		II (UATS [b])	-	0.3
benz(a)anthracene		II (UATS [b])	0.0091	0.3
benzo(b)fluoranthene		II (UATS [b])	0.0091	0.3
benzo(e)pyrene		II (UATS [b])	-	0.3
benzo(k)fluoranthene		II (UATS [b])	0.0091	0.3
chrysene		II (UATS [b])	0.091	0.3
dibenz(a,h)anthracene		II (UATS [b])	0.0091	0.3
fluoranthene		II (UATS [b])	-	0.3
fluorene		II (UATS [b])	-	0.3
indeno(1,2,3-cd)pyrene		II (UATS [b])	0.0091	0.3
phenanthrene		II (UATS [b])	-	0.3
pyrene		II (UATS [b])	-	0.3

[a] These values are per the NATTS Workplan Template, March 2015 [3]

[b] PAHs compounds included in the UATS list as polycyclic organic matter (POM)

1.3 Importance of Adherence to Guidelines

The overall data quality objective (DQO) of the NATTS Program is to detect trends in HAP concentrations covering rolling three-year periods with uniform certainty across the 27-site network with a coefficient of variation (CV) not to exceed 15 percent.[4] Stated another way, the DQO is to be able to detect a 15% difference (trend) in non-overlapping three-year periods within acceptable levels of decision error. This is accomplished by generating representative concentration data for the various HAPs with appropriate sensitivity within acceptable limits of imprecision and bias. For overall trends to be discernable, concentration data must be generated with methods which meet minimum performance criteria. The DQO, data quality indicators

(DQIs), and their associated measurement quality objectives (MQOs), or acceptance criteria, are presented in detail in Sections 2.1 and 3.2. EPA recognizes there is a disconnect in the NATTS bias MQO, which may not exceed 25%, and bias criteria in individual methods, notably TO-13A and TO-15, which exceed 25%. These methods are currently undergoing refinement by EPA's Office of Research and Development (ORD). For information regarding the determination of the DQO, DQIs, and MQOs, please refer to the following background reports and 2013 DQO reassessment report:

- Air Toxics Monitoring Concept Paper, Revised Draft February 29, 2000: https://www3.epa.gov/ttnamti1/files/ambient/airtox/cncp-sab.pdf

- Draft Report on Development of Data Quality Objectives (DQOs) for the National Ambient Air Toxics Trends Monitoring Network, September 27, 2002 (Appendix A of this TAD)

- Analysis, Development, and Update of the National Air Toxics Trends Stations (NATTS) Network Program-Level Data Quality Objective (DQO) and Associated Method Quality Objectives (MQOs), Final Report, June 13, 2013 https://www3.epa.gov/ttnamti1/files/ambient/airtox/nattsdqo20130613.pdf

Together, these documents provide a roadmap for determining and verifying the NATTS DQO and supporting MQOs.

A review of data during Phase I of the NATTS pilot project identified that variations in sampling, analysis, data reporting, and quality assurance resulted in a large amount of data inconsistency.[2] This TAD was developed and revised to increase consistency across the network and facilitate attainment of the NATTS DQO. Failure to attain the prescribed NATTS MQOs limits the ability to detect trends. Trends must be assessed so that EPA, as outlined in the EPA's Integrated Urban Air Strategy, may verify that the cumulative health risks associated with air toxics are in fact decreasing.[5]

1.4 Overview of TAD Sections

This document is organized so as to present guidance and requirements in the likely order in which they are needed when establishing a network site or network sites and laboratory, i.e., planning, implementation, and data verification. Background information, the NATTS DQO, and the framework and requirements for quality systems are addressed first, followed by collection and analysis of air samples, with data handling and validation tables completing the document. Each section is briefly described below.

1. Background – Brief overview of the history of the NATTS Program, NATTS analytes, and critical changes from Revision 2
2. Metrics Defining Data Quality for the NATTS Program – Importance of data consistency, NATTS monitoring objectives, quality systems, and siting criteria

3. Quality Assurance and Quality Control – Quality Assurance Project Plan (QAPP) development, QAPP elements including standard operating procedures (SOPs), corrective action, equipment calibration, document control, training, chain of custody (COC), traceability, labeling, control charting, software, records review, data verification and validation, and air quality subsystem (AQS) reporting
4. Collection and Analysis Methods – method detection limit (MDL) procedures, VOCs, carbonyls, PM_{10} metals, and PAHs
5. Meteorology – Brief description of required meteorological measurements
6. Data Handling – Procedures and policies for collection, manipulation, backup, archival, and calculations
7. Data Validation Tables – A series of tables detailing method specific critical criteria

1.5 Critical Changes and Updates from Revision 2 of the NATTS TAD

With this revision, the NATTS TAD has not only been reorganized and streamlined, but it has been substantially updated compared to Revision 2. Specific changes include:

- Specification of detailed requirements and recommendations for quality system development and implementation
- Specification of calibration requirements and recommendations for all instruments, including support equipment
- Recommendations for conducting and documenting of training
- Revision to the MDL determination procedure to be inclusive of the contribution from the collection media background
- Clarification of precision for sample collection and analysis
- Relaxation of certain VOCs sample collection requirements
- Provision of updated guidance on collection and analysis of VOCs, carbonyls, PM_{10} metals, and PAHs
- Exclusion of hexavalent chromium sampling and analysis methods
- Clarification on data handling practices
- Provision of data validation templates

Updating the guidance and requirements for the air sampling and analysis methods is the primary goal of this TAD revision. The secondary goal is to provide a more user-friendly guidance document with discrete sections organized in a manner so as to allow users to quickly locate the desired information. Of note, data validation template tables have been provided as an appendix in Section 7.

With the removal of hexavalent chromium as a NATTS core HAP in June 2013, guidance for sample collection and analysis for this analyte are not provided within this TAD revision.

1.6 Good Scientific Laboratory Practices

Good scientific practices, including instrument calibration and proper recording of observations, measurements, and instrument conditions, are equally important in both the field and in the laboratory. Such practices are necessary to generate data which are consistent, comparable, standardized, traceable, and defensible. Appropriate aspects of good laboratory and field practices are to be detailed in each agency's NATTS quality system. The need for, and examples of such practices are given below and in Section 2.

1.6.1 Data Consistency and Traceability. To be able to verify that the NATTS network generates data of quality sufficient to evaluate the main NATTS Program DQO, data collection and generation activities must be traceable to calibrated instruments, certified standards, and to activities conducted by individuals with the appropriate and documented training. Traceability in this case refers to ensuring the existence of a documentation trail which allows reconstruction of the activities performed to collect and analyze the sample and to the certified standards and calibrated instrumentation employed to determine analyte concentrations. To specifically ensure attainment of overall network bias requirements, each reported concentration must be traceable to a measurement of known accuracy, be it from an analytical balance, volumetric flask, gas chromatography/mass spectrometer (GC/MS), mass flow controller, critical orifice calibration plate, etc. Maintaining this traceability from sample collection to final results reporting assures that NATTS data are credible and defensible, and that the root cause of nonconformances may be found and corrected which thereby enables continuous improvement in NATTS program activities. Instrument calibration specifications and frequencies are provided in Section 3.

1.7 NATTS as the Model for Air Toxics Monitoring

Air toxics monitoring is an important, but often secondary, consideration for many air quality agencies. One reason for such is that there are no national ambient air quality standards (NAAQS) for air toxics for which regulatory compliance efforts would be required. Guidance for conducting air toxics sample collection and analysis is not as widely available as for criteria pollutants and is limited to performance-based compendium methods as compared to Federal Reference Methods (FRMs). This TAD is intended to primarily provide guidance and delineate requirements for NATTS sites and their associated laboratories; however, aspects of sampling, analysis, and quality assurance could be applied by agencies conducting air toxics monitoring outside of the NATTS network. This TAD incorporates feedback provided by the air toxics community with vast and varied experience conducting air toxics measurements. Feedback and input provided by the air toxics community were carefully reviewed and considered by a small workgroup of EPA and state/local/tribal (SLT) stakeholders in reviewing and revising this TAD. The NATTS network is a collaboration of SLT monitoring organizations with EPA. With an extensive network of experienced site operators and laboratory staff, the NATTS network strives to be the exemplar of air toxics monitoring.

1.8 References

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.

2. *National Monitoring Strategy Air Toxics Component, Final Draft.* United States Environmental Protection Agency, July 2004. Available at (accessed October 18, 2016): https://www3.epa.gov/ttnamti1/files/ambient/monitorstrat/atstrat804.pdf

3. National Air Toxics Trends Station Work Plan Template. United States Environmental Protection Agency, Revised: March 2015. Available at (accessed October 18, 2016): https://www3.epa.gov/ttn/amtic/files/ambient/airtox/nattsworkplantemplate.pdf

4. *Quality Management Plan for the National Air Toxics Trends Stations.* Quality Assurance Guidance Document, EPA 454/R-02-006. September 2005. Available at (accessed October 18, 2016): https://www3.epa.gov/ttnamti1/files/ambient/airtox/nattsqmp.pdf

2.0: IMPORTANCE OF DATA CONSISTENCY

As the main goal of the NATTS Program is to detect long-term trends in ambient air toxics concentrations across the continental United States, sample data collected at each site must be comparable over time and from one site to the next. The ability to detect and evaluate trends on a nationwide basis requires the standardized operation of the NATTS Program based upon four key components:

- Known and specific MQOs for the program;
- Specified measurement (collection and analysis) methods performed in a standardized and consistent manner across the network;
- Known and specific acceptance criteria for various aspects of the specified monitoring methods; and
- Stability of monitoring sites including location and operation over the required period of time.

In short, each site's concentration data must meet the MQOs and be generated with standardized methods that are appropriately sensitive, show minimal bias, and are sufficiently precise. Moreover, the collected samples taken together must be representative of the ambient conditions at the site over the course of a year and the annual dataset must be adequately complete. If program MQOs are not attained at each site, the network data will not be consistent across all sites and the ability to detect concentration trends will be compromised. MQOs related to each of the specific DQIs are discussed in more detail in Section 2.1.

This TAD is written such that requirements are described as "must" and recommendations are described as "should." It is expected that monitoring agencies will make good faith efforts to comply with the requirements and adopt recommendations, where feasible.

2.1 Data Quality Objectives and Relationship to the Quality Assurance Project Plan

The DQO process ensures that the type, quantity, and quality of data used in decision making are appropriate to evaluate the overall DQO of the NATTS Program. Discussion of the determination of the NATTS DQO is addressed in the NATTS Quality Management Plan (QMP)[1] and is not reproduced here. Background information on the development of the NATTS DQO process is detailed in the initial DQO report[2] and a follow up assessment was completed in 2013[3] to verify that the DQO and supporting MQOs remained applicable and suitable to attain network goals.

Each monitoring organization must develop a QAPP that describes the framework of the resources, responsible individuals, and actions to be taken to attain the NATTS DQO. QAPP development is described further in Section 3.3.

There is a single main DQO for the NATTS Program, which is:

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

This main DQO is directly related to demonstrating a reduction in health-based risk related to air toxics inhalation exposure. To achieve this main DQO, the NATTS Program network was designed to meet the following primary monitoring objectives, which are to:

- Measure concentrations of the NATTS Tier I core analytes and Tier II analytes of interest in ambient air at each NATTS site. These analytes are listed in Table 1.2-1.
- Generate data of sufficiently high and known quality that are nationally consistent. Such requires the implementation and maintenance of a robust and functional quality system, the proper execution of the applicable sampling and analysis methods, and that the specified methods provide sufficient sensitivity to obtain a limit of detection at or lower than that at which adverse health effects have been determined.
- Collect sufficient data to represent the annual average ambient concentrations of air toxics at each NATTS site. Collection of one sample every six days results in 60 or 61 samples per year exclusive of additional quality control (QC) samples such as blanks, collocated samples, duplicates, etc.

In addition to these primary monitoring objectives, the NATTS network was designed to address the following secondary monitoring objectives, which are to:

- Complement existing programs. The NATTS network is integrated with existing programs such as criteria pollutant monitoring, Photochemical Assessment Monitoring Stations (PAMS), National Core (NCore), etc., and to take advantage of efficiencies of scale to the extent that methodologies and operations are compatible. Establishment of NATTS sites at existing sites leverages the existing resources of experienced operators and infrastructure to achieve program objectives.
- Reflect community-oriented population exposure. Stationary monitors are sited to be representative of average concentrations within a 0.5- to 4-kilometer area (i.e., neighborhood scale). These neighborhood-scale measurements are more reflective of typical population exposure, can be incorporated in the estimation of long-term population risk, and are the primary component of the NATTS Program. Note that some NATTS sites may no longer truly represent neighborhood scale due to source or infrastructure changes. While new near-field sources may impact the measured concentrations, stability of the site location is necessary to detect trends which may still be discernable even when sites are impacted by such sources.
- 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 and the determination of the relationships between emissions and air quality under different circumstances, and allows for tracking of changes in emissions.[4] National assessments must reflect the differences among cities and

between urban and rural areas for selected HAPs, so the network:

- Includes cities with high population risk (both major metropolitan areas and other cities with high or potentially high anticipated air toxics concentrations);
- Distinguishes differences within and between geographic regions (to describe characteristics of areas affected by high concentrations (e.g. urban areas) versus low concentrations (e.g. rural areas);
- Reflects the variability among pollutant patterns across communities; and
- Includes background monitoring (i.e., sites without localized sources).

The above monitoring objectives are supported by the DQIs as described in the following subsections:

2.1.1 Representativeness. To adequately characterize the ambient air toxics concentrations over the course of a year, sample collection must occur every six days per the national sampling calendar for a 24-hour period beginning and ending at midnight local standard time (without correction for daylight savings time, if applicable). This sample collection duration and frequency provides a sufficient number of data points to ensure that the collected data are representative of the annual average daily concentration at a given site. Collection methods are designed to efficiently capture airborne HAPs over this time period in order to measure concentrations representative of the ambient air during sample collection.

2.1.2 Completeness. Comparison of concentration data across sites and over time requires that a minimum number of samples be collected over the course of each calendar year. The MQO for completeness prescribes that ≥ 85% of the annual air samples must be valid, equivalent to 52 of the annual 61 expected samples (51 during years when there are only 60 collection events).

A valid sample is one that was collected, analyzed, and reported to AQS without null flags. If a collected sample is voided or invalidated for any reason, a make-up sample collection should be attempted as soon as practical according to the make-up sampling policy below.

2.1.2.1 Make-up Sample Policy. Samples and sample results may be invalidated for a number of reasons. In all cases, the concentration data are entered in AQS flagged with a null code indicating the data are invalid. In order to increase the likelihood of attaining the completeness MQO of ≥ 85%, make-up samples should be collected when a sample or sample result is invalidated.

A replacement sample should be collected as close to the original sampling date as possible, and preferably before the next scheduled sampling date. When scheduling make-up sample collection, consideration should be given to minimize bias introduced to the annual concentration average due to differences in concentration from the originally scheduled sample date. Such considerations include concentration differences due to sample collection on a particular day of the week (weekday versus weekend) and potential seasonal effects. If it is not feasible to collect the make-up sample prior to the next scheduled sampling date, the sample should be collected within 30 days of the original sampling date. In all cases, the make-up sample should be

collected within the calendar year averaging period that starts January 1 and ends December 31. Note: For sampling units employing six-day timers, failure to reset the timer following a make-up sample can result in mistakenly collecting samples on dates that do not follow the national sampling calendar.

To summarize, make-up samples should be collected as close to the original sampling date as possible, and should be collected according to the following, in order of most preferable to least preferable:

1. Before the next scheduled sampling date
2. Within 30 days of the missed collection date
3. Within the calendar year.

In order to be temporally representative of the annual concentration at a given site, the sample dates must be as evenly distributed as possible to capture concentrations that fluctuate seasonally or according to weather patterns. It is not acceptable to delay make-up sampling until the end of the calendar year, as this may bias the data to be more seasonally than annually representative.

2.1.3 Precision. Reproducibility is a key component of ensuring concentration results at one site are comparable to those at other sites and are comparable over time. For the NATTS Program, precision of field and laboratory activities (inclusive of extraction and analysis) may be assessed by collection of collocated and/or duplicate field samples; the precision of laboratory handling and analysis may be estimated by the subdivision of a collected sample into preparation duplicates which are separately taken through all laboratory procedures (digestion or extraction and analysis) and includes instances in which target analytes may be added to a subsample to prepare matrix spike duplicates; and analytical precision is assessed by the replicate analysis of a sample or sample extract/digestate. Note that the previous revision of this TAD required that collocated and duplicate samples be analyzed in replicate. This has been relaxed to permit replicate analysis on any sample chosen by the laboratory. A summary of possible precision assessments is shown in Table 2.1-1. Precision sample collection and replicate analysis requirements will be detailed in each site's annual NATTS workplan.

The network MQO is based on an evaluation of at least an entire year's data. In all cases a coefficient of variance (CV) of $\leq 15\%$ must be met. For more information on how the CV is calculated, see the 2011-2012 NATTS Quality Assurance Annual Report.[5] Note that this precision MQO is different than the precision acceptance criteria for the individual collection and analysis methods; imprecision of the latter may be permitted to be larger than 15%. Such method-specific precision requirements apply to comparing two measurements and do not apply to larger ($N > 2$) sample sets.

Table 2.1-1. Possible Assessments of Precision through Field and Laboratory Activities

HAP Class	Collocation *	Duplicate Field Samples *	Preparation (Digestion/ Extraction) Duplicate	Matrix Spike Duplicate	Analysis Replicate
VOCs	yes	yes	no	no	yes
Carbonyls	yes	yes	no	no	yes
PM_{10} metals – high volume collection	yes	no	yes	yes	yes
PM_{10} metals – low volume collection	yes	no	no	no	yes
PAHs	yes	no	no	no	yes

*Note: Collection of collocated and duplicate field samples is highly desired, but not required, and will be detailed in the site's annual workplan.

2.1.4 Bias. Bias is the difference of a measurement from a true or accepted value and can be negative or positive. As much as possible, bias should be minimized as biased data may result in incorrect conclusions and therefore incorrect decisions. Bias may originate in several places within the sample collection and analysis steps. Sources of sample collection bias include, but are not limited to, incorrectly calibrated flows or out-of-calibration sampling instruments, elevated and unaccounted for background on collection media, poorly maintained (dirty) sampling inlets and flow paths, and poor sample handling techniques resulting in contamination or loss of analyte. Sources of sample analysis bias include, but are not limited to, poor hygiene or technique in sample preparation, incorrectly calibrated or out of tolerance equipment used for standard materials preparation and analysis, and infrequent or inappropriate instrument maintenance leading to enhanced or degraded analyte responses.

2.1.4.1 Assessing Laboratory Bias - Proficiency Testing. Each laboratory analyzing samples generated at NATTS sites must participate in the NATTS proficiency testing (PT) program. PT samples for each of the four sample classes, VOCs, carbonyls, PM_{10} metals, and PAHs, are generated at a frequency determined by EPA Office of Air Quality Planning and Standards (OAQPS), typically twice annually for each class. Participating laboratories are blind to the spiked concentrations and analyze the PT samples via methods and procedures identical to those employed for field-collected air samples.

PT target analytes, which include all Tier I analytes, among others, are identified in the following tables in Section 4:

VOCs	Table 4.2-1
Carbonyls	Table 4.3-1
PM_{10} Metals	Table 4.4-1
PAHs	Table 4.5-1

Each laboratory's PT results, on an analyte-by-analyte basis, must be within ± 25% of the assigned target value, defined as the NATTS laboratory average, excluding outliers. In the event

there is a problem with the NATTS laboratory average such as a contamination issue, the assigned target value may be changed to the nominal concentration or referee laboratory average, as applicable, and will be detailed in the PT results. Laboratories which fail to meet the bias acceptance criterion on an analyte-by-analyte basis must identify the root cause of the bias for the failed analyte, take corrective action, as appropriate, to eliminate the cause of the bias, and must evaluate the potential for bias in reported field sample data going back to last acceptable PT result. In the event of two consecutive failed PTs for a given analyte, laboratories must qualify field collected sample results as estimated when reported to AQS. EPA recognizes that the NATTS MQO bias criterion of ± 25% established through the DQO process is narrower than the bias criteria for some of the analytical methods, namely TO-15 and TO-13A. In order for the main NATTS DQO to be achieved, the bias MQO criterion must be achieved.

2.1.4.2 Assessing Field Bias. The direction of the flow rate bias in carbonyls, PM_{10} metals, and PAHs samplers is opposite that to the bias introduced in the reported concentrations. That is, flow rates which are biased low result in overestimation of air concentrations whereas flow rates which are biased high result in underestimation of air concentrations. As VOCs collection methods involve collection of whole air into the canister, the flow rate accuracy is of less importance and does not directly correlate to errors in measured concentrations. Rather, it is important that the flow rate into the canister be constant over the entire 24-hour collection period so as to best characterize the average burden of VOCs over the entire sampling duration.

Indicated flow rates for carbonyls and PAHs must be within ± 10% of both the flow transfer standard and the design flow rate (where applicable). The indicated flow rate for the low volume PM_{10} metals method must be within ± 4% of the flow transfer standard and within ± 5% of the design flow rate. The indicated flow rate for the high volume PM_{10} metals method must be within ± 7% of the transfer standard and within ± 10% of the design flow rate. Failure to meet these criteria must result in corrective action including, but not limited to, recalibration of the sampling unit flow or resetting of flow linear regression response, where possible. Sampling units which cannot meet these flow accuracy specifications must not be utilized for sample collection. Additionally, following a failing calibration or calibration check, agencies must evaluate sample data collected since the last acceptable calibration or calibration check, and such data may be subject to invalidation. Corrective action is recommended for flow calibration checks which indicate flows approaching, but not exceeding the appropriate flow acceptance criterion. Calibration flow checks must be performed at minimum quarterly; however, to minimize risk of invalidation of data, monthly flow calibration checks are recommended.

Sampling bias for VOCs and carbonyls is also characterized by evaluating sample media collected by providing analyte-free zero air or nitrogen to the sampling unit (zero checking) and by providing a known concentration analyte stream to VOCs sampling units (known standard check). These zero checks and known standard checks are discussed further in Sections 4.2.5.5 and 4.3.7.1.1, for VOCs and carbonyls, respectively.

2.1.5 Sensitivity. Following promulgation of the CAA and its amendments, ambient air toxics concentrations have been decreasing. As concentrations decrease, they become increasingly difficult to measure and, as a result, measurement methods must become increasingly sensitive. Concurrent with decreases in ambient air toxics concentrations, health

risk assessments for exposures to air toxics are driving health risk-based concentrations lower, which also precipitates a need to increase method sensitivity. In order to ensure that methods are sufficiently sensitive, MDL MQOs have been established which prescribe the maximum allowable MDL for each required NATTS core/Tier I analyte. As concentrations for HAPs decrease in the ambient atmosphere and are measured closer to the MDL or below the MDL, this results in a decrease in the accuracy (decrease in precision and increase in bias) of the percent change estimate in evaluating a trend.

The MDL and sample quantitation limit ([SQL], defined as 3.18 times the MDL concentration) provide information on the concentration at which both positive identification and accurate quantification is expected, respectively. While all measured concentrations (even those less than the MDL) must be reported to AQS, the confidence associated with each reported concentration is correlated to its relationship to the corresponding MDL and SQL.

The SQL is equivalent to ten-fold the standard deviation of seven measurements of MDL samples, which was defined in draft EPA guidance in 1994[6] as the minimum level (ML). The 3.18-fold was derived by dividing 10 standard deviations by 3.14 (the student's T value for 7 replicates). The MDL process in 40 Code of Federal Regulations (CFR) Part 136 Appendix B is protective against reporting false positives such that 99% of the measurements made at the determined MDL value are positively detected (determined to be different from the detectors response in the absence of the analyte), but does not attempt to characterize precision or address accuracy at the determined MDL concentration. The SQL (ML) concentration provides more confidence to the accuracy of the measurement with precision that is well-characterized.

MDL MQOs that must be met (as of the promulgation of this document in October 2016) are given in Table 4.1-1. Further discussion of MDL background, determination, and importance are discussed in in Section 4.1.

2.2 NATTS Workplan

Each year the EPA will submit a workplan to each agency conducting NATTS Program work covering the grant period from July 1 through June 30 of the following calendar year. This workplan details the sample collection, sample analysis, and data reporting responsibilities and the associated budget with which each agency must comply. The workplan briefly describes the NATTS main DQO and associated outputs and outcomes as related to the EPA's strategic goals. The workplan will prescribe the quantity of quality assurance samples (collocated, duplicate, or analysis replicate) to be collected at each site for the grant funding year. The workplan also specifies the required MDL MQOs for the Tier I Core analytes.

2.3 Quality System Development

There are 11 quality management specifications defined in EPA Order CIO 2105.0 (https://www.epa.gov/sites/production/files/2015-09/documents/epa_order_cio_21050.pdf) for all EPA organizations covered by the EPA Quality System. It is EPA policy that each agency conducting NATTS Program work must have a quality system that conforms to the minimum specifications of the American National Standards Institute (ANSI)/American Society for

Quality (ASQ) E4 "Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs.[7] ASQ E4 is based on the general principle that the quality system provides guidelines for quality assurance (QA) and quality control (QC) based on the continuous cycle of planning, implementation, documenting, and assessment.[8] Each agency's quality system must also comply with the requirements as given in this TAD, which complements the requirements in ASQ E4. The purpose of defining the quality systems requirements in this manner is to provide a single source for developing or revising quality systems for NATTS Program work. Quality systems documents, including QAPPs and SOPs, must be revised to reflect the requirements. The quality system and associated functions are described in the plan-do-check-act feedback loop to ensure continuous improvement to ensure NATTS MQOs are met.

Plan - The planning portion of the quality system incorporates development of quality systems documents such as a QMP, QAPP, and SOPs which define the activities to be conducted, who they are conducted by, when activities are conducted, and how they must be documented. These documents must adapt and incorporate adjustments to procedures and policies when changes are needed or when procedures and policies become obsolete. Quality systems documents serve a dual purpose in that they describe how activities will be conducted and serve to document policies and procedures for reconstructing past activities.

Do - Activities described in the quality systems documents must be implemented and executed as prescribed. Staff training is a necessary element of a functional quality system, ensuring that each individual conducting activities has the experience and skills required to generate work product of a known and adequate quality. Appropriate training combined with up-to-date quality systems documents ensure that staff have both the skills and procedures to conduct activities as required.

Check - Assessments are conducted during and after planning and implementation to ensure that work products meet the objectives and needs of the program as defined during planning. Additionally, assessments ensure that quality systems documents sufficiently describe the activities to be performed, that measurements and calculations are accurate, that staff perform activities per the current quality systems documents, that staff training is up to date, and that nonconformances are communicated to those ultimately responsible for the program.

Act - Following assessments, root cause analysis is performed and corrective action is taken to address nonconformances such that the NATTS program may be continuously improved.

Each agency must have a robust and fully-functioning quality system to ensure that NATTS Program MQOs for the various DQIs are met. When MQOs are met across the entire network, the NATTS program DQO will be attained. A fundamental part of a functional quality system is the QAPP, which each agency must develop and maintain for NATTS program work. Details and specific quality system elements that must be incorporated in the NATTS QAPP are presented in Section 3.

2.4 Siting Considerations

Urban concentration data are needed to address the range of population exposures across and within urban areas. Conversely, rural concentration data are needed for characterization of exposures of non-urban populations, to establish non-source impacted concentrations (as practicable), and to better assess environmental impacts of emissions of air toxics. The NATTS network at the time of this TAD revision consists of 20 urban sites and seven rural sites. Each of these sites has been established since 2008, and only modest modifications involving relocation within a small geographic area have occurred over the past several years. Long-term monitoring needed to measure average concentrations over successive three-year periods requires that sites are maintained at, or in very close proximity to, their current location. This long-term data generation from each site is integral to discerning trends in air toxics concentrations.

For each of the 27 sites currently in the NATTS network, sampling unit siting may have changed little, if at all, from when sample collection for the NATTS Program began at the specific site. Nonetheless, site operators should evaluate instrument siting annually to ensure that requirements continue to be met consistently across the network. Siting criteria to consider relate to changes at the site such as tree growth, construction or development on property near the site, new sources, and other changes which may impact sample collection and the resulting measured concentrations. Particular attention should be paid to vertical placement of inlets, spacing between sampling inlets, proximity to vehicle traffic (especially where traffic levels have increased due to housing or business development), and proximity to obstructions or other interferences. Additionally, monitoring agencies should be aware of changes in sources, population, and neighborhood make-up (businesses, industry, etc.) which may impact sampler siting or sample concentrations.

Monitoring unit inlet placement must conform to the specifications listed in 40 CFR Part 58 Appendix E and the additional guidance given below.

2.4.1 Sampling Instrument Spacing. Requirements for sampler spacing are relative to the sampling unit inlet (edge) and must conform to the criteria listed in Table 2.4-1.

As an example, per the table above, an inlet to a carbonyls sampler must be no less than 2 m and no more than 15 m above the ground and it may be no closer than 2 m to any high volume sampler. Moreover, the inlets of collocated samplers may be no further than 4 m in the horizontal direction, and no more than 3 m apart vertically.

Note that for gaseous HAPs (VOCs and carbonyls) there is no minimum collocation distance as gases are much more homogeneous in the ambient air than particulate matter, and are not likely to influence one another, particularly at the low flow rates utilized.

Table 2.4-1. Sampling Unit Inlet Vertical Spacing Requirements

Parameter	Flow Rate	Inlet Above Ground Level Height Requirement [a]	Horizontal Collocation Requirement	Vertical Collocation Requirement
VOCs	Low volume (< 1000 mL/min)	2-15 m	0-4 m	≤ 3 m
Carbonyls	Low volume (~ 1 L/min)	2-15 m	0-4 m	≤ 3 m
PM_{10} Metals	Low volume (~16.7 L/min)	2-15 m	1-4 m [b]	≤ 3 m
	High volume [c] (~ 1.1 m^3/min)	2-15 m	2-4 m [b]	≤ 3 m
PAHs	High volume [c, d] (> 0.139 m^3/min)	2-15 m	2-4 m	≤ 3 m

[a] Many standalone sampling unit inlets do not meet the minimum height and must be installed on a support structure such as a riser or rooftop to elevate the inlet to the proper height.
[b] 40 CFR Part 58 Appendix A Section 3.3.4.2(c).
[c] These high volume sampling units must be minimally 2 m from all other sampling inlets.
[d] 40 CFR Part 58 Appendix E states that high volume sampling units are those with flow > 200 L/minute. However the regulations are silent on high volume PAHs sampling units, which operate > 139 L/minute; in this TAD they are conservatively being treated as high volume sampling units such that they must minimally be 2 m horizontally from other instrument inlets.

2.4.2 Interferences to Sampling Unit Siting. Interference from other samplers, particularly high volume sampling units for PAHs and PM_{10} metals, must be avoided by ensuring that all inlets are minimally 2 meters from any high volume inlet. Additionally, to eliminate recollection of already sampled "scrubbed" air, exhausts (when so equipped) from high volume sampling units must be directed away from air samplers in the primary downwind direction via hose that terminates minimally 3 meters in distance from any sampler.

PM_{10} metal sampling unit sites must not be in an unpaved area unless covered by vegetation year round, so the impacts of wind-blown dusts are kept to a minimum.[9]

Tarred or asphalt roofs should be avoided for the install of inlets for carbonyls, VOCs, and PAHs air samplers as these materials may emit target analytes during warmer sampling periods. If installation is performed on such a roof, it is recommended that the tar or asphalt be encapsulated or sufficiently weathered and that collected samples be evaluated for marker compounds indicative of contamination or influence from the tar or asphalt.

2.4.3 Obstructions. An inlet of standalone sampling units and inlet probes must be at least 1 meter vertically or horizontally away from any supporting structure, wall, parapet, or other obstruction. If the probe is located near the side of a building, it should be located on the windward side relative to the prevailing wind direction during the season of highest concentration potential.

Inlets must have unrestricted airflow and be located away from obstacles so that the distance from the obstacle to the inlet is at least twice the height difference the obstacle protrudes above the inlet. For instance, if a monitoring trailer is 4 meters above the inlet of a PM_{10} metals sampling unit, the inlet must be minimally 8 meters from the monitoring trailer.

All sampling inlets must be minimally 10 meters from the dripline (end of the nearest branch) of any tree.

2.4.4 Spacing from Roadways. Sampling unit inlets for VOCs, carbonyls, PM_{10} metals, and PAHs must meet or exceed the minimum distance from roadways according to Table 2.4-2.

Table 2.4-2. Sampling Unit Inlet Required Minimum Distances from Roadways

Roadway Average Daily Traffic (ADT), Vehicles per Day	Minimum Distance to Inlet (m) [a]
≤ 15,000	15
20,000	20
40,000	40
60,000	60
80,000	80
≥ 100,000	100

[a] Distance from the edge of the nearest traffic lane. The distance for intermediate traffic counts should be interpolated from the table values based on measured traffic counts. Values in this table taken from 40 CFR Part 58 Appendix E, Figure E-1 for neighborhood scale sites.

2.4.5 Ongoing Siting Considerations. Agencies must be mindful of conditions at the site that may impact siting criteria.

Infrequent, non-characteristic, or non-representative sources such as road and building construction may impact measured sample concentrations due to increased dust, emissions from materials utilized (paints, paint strippers, asphalt, etc.), and heavy machinery operation. Other such sources include demolition operations (e.g. buildings or roadways) generating dust which may impact PM_{10} metals concentrations. Application of fresh pavement and painting of traffic lanes generates substantial concentrations of PAHs and VOCs. For sites in residential areas, storage of fuels, operation of charcoal grills, backyard fire pits, and fireplaces can contribute to elevated measured concentrations of PAHs and PM. Concentrations of HAPs measured at rural sites may be affected by forest fires, logging operations, etc. Observation of such conditions must be noted on the sample collection records or site log and may require qualification of results.

Fast growing trees, newly constructed buildings or traffic routes, and other interferences must be noted and recorded in the site log and data must be qualified, as appropriate. When these items negatively impact the siting criteria, the obstruction or interference must be addressed. Such necessary changes to instrument siting should be included in each site's annual network plan. For unavoidable impacts to the site (such as a business acting as a significant source), these should be addressed in the network plan and may require relocation of the site. Such interferences and potential relocation should be discussed and addressed in concert with the EPA Region office.

2.5 References

1. *Quality Management Plan for the National Air Toxics Trends Stations.* Quality Assurance Guidance Document, EPA 454/R-02-006. September 2005. Available at (accessed October 18, 2016): https://www3.epa.gov/ttnamti1/files/ambient/airtox/nattsqmp.pdf

2. Draft Report on Development of Data Quality Objectives (DQOs) for the National Ambient Air Toxics Trends Monitoring Network, September 27, 2002
(Appendix A of this TAD)

3. Analysis, Development, and Update of the National Air Toxics Trends Stations (NATTS) Network Program-Level Data Quality Objective (DQO) and Associated Method Quality Objectives (MQOs), Final Report, June 13, 2013. Available at (accessed October 18, 2016): https://www3.epa.gov/ttnamti1/files/ambient/airtox/nattsdqo20130613.pdf

4. *National Air Toxics Program: The Integrated Urban Strategy*, Report to Congress, EPA 453/R-99-007, July 2000. Available at (accessed October 18, 2016): https://www.epa.gov/sites/production/files/2014-08/documents/072000-urban-air-toxics-report-congress.pdf

5. *National Air Toxics Trends Stations Quality Assurance Annual Report, Calendar Years 2011 and 2012, Final*, December 12, 2014. Available at (accessed October 18, 2016): https://www3.epa.gov/ttnamti1/files/ambient/airtox/NATTS20112012QAARfinal.pdf

6. *National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-based Effluent Limitations Set Below Analytical Detection/Quantitation Levels*, Draft Report. United States EPA, 1994

7. *Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs*, American National Standards Institute (ANSI)/American Society for Quality (ASQ) E4, 2004.

8. *Overview of the EPA Quality System for Environmental Data and Technology. EPA/240/R-02/003; U.S. Environmental Protection Agency: Office of Environmental Information. Washington, DC. November 2002.* Available at (accessed October 18, 2016): https://www.epa.gov/sites/production/files/2015-08/documents/overview-final.pdf

9. Ambient Air Quality Surveillance, Probe and Monitoring Path Siting Criteria for Ambient Air Quality Monitoring, 40 CFR § 58 Appendix E, 201

3.0: QUALITY ASSURANCE AND QUALITY CONTROL

3.1 NATTS Quality Management Plan

EPA OAQPS developed the NATTS Program QMP to provide a set of minimum requirements that must be followed by all monitoring organizations (state, local, or tribal organization; or company) conducting NATTS Program work. Development of the QMP began in 2002 and was completed, approved, and implemented in 2005. Essential QA and QC elements are defined within the NATTS QMP[1] and are excerpted and presented in this document.

3.2 NATTS Main Data Quality Objective, Data Quality Indicators, and Measurement Quality Objectives

There is a single main DQO for the NATTS Program, which is stated as:

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

To achieve this primary DQO, the DQIs of representativeness, completeness, precision, bias, and sensitivity must meet specific MQOs, or acceptance criteria. The MQOs for each of the DQIs are as follows:

- **Representativeness:** Sampling must occur at one-in-six day frequency, from midnight to midnight local time, over 24 ± 1 hours
- **Completeness:** At least 85% of all data available in a given quarter must be reported
- **Precision:** The CV must be no more than 15%
- **Bias:** Measurement error must be no more than 25%
- **Sensitivity:** MDLs must meet the network requirements.

Each entity supporting NATTS Program data collection must ensure that these MQOs are met for each of the DQIs. Implementation of a robust quality system is part of the process to attain such.

3.3 Monitoring Organization QAPP Development and Approval

As discussed in Section 2.3, the monitoring organization quality system is the framework that ensures that defensible data of appropriate quality – those that meet the network MQOs for the various DQIs – are generated and reported to EPA so that the NATTS DQO is attained. The NATTS QAPP is the roadmap for design of each organization's quality system.

Given the importance of the QAPP, each monitoring organization operating a NATTS monitoring site and/or laboratory performing analysis of NATTS Program samples must have an up-to-date and fully approved QAPP which covers all aspects of the sample collection, analysis,

and QA/QC activities performed by the specific agency and at the associated laboratory at which samples are analyzed. All major stakeholders involved in the monitoring organization's and/or laboratory's NATTS Program work should provide input to and review the QAPP to ensure that aspects of the QAPP for which they are responsible are accurately and adequately described. The QAPP must minimally be approved and signed by the monitoring organization's NATTS Program Manager (however named) and the EPA Regional office (or EPA Regional office delegate as defined in the grant language) in which the monitoring site and/or laboratory exists and the QAPP must be on-file.

The NATTS QAPP must provide an overview of the work to be conducted, describe the need for and objectives of the measurements, and define the QA/QC activities to be applied to the project such that the monitoring objectives are attained. The QAPP should include information for staff responsible for project management, sample collection, laboratory analysis, QA, training, safety, data review, and data reporting.

The NATTS QAPP for each monitoring organization is the starting point or roadmap to ensure that the NATTS MQOs, and therefore NATTS monitoring objectives, are achieved. Review of the NATTS QAPP on an annual basis (or as required by the Region), conduct of audits and assessments, and implementation of effective corrective action ensure that NATTS sites and supporting labs are in fact achieving NATTS program objectives, and, if not, are implementing corrective actions, as needed.

The NATTS QAPP for each monitoring organization must include the NATTS DQO, DQIs, and MQOs listed above in Section 3.2, and should include elements listed in Section 3.3.1.3 to ensure that data of sufficient quality are generated over time such that concentration trends may be successfully detected and that monitoring data of comparable quality are generated across the entire NATTS network. The NATTS Program DQO, DQIs, and MQOs take precedent over regional, state, local, or tribal monitoring objectives for the associated air toxics sampling that is performed unless the SLT requirements are more stringent than those indicated for NATTS. Monitoring agencies are free to prescribe more conservative acceptance criteria (e.g. lower blank acceptance concentrations, tighter recovery ranges, etc.).

3.3.1 Development of the NATTS QAPP. EPA has developed a model QAPP as described in *EPA QA/R-5, EPA Requirements for Quality Assurance Project Plans*[2] and the accompanying document, *EPA QA/G-5, Guidance for Quality Assurance Project Plans*.[3] This model QAPP may be a useful starting point in the development of the QAPP for each monitoring agency conducting NATTS Program work.

3.3.1.1 NATTS QAPP – Program DQOs, DQIs, and MQOs. The NATTS DQOs, DQIs, and MQOs, which are given in Section 3.2 of this TAD, must be included in the NATTS QAPP.

3.3.1.2 NATTS QAPP – Performance Based Method Criteria. NATTS Program work must comply with the requirements listed in this TAD and with the collection and analysis methods specified in Section 4. Acceptance criteria specified in the methods must be met as prescribed; however, method deviations are permitted provided the acceptance criteria for precision and bias are met and can be demonstrated to be scientifically sound and defensible. The NATTS Program

is designed according to the EPA's Flexible Approaches to Environmental Measurement (FAEM). The FAEM is a performance-based measurement systems approach which prescribes specific methods or approaches to be implemented, but permits deviations in the manner in which the specified methods are performed provided that the resulting data meet the data quality acceptance criteria for precision and bias.

Planned method deviations must be described in the monitoring organization's QAPP and must be approved by the cognizant EPA regional office (or delegate as detailed in the grant language). Adjustments to storage conditions and holding times are not permitted, nor are deviations which permit exceedances to the specified method acceptance criteria or to NATTS MQOs as such would allow data of a quality lower than, and not comparable to, that required to be generated in the NATTS network per the NATTS QMP and per this TAD. Agency QAPPs should incorporate much of the guidance listed in this TAD.

3.3.1.3 NATTS QAPP – Incorporating Quality System Elements. In addition to the example information contained in the model QAPP listed in Section 3.3.1, monitoring organizations should develop and prescribe within the QAPP the following quality system elements which are described in more detail in the following sections:

- Pertinent SOP documents
- Corrective action procedures
- QA unit and internal audit procedures
- Calibration of instruments
- Document control
- Training requirements and documentation, and demonstration of capability
- Sample custody and storage
- Traceability of reagents and standard materials
- Labeling
- Early warning systems – control charts
- Spreadsheets and data reduction algorithms
- Software validation, updating, and upgrading
- Review of records
- Data verification and validation
- Reporting of results to AQS
- Records retention and archival
- Safety

3.3.1.3.1 Standard Operating Procedure Documents. The NATTS QAPP must list the pertinent SOPs, however named, to be followed to conduct all NATTS Program work. SOPs must prescribe the details of the activities applicable to sample collection in the field, preparation and analysis of the samples in the laboratory, and data review, reduction, and reporting. SOPs must minimally cover the following aspects of the NATTS program:

- Sample collection for VOCs, carbonyls, PM_{10} metals, and PAHs;
- Sample preparation and analysis for VOCs, carbonyls, PM_{10} metals, and PAHs;

- Calibration, certification, and maintenance of each type of sample collection and analysis instrument;
- Calibration of critical support equipment; and
- Data review.

Additional SOPs should be prepared as necessary to cover routine procedures and repetitive tasks which, if performed incorrectly, could affect data quality such as COC and performing numerical calculations (describing rounding, significant figures, etc.).

Refer to Section 3.3.2 for further guidance on preparation of SOPs.

For portions of the sample collection and analysis which are contracted or otherwise performed elsewhere (not by the cognizant NATTS monitoring agency), the monitoring organization must reference the SOP of the third party in its NATTS QAPP and if the laboratory is other than the national contract laboratory (which are maintained by EPA), must maintain a current, approved copy of the third party's SOP(s) on file. Monitoring agencies must ensure that third-party laboratory QAPPs and SOPs are available.

3.3.1.3.2 Corrective Action Process. Each monitoring organization must have a corrective action process in place that is executed upon discovery of nonconformances to the NATTS TAD, NATTS agency QAPP, and/or applicable agency SOPs. Each monitoring organization should ideally have a corrective action tracking procedure so that all corrective actions are available in a single location (e.g., binder, database, etc.) and may be readily referenced. Corrective actions are taken to remedy nonconformances found during audits or assessments; however, corrective action must also be performed and documented for nonconformances or problems noted during routine, everyday operations.

For each nonconformance, a corrective action report should be prepared which includes the following components:

- Unique corrective action report (CAR) identifier
- Identification of the individual initiating the CAR (staff person's name)
- Date of discovery of nonconformance
- Date of CAR initiation
- Area or procedure affected (e.g., PM_{10} metals sample collection)
- Description of the nonconformance (what happened and how it does not conform)
- Investigation of the nonconformance (how discovered, what is affected by the nonconforming work)
- Root cause analysis (what caused the nonconformance)
- Investigation for similar areas of nonconformance

- Immediate and long-term (if needed) remedial corrective actions (and documentation of when completed)
- Due date for remedial action completion
- Impact assessment of nonconformance
- Assessment of corrective action effectiveness
- Demonstration of return to conformance
- Follow up audit to ensure corrective actions were effective (with date completed)

Situations which would require a corrective action report include, but are not limited to:

- Repeated calibration failure
- Incorrect sample storage conditions
- Blank contamination
- Incorrect procedures followed
- Repeated QC acceptance criteria failures

Root cause analysis should be performed as soon as possible so remedial actions may be taken to correct the problem before it affects other procedural areas or additional samples and to minimize recurrence of the problem. For problems where the root cause is not immediately obvious, a stepwise approach should be taken to isolate the specific cause(s) of the nonconformance(s). Incorrect conclusions may result if too many variables are altered at one time, rendering the corrective action process ineffective.

An example CAR form is shown below in Figure 3.1-1.

Corrective Action Report

Corrective Action Report ID (CAR-YYYYMMDD-XXX):	
Initiated By:	
Area(s) or Procedure(s) Affected:	
Description of Nonconformance:	
Investigation of Nonconformance:	
Root Cause:	
Investigation for Similar Instances of Nonconformance:	
Immediate Corrective Action(s):	Date(s) completed
Impact Assessment of Nonconformance:	
Long-term Corrective Action(s):	Date(s) completed
Assessment of Effectiveness of Corrective Action:	
Additional Corrective Action Necessary: (optional – Provide CAR ID)	Date(s) completed
Return To Conformance (if applicable):	Date(s) completed
Follow-up Actions (if any): Date(s) completed	
Corrective Action Completion Date:	
Approval of Corrective Action Completion	
QA Manager Representative:	

Figure 3.1-1. Example Corrective Action Report

3.3.1.3.3 Quality Assurance Unit and Internal Audit Procedures. Each monitoring organization should have a QA group, or, minimally, an individual quality assurance officer (however named). This quality assurance unit is typically responsible for performing assessments (audits) of sample collection procedures, sample analysis procedures, data records, and the quality system as well as managing and overseeing the corrective action process, managing document control, performing QA training, and reviewing QC data as applicable. Monitoring organizations which contract laboratory analysis should ensure that the laboratory operates a QA program to oversee and conduct audits of these aspects for which the laboratory is responsible.

QA staff should be independent from project management to best ensure that nonconformances are addressed and remedied and to maximize the likelihood that data of sufficient quality are generated. Moreover, independent QA oversight is integral to ensuring that internal audits are objective. For agencies which may not have sufficient resources to dedicate an independent QA staff member, an individual not affiliated with a given activity may serve to perform QA functions. The quality assurance staff should conduct three types of audits:

- Technical systems audits (TSAs): An onsite review and inspection of the monitoring agency's monitoring program to assess compliance with the established regulations governing the collection analysis, validation, and reporting of ambient air quality data.[4] The auditor observes staff conducting sample collection and analysis activities and compares the activities performed against procedures codified in the agency QAPP and applicable SOPs, ensures proper documentation practices, verifies staff training records, verifies proper data reporting, and ensures all operations are performed in accordance with appropriate safety practices.

- Audits of Data Quality (ADQs): The auditor reviews reported data to ensure traceability of all measurements and calculations from initial receipt of sample collection media through to the final reported results. Calculations and data transformations are verified to be accurate.

- Quality Systems Audits (QSAs): The auditor reviews quality systems documents such as the agency QMP, QAPP, and SOPs to ensure they are current and to assess compliance with program requirements, such as those stipulated in this TAD.

The monitoring organization QAPP, SOP, or other suitable controlled document should define the schedule for audit frequency, the scope of each type of audit (i.e., which operational areas must be observed, which records must be reviewed, etc.), the timeline for following up on audit nonconformances, the timeline for conducting follow-up audits that ensure that nonconformances are being remedied in a satisfactory and timely manner, and the method for reporting audit outcomes to agency management and staff. For monitoring organizations which utilize contract laboratory analysis services, the laboratory QAPP, QMP, or similar controlled document should define these frequencies.

3.3.1.3.4 Calibration of Instruments. Each agency must define in the NATTS QAPP, SOP, or similar controlled document the frequency at which critical instruments must be calibrated and the acceptable tolerance for such calibrations. Critical instruments are defined as those whose measurements directly impact the accuracy of the final reported concentrations. The calibration of such instruments must be traceable to a certified standard and a standard calibration process. Critical instruments include, but are not limited to:

- Flow transfer standards
- Mass flow controllers, mechanical flow controllers, and meters generating flow readings for calculating total collected sample volumes and diluting standard gases
- Thermometers and barometers

- Volumetric delivery devices such as fixed and adjustable pipettes, bottletop dispensers, etc.
- Balances
- Pressure gauges and transducers when measuring pressures for dilution or standard preparation

Such critical instruments must be calibrated initially and the calibration verified (checked) periodically to ensure the calibration remains valid. Instruments must be recalibrated (or removed from service and replaced with a properly calibrated unit) when calibration verifications fail. Data generated with the failing equipment since the last acceptable calibration or calibration verification must be examined and considered for qualification. Monitoring agencies are encouraged to perform more frequent calibration checks (identified as recommendations) to limit the amount of data subject to qualification when calibration checks fail acceptance criteria. Frequency of calibration verifications must conform to Table 3.3-1 and must be addressed within the agency NATTS QAPP, SOPs, or similar controlled document.

Table 3.3-1. Calibration and Calibration Check Frequency Requirements for Standards and Critical Instruments

Instrument or Standard	Area of Use	Required Calibration Check [a] Frequency and Tolerance	Required Calibration [b] Frequency
Balances	Laboratory – Weighing standard materials, calibration of pipettes, determining mass loss for microwave metals digestion, weighing PAHs sorbent resin (XAD-2)	Each day of use with certified calibration check weights bracketing the balance load; Must be within manufacturer-specified tolerance covering the range of use	Initially, annually, and when calibration checks demonstrate an out of tolerance condition
Certified Weights	Laboratory – Calibration verification of balances	Check not required.	Annual certification by accredited metrology laboratory; Must be within manufacturer-specified tolerance
Mechanical Pipettes	Laboratory – Dispensing liquid volumes	Minimally quarterly, recommended monthly, by weighing delivered volumes of deionized water bracketing those dispensed; Must be within manufacturer-specified tolerance covering the range of use	Initially and when calibration checks demonstrate an out of tolerance condition
Bottletop Dispensers	Laboratory – Dispensing critical liquid volumes	Each day of use by delivery into a To Contain (TC) graduated cylinder Must be within ± 5%	When delivery volumes are set and when calibration checks fail criteria
Thermometers – Laboratory	Laboratory – Temperature monitoring of water baths, metals digestion, refrigerated storage units, canister cleaning ovens, and water for pipette calibration	Check not required.	Annual at temperature range of use or at not-to-exceed temperature – Correction factors applied to match certified standard

Table 3.3-1. Calibration and Calibration Check Frequency Requirements for Standards and Critical Instruments (Continued)

Instrument or Standard	Area of Use	Required Calibration Check [a] Frequency and Tolerance	Required Calibration [b] Frequency
Thermometers – Meteorological	Field – Recording environmental conditions during sample collection	Minimally quarterly, monthly recommended Must be within ± 0.5°C of certified standard at working temperature	Initially and when calibration checks indicate readings out of tolerance
Barometers	Field – Recording environmental conditions during sample collection Laboratory – Recording environmental conditions during instrument calibration	Minimally quarterly, monthly recommended Must be within ± 10 mm Hg of certified standard at typical barometric pressure	Initially and when calibration checks indicate readings out of tolerance
Flow Transfer Standards	Field – Critical flow orifices and volumetric flow meters for calibrating and verifying sampling unit flows Built-in thermometers and barometers must be calibrated	Check not required.	Annual; Must be within manufacturer-specified tolerance and cover the range of use
Pressure Gauges or Transducers	Field and Laboratory – Measure canister pressure/vacuum before and after collection, measure final canister vacuum following cleaning	Annual. Must be within 0.5 psi or manufacturer-specified tolerance and cover the range of use	Initially and when calibration checks show out of tolerance. Must cover the range of use
Flow Controllers and Meters – Laboratory	Laboratory – Mass flow controllers (MFCs), flow rotameters, or similar devices for measuring/metering gas flow rates for critical measurements (standard gas mixing)	Minimally quarterly, monthly recommended Flow within ± 2% of certified standards	Initially and when calibration checks demonstrate flows are out of tolerance
VOCs Sampling Units	Field – Collection of VOCs in canisters Flow control (such as MFC) Pressure gauge/transducer	If performed, minimally quarterly, for flow control, annually for pressure gauge/transducer Flow control (check is optional) within ±10% of certified flow If needed for critical measurements (canister starting/ending pressure), pressure gauge/transducer within ± 0.5 pounds per square inch (psi) of certified standard	Flow control - Initially and when components affecting flow are adjusted or replaced, or when calibration checks demonstrate flows are out of tolerance Pressure gauges/transducers – initially and when calibration checks demonstrate flows are out of tolerance
Carbonyls Sampling Units	Field – Collection of carbonyls on 2,4-dinitrophenylhydrazine (DNPH) sorbent cartridges Flow control (such as MFC)	Minimally quarterly, monthly recommended Flow within ±10% of certified flow and design flow	Initially, when calibration checks demonstrate flows are out of tolerance, and when components affecting flow are adjusted or replaced

Table 3.3-1. Calibration and Calibration Check Frequency Requirements for Standards and Critical Instruments (Continued)

Instrument or Standard	Area of Use	Required Calibration Check [a] Frequency and Tolerance	Required Calibration [b] Frequency
PM_{10} Metals Sampling Units	Field – Collection of PM_{10} on filter media for metals analysis Flow control must be within tolerance If equipped, thermometer and barometer must be within field tolerances specified above	Minimally quarterly, monthly recommended Low volume flows within ±4% of transfer standard and ±5% of design flow High volume flows within ±7% of transfer standard and ±10% of design flow	Initially, when calibration checks demonstrate flows are out of tolerance, and when components affecting flow are adjusted or replaced
PAHs Sampling Units	Field – Collection of carbonyls on QFF, PUF, and XAD-2 media sampling modules Flow control must be within tolerance If equipped, thermometer and barometer must be within field tolerance specified above	Minimally quarterly, monthly recommended Flow within ±10% of certified flow and design flow	Initially, when calibration checks demonstrate flows are out of tolerance, and when components affecting flow are adjusted or replaced
GC/MS for VOCs analysis	Laboratory – Analysis of VOCs from stainless steel canisters	Refer to Table 4.2-3	Initially, following failed continuing calibration verification (CCV) check, following failed bromofluorobenzene (BFB) tune check, or when changes/maintenance to the instrument affect calibration response
HPLC for carbonyls analysis	Laboratory – Analysis of carbonyl-DNPH extracts	Refer to Table 4.3-4	Initially, following failed continuing calibration verification (CCV) check, or when changes/maintenance to the instrument affect calibration response
ICP/MS for metals analysis	Laboratory – Analysis of PM_{10} digestates for metals	Refer to Table 4.4-3	Each day of analysis
GC/MS for PAHs analysis	Laboratory – Analysis of polyurethane foam (PUF)/resin/quartz fiber filter (QFF) extracts for PAHs	Refer to Table 4.5-3	Initially, following failed continuing calibration verification (CCV) check, following failed decafluorotriphenylphosphine (DFTPP) tune check, or when changes/maintenance to the instrument affect calibration response

[a] Calibration verification checks are a comparison to a certified standard, typically at a single point at which the instrument is used, to ensure the instrument or standard remains within a prescribed tolerance. Instruments or standards which exceed the tolerance must be adjusted to be within prescribed tolerances or replaced.

[b] Calibration refers to resetting the reading or setting or applying a correction factor to the instrument or standard to match a certified standard, typically at three or more points bracketing the range of use.

3.3.1.3.4.1 Calibration Verification (Checks)

Following instrument calibration, critical instruments must undergo periodic calibration verification (check) to ensure bias meets the assigned acceptance criterion. Calibration checks typically challenge the instrument at a single point typical of use or toward the middle of the calibration range. Calibration checks may also include multiple points bracketing the range of use. Instruments for which calibration checks are required include, but are not limited to:

- Mass flow controllers, mechanical flow controllers, and meters generating flow readings for calculating total collected sample volumes and diluting standard gases
- Volumetric delivery devices such as fixed and adjustable pipettes, bottletop dispensers, etc.
- Balances
- Analytical instruments generating concentration data (e.g. GC/MS, HPLC, ICP-MS)

3.3.1.3.5 Document Control System. Each monitoring organization must have a prescribed system defined in its NATTS QAPP or QMP for control of quality system documents such as QMPs, QAPPs, and SOPs. A properly operating document control system ensures that all documents integral in defining performance criteria and prescribing procedures are current, and that outdated or superseded documents are not available for inadvertent reference. All such controlled documents must minimally be approved by a cognizant manager (however named) who is ultimately responsible for the conduct of the work (e.g., monitoring agency director for an agency QMP, NATTS program manager for the NATTS QAPP, monitoring manager or laboratory manager for a field or analytical SOP, etc.), and by a QA staff member responsible for overseeing the work. Current versions of controlled documents must be readily available to each staff member conducting NATTS Program work.

To increase the likelihood that all applicable NATTS activities are performed according to current, approved procedures, the distribution of controlled documents should be managed and tracked such that only the current, approved versions are available in areas in which such documents are needed (for example, at field sites and in laboratories) and that outdated versions are removed once superseded. With the proliferation of networked computers at monitoring sites and within laboratories, it is convenient to have electronic versions of controlled documents available which are write-protected. Printing privileges of such read-only electronic documents should be disallowed, or, if printing is permitted, such documents should be identified via watermark with the date of printing and their expiration.

Procedures and frequency for changing and updating controlled documents should be clearly described in the QAPP, SOP, or similar controlled document. Preparing amendments is an efficient way to address minor changes to controlled documents. An amendment describes the change and rationale for the change, and may be appended to the document without requiring a complete revision of the document. Such amendments should be approved minimally by the cognizant manager (field operations manager or laboratory manager) responsible for the conduct of the work, and by a member of QA staff responsible for the document and overseeing the

work. For major changes to controlled documents, such as those required for a new sampling unit or updated laboratory information management system (LIMS), a new revision should be prepared and approved by all required signatories. A system for identifying revisions should be prescribed to allow tracking of versions. A typical example system uses whole numbers to designate major revisions and decimals to indicate minor revisions. For example, the first version of a QAPP would be version 1.0, a minor revision would update to version 1.1, and the next major revision would be version 2.0, and so on.

An effective date must be included on all controlled documents and they should include an issue date if this is different from the effective date. A period between the issue date and effective date permits staff to become familiar with the SOP prior to its becoming effective. A header or footer should indicate the effective date, version number, page number, and total number of pages included in the document. A best practice is to include a revision history section for each controlled document so that readers can quickly and efficiently ascertain changes from the previous version of the document.

Monitoring agencies (and laboratories) should forbid uncontrolled excerpts to be printed from controlled documents such as operation instructions or calibration standard preparation tables. These excerpts are then uncontrolled and may inadvertently be referenced when the version of origin is no longer effective. For the same reason, unless permitted by the agency's controlled document policy, uncontrolled shortcut procedural summary documents (summarizing SOP procedures) similarly should not be permitted. Such procedure summaries may be included in the NATTS QAPP or applicable SOP to ensure they are updated when the document is revised. Similarly, notes should not be recorded on controlled document hard copies unless permitted by the monitoring organization's controlled document revision or amendment process.

The review frequency for controlled documents should be described within the QMP, QAPP, or similar controlled document. Periodic review of controlled documents must be performed to ensure that they adequately describe current agency policies and procedures. Each such review and outcome of the review (e.g., adequate, minor revision needed, major revision needed, etc.) should be documented. The agency NATTS QAPP must be reviewed annually and associated SOPs are recommended to be reviewed annually, but must minimally be reviewed every three years. SOPs must be reviewed following major changes to network guidance to ensure they are compliant with the updated guidance.

3.3.1.3.6 Training Requirements and Documentation, and Demonstration of Capability. The training required for each staff member who conducts NATTS Program work must be prescribed in the agency NATTS QAPP, SOP, or similar controlled document, and the completion of each required training element must be documented. Specifically, staff must read, and document that they have read and understood, the most recent versions of the NATTS quality system documents (QAPP, SOPs, etc.) pertaining to their responsibilities.

Each monitoring organization must have minimum requirements for staff position experience including a combination of education and previous employment experience. In addition to documented experience, each staff member must be approved by cognizant management to conduct the activities for which they are responsible. Such approval should be granted initially

before beginning work and periodically thereafter, and should be minimally based on successful completion of a demonstration of capability (DOC) process. DOCs are described in the subsections below.

Each staff member must have training documented which indicates the staff member's training is current for each procedure performed, as required by the agency QMP, NATTS QAPP, SOP, or similar controlled document. Training documentation can consist of hard copy or electronic documentation and may be located in numerous files or locations, provided it can be retrieved for auditing purposes. In addition to relevant DOC documentation, the training records should include items related to experience such as a resume or curriculum vitae, certificates from training coursework, and a job description specific to the monitoring organization.

3.3.1.3.6.1 Initial Demonstration of Capability

Once the staff member has read the relevant current SOP, and documented such, the staff member must demonstrate proficiency with a given procedure prior to performing activities to generate or manipulate NATTS program data. One method by which such could be accomplished is as follows. First, the staff member observes an experienced staff member performing the procedure. Next, the trainee conducts the activity under the immediate supervision of and with direction from an experienced staff member. Finally, the trainee performs the activity independently while being observed by an experienced staff member. To ensure all aspects of a procedure are captured in the initial DOC, it is recommended that a checklist be developed that includes all required steps consistent with the applicable quality system document(s) to perform the activity. Regardless of the actual initial DOC process selected for implementation, the process to be implemented and its acceptance criteria must be defined in the QAPP, SOP, or similar controlled document.

3.3.1.3.6.2 Ongoing Demonstration of Capability

Each staff member performing NATTS Program field work must demonstrate continued proficiency with tasks for which they are responsible, minimally every three years, but recommended to be annually. The staff member should be observed by a QA staff member (as part of an audit), experienced staff member, or responsible manager.

Laboratory staff must annually demonstrate continued proficiency by completing one of the following:

- Repeat of the IDOC procedure.
- Acceptable performance on one or more blind samples (single blind to the analyst) following the approved method for each target analyte. Acceptable performance is indicated by demonstrating recovery within limits of the method LCS for each target analyte.
- Analysis of at least four consecutive LCSs with acceptable levels of bias. Acceptable performance is indicated by demonstrating recovery within limits of the method LCS for each target analyte.

- Acceptable performance on a PT sample. Acceptable performance is defined by the provider of the PT sample, as indicated by no results marked as "Unacceptable" or equivalent, for target analytes.

As with the initial demonstration of capability, the continuing DOC process and its applicable process acceptance criteria must be prescribed in the agency NATTS QAPP, SOP, or similar controlled document.

3.3.1.3.7 Sample Custody and Storage. Procedures and details related to sample custody and sample storage must be included in each monitoring organization's NATTS QAPP or similar document such as a sample handling SOP.

The COC is a documented trail of who had possession of a sample or group of samples at any specific point from collection through receipt at the laboratory. Custody records must include details of transfers of possession between individuals, between individuals and shippers (when applicable), and to storage at the laboratory and any pertinent details such as storage location and conditions. It is strongly recommended to maintain sample integrity that samples be protected and access to the samples be limited to those responsible for the samples.

Sample custody begins when media are readied for dispatch to the field monitoring site. At this point, a COC form, sample collection form with portions dedicated to documenting custody transfers, or other form as defined by the monitoring agency, must accompany the sampling media until they are received at the laboratory for analysis. Each time the sampling media are transferred, the individual relinquishing the sample and receiving the sample, the date and time, and the storage conditions (for carbonyls and PAHs samples) should be documented so the history of the sample is traceable and can be reconstructed. Storage conditions for carbonyls and PAHs samples must be monitored with a calibrated thermometer and storage records should include unique identifiers for the thermometers monitoring the storage units.

Sample collection forms or other forms as defined by the monitoring agency may double as a COC form provided they include sufficient space for documenting all sample transfers and storage conditions.

If not already assigned prior to dispatching to the field, upon receipt at the laboratory each specific field-collected sample medium (cartridge, filter, canister, etc. including all field QC) must be uniquely identified for tracking within the laboratory. This unique identifier allows each sample to be tracked to ensure proper storage within the laboratory and to avoid switching of samples which can invalidate sample data.

3.3.1.3.8 Traceability of Reagents and Standard Materials. Each monitoring organization must prescribe in its NATTS QAPP, or similar controlled document, the information to be recorded and maintained for traceability of reagents and standard materials and must codify the requirements for their labeling.

All reagents and standard materials utilized in the preparation and analysis of NATTS Program samples must be of known concentration or purity as documented by a certificate of analysis

(COA) or similar certification. Such certification documents must be retained. The one exception to this is for deionized water which is sourced from a water polisher, for which records of the maintenance must be maintained to demonstrate that the water is of appropriate quality. When prepared in the laboratory, the source of all reagents must be documented (in a logbook or similar) and be traceable to the certificates of analysis. Lot or batch numbers for each reagent (acid, solvent, etc.) must be documented for all preparations. Critical volume measurements (e.g. delivered volumes of stock standards, final volumes of diluted standards) must be documented in the preparation log when used for reagent or standard preparation, including unique identifiers (where applicable) for measurements by way of volumetric syringes, mechanical pipettes, and volumetric flasks, among other methods. The conditions at which the reagents and standards are stored must be documented, particularly for those reagents and standards which require special conditions such as refrigeration or protection from light. If maintenance of a specific temperature range or not-to-exceed temperature is required, the temperature(s) of storage container(s) must be measured and documented at a prescribed frequency (recommend minimally daily during normal working hours) and the calibration of thermometers must be certified and traceable at the critical temperature (e.g. for a carbonyls sample storage refrigerator, the thermometer must be calibrated at 4ºC). A calibrated min-max type thermometer or continuous monitoring is recommended to ensure that the not-to-exceed temperature is maintained.

Expiration dates must be assigned to reagents and standards and must be set as the earliest expiration date among any component comprising the reagent or standard. If the expiration date is given as a month and year, the date after which the reagent or standard may not be used is understood to be the last day of the indicated month. For reagents or standards which were not assigned an expiration by the supplier, the monitoring agency may assign an expiration (recommended not to exceed five years). The policy for assigning the expiration date when not provided by the manufacturer must be prescribed in the monitoring agency QAPP, SOP, or similar controlled document.

3.3.1.3.9 Labeling. Each NATTS monitoring organization must have a prescribed procedure for labeling of all samples, standards, and reagents. Each must be uniquely identified and the identifier clearly labeled on the applicable container (e.g., VOCs canister tag, DNPH cartridge foil pouch, metals filter holder, PAHs cartridge transport jar, GC vial containing solvent, etc.).

Standards and reagents must be minimally labeled to identity the contents (e.g., 69-component VOC blend in nitrogen, 2 µg/mL benzo(a)pyrene in hexane, 2% v/v nitric acid, etc.), and should include the preparation date and expiration date. All standards and reagents prepared or mixed in the laboratory must be traceable to a preparation log.

3.3.1.3.10 Early Warning Systems – Control Charts. Laboratories should employ control charting where practical to track QC parameters. If used, the process of control charting should be described in the NATTS QAPP, SOP, or similar controlled document. Parameters suitable for control charting include concentrations measured in QC samples such as blanks, laboratory control spikes, matrix spikes, secondary source calibration standards, internal standards, and proficiency test results. Control charts may be prepared with spreadsheets and

many LIMS incorporate control charting capabilities. Once implemented, control charts are simple to maintain and are a valuable tool for evaluating trends and may provide an alert before nonconformances occur. Control charts should be periodically updated and reviewed to ensure data inputs are current and that associated control limits meet method-specified criteria. The update frequency should be prescribed in the applicable controlled document.

3.3.1.3.11 Spreadsheets and Other Data Reduction Algorithms. While spreadsheets and other automated or semi-automated data reduction algorithms, for instance, those contained in LIMS software, are valuable tools for transforming and reducing data generated by sampling and analysis instruments, they have limitations and may be sources of error. If a NATTS agency in fact employs such processes it should prescribe the NATTS QAPP, SOP, or similar controlled document the details for preparation, review, and control of data reduction spreadsheets or of other non-commercial automated and/or semi-automated data transformation and reduction algorithms and processes. Implementation of such processes will require an initial time investment, but should minimize errors and subsequently increase the efficiency and speed of data reporting. If an agency were to implement such processes, it should codify the relevant procedures into its QAPP or other quality system document and may consider adoption of the following best practices.

Where possible, manual entry of instrument data into spreadsheets and/or non-commercial automated data transformation/reduction algorithms must be minimized. Rather, the direct importation of data outputs from instruments into such systems is preferable so as to avoid transcription errors. Furthermore, data reduction spreadsheets or other non-commercial algorithms must be validated and locked/non-editable to ensure that critical formulas are not inadvertently altered. The process of validation of the spreadsheet or non-commercial algorithm must be codified in the quality system document such that it is known and verifiable that all critical aspects of the data reduction procedure have been confirmed to be technically defensible, valid, and error-free. This validation should be performed when the spreadsheet or non-commercial algorithm is revised.

3.3.1.3.12 Software Validation, Testing, Updating, and Upgrading. Each agency performing NATTS Program work should have prescribed within the agency NATTS QAPP, SOP, or similar controlled document policies and procedures for testing, updating, and upgrading computer software systems employed for data generation and manipulation such as chromatography data systems (CDSs), LIMS, and other instrument software where applicable. The policies and procedures should detail the responsible individuals, testing required, and documentation to be maintained.

3.3.1.3.12.1 Software Validation

Off-the-shelf software packages such as spreadsheet programs are presumed to be validated. It is strongly recommended that individual spreadsheets should be validated as described in Section 3.3.1.3.11. Other software packages such as CDS should undergo validation by manually calculating values to ensure that software outputs match the expected result. Due to the differences in algorithms or limitations to how software packages handle calculations, there may be slight differences between commercial software package outputs and spreadsheets or other

software systems. Such differences should be noted and addressed where possible if they impact digits which are significant in the calculations. Records of software validation must be maintained.

3.3.1.3.12.2 Software Testing

Once validated, software packages should be tested minimally annually and when updated or upgraded to ensure that calculations are being performed as expected. This may be performed by processing a previous dataset through the software and comparing the outputs for parity. The rationale behind such testing is to ensure that software systems and calculation regimes have not become corrupted. Discrepancies in outputs must result in corrective action to rectify the discrepancies.

3.3.1.3.12.3 Software Updating and Upgrading

Software manufacturers periodically release software updates to correct bugs, improve the user interface, or include new functionality, etc. Updates or upgrades installed should be documented in a log and be verified for proper operation by the testing regime prescribed in Section 3.3.1.3.12.2. Agencies should verify that upgrades were performed and the date they were performed.

3.3.1.3.13 Review of Records. To ensure that sample collection and analysis activities were performed as prescribed, are documented completely and accurately, and to identify potential nonconformances that may invalidate data, all logbooks, forms, notes, and data must be reviewed by a second individual who has familiarity with the procedure but who did not generate the record. Field site notebooks, site equipment maintenance logs, sample collection forms, COC forms, laboratory preparation logs, analysis instrument logs, storage temperature logs, and all other critical information must be reviewed on a periodic basis by an individual who did not record the documentation. Each record should minimally be reviewed for legibility, completeness, traceability, and accuracy (including hand calculations not performed by a validated spreadsheet). It is also recommended that reviews should determine if the procedures followed were codified and appropriate. These reviews must be documented, either within the records themselves, or in a separate review notebook or form indicating the individual performing the review, the materials reviewed, and when the review was performed. Details of the review scope, schedule, responsible individuals, and required documentation must be described in the NATTS QAPP, SOP, or similar controlled document. These reviews should occur minimally quarterly and a best practice would be to conduct reviews monthly.

If documentation errors are noted during review, they should be corrected as soon as practical. Correction of handwritten entries must be performed with a single line, the correct entry must be made nearby or be traceable to an annotated footnote, the individual making the correction must be identified by signature or initials, the notation must include the date the correction was made, and the notation should include the rationale for the correction. Corrections to electronic logs must likewise not overwrite the original record, must identify the individual making the correction, must include the date of the correction, and should include the rationale for the

correction. Further guidance on maintaining electronic logs is available in the EPA Technical Note - Use of Electronic Logbooks for Ambient Air Monitoring. [5]

Note that reviewing records as described in this section is a component of the data verification process described in the next section, but should not be substituted for the data verification process.

3.3.1.3.14 Data Verification and Validation. Data verification is the systematic process for evaluating objective evidence (data) for compliance with requirements for completeness and for correctness as stipulated by a specific method. Objective evidence consists of the records such as sample collection forms, sample storage records, laboratory preparation records, calibration records, analysis results, etc. Validation is the confirmation that verified data have met specific intended use requirements, i.e., meeting DQO requirements prescribed in the NATTS QAPP.[6]

Spurious data have an outsized influence on statistical analysis and modeling; thus, data must be closely examined to ensure that concentration values accurately reflect air quality conditions at the monitoring site through verification and validation. Monitoring organizations must not censor (invalidate) data they consider to be anomalous or spurious. Data should only be invalidated if they do not meet the critical specifications in the validation tables in Section 7 or when there is a known problem with the data which would invalidate them. For data suspected to be spurious or anomalous, they should be qualified appropriately when entered into AQS so the end data user can decide the most suitable manner for handling the data.

Each monitoring organization must have processes and policies which must be described within its NATTS QAPP or other quality systems document for data verification, data validation, and the associated documentation that is generated and retained during the processes of verification and validation of data. It is a best practice that NATTS agencies perform data verification in accordance with the tables in Section 7 of this TAD where method-specific criteria may be found. Additional information on implementing and structuring data validation and verification policies and procedures is available in *Guidance on Environmental Data Verification and Data Validation, EPA QA/G-8, EPA/240/R-02-004.*[6]

3.3.1.3.14.1 Data Verification

The data verification process begins when sample media are dispatched to the field for collection and ends following final review of a completed data package. Verification includes many of the aspects of data review discussed in Section 3.3.1.3.13 as well as additional QC checks such as verification of proper sample handling and verification of calculations. Once data verification is completed, data validation is conducted. Given in this section is a generic data verification process that a NATTS agency may adopt. Data verification is not required, but is *strongly recommended*.

Upon retrieval of samples in the field, the field operator verifies that sample collection parameters comply with SOPs and documents the collection details on the field sample collection form. At the laboratory, custody documentation is reviewed to ensure that sample

collection documentation meets specification and does not exhibit anomalies which would invalidate the collected sample. Laboratory analysts ensure that media have been stored properly and that QC samples are prepared according to method specifications. Following acquisition of the analytical data, the analyst reviews QC results as well as the acquired data to ensure proper analyte identification and to verify that method-specified acceptance criteria are met. A peer then reviews the entire data package beginning with sample collection and custody documentation through preparation, analysis, and concentration calculations so as to ensure that method procedures were properly followed, calculations are correct, and method-specific acceptance criteria are met. At any point during the initial and/or peer review, errors must be corrected and additional notes added to describe problems or anomalies in the sample collection and analysis processes. QC failures or method deviations must be documented and appropriate flags applied to the results so staff performing data validation may be alerted regarding data which may be compromised or require invalidation.

3.3.1.3.14.2 Data Validation

Data validation is performed following the data verification process and is a separate process from the network-wide assessments made by data users to evaluate trends and assess whether data meet MQOs. During validation data are evaluated by the monitoring agency for compliance with specific use requirements which may include comparison of collocated sample results, examination of meteorology data, sample collection notes, and custody forms, and review of historical data for trends analysis and identification of outlier data. Attainment of the NATTS MQOs should also be assessed by monitoring agencies to determine if the data will support attainment of the NATTS DQO. Failure to attain the NATTS MQOs must prompt corrective action. Given in the remainder of this section is a generic data validation process that a NATTS agency may adopt. Note that data are not being validated if the monitoring agency is not performing data validation since he EPA does not perform subsequent data validation.

An appropriate starting point for validating data involves preparing summary statistics by calculating the central tendency of the dataset along with the standard deviation and relative standard deviation of the concentrations of each HAP. The central tendency may be calculated as the arithmetic mean, geometric mean, median, or mode:

- Arithmetic mean: The sum of the measured concentration values divided by the total number of samples in the dataset.
- Geometric mean: The *nth* root of the product of *n* concentration values.
- Median: The concentration value represented by the midpoint of the dataset when the concentration values are placed in numerical order. Fifty percent of the resulting concentration values will be above this value and 50% will be below.
- Mode: The concentration value with the highest frequency.

Once the summary statistics have been prepared, each HAP and combination of HAPs may be evaluated using graphical techniques to identify anomalous data and outliers. Graphical techniques permit comparison of concentrations of each HAP to the expected concentrations and

relative concentrations of other HAPs to inspect for values which stand out. Time series plots, scatter plots, and fingerprint plots, described below, are valuable tools for validating data.

- Time series plots: Concentrations are plotted on the y-axis against collection date (time) on the x-axis. Extreme or anomalous values are immediately identifiable in individual HAP plots, and may be more powerful when multiple HAPs are plotted together. HAPs which are typically emitted from the same type of source (i.e., benzene and toluene from mobile sources) and from different sources (i.e., formaldehyde and PM_{10} nickel) can provide insight on whether concentration anomalies are realistic to the collected sample or may be an artifact of the collection or analysis of the sample.
- Scatter plots: Concentrations of pairs of HAPs are plotted such that each HAP (e.g., benzene and toluene) is dedicated to the y-axis or x-axis such that the coordinates of each plotted point are set by the benzene and toluene concentrations measured during a given sampling event. The resulting plots generally show points which are clumped together such that they have a well-defined relationship. Points which lie outside of the well-defined area are then generally identifiable and can be further investigated.
- Fingerprint plots: Concentrations of all HAPs within a given class (e.g., VOCs, carbonyls, etc.) are plotted on the y-axis against the molecular weight, alphabetical order, or some other consistent order on the x-axis which enable discerning patterns or identifying anomalies. Fingerprints prepared for each sampling event are compared and will typically be very similar among events. Plots which show markedly different patterns may indicate anomalous results. For instance, during a specific sampling event a HAP may be observed at a concentration much higher or much lower than expected given the typically observed pattern between concentration and molecular weight (alphabetical order, etc.), and such is evidence of a spurious result for this HAP for this sampling event.

Confidence is increased for concentration data which do not appear anomalous when plotted using these graphical tools. For data which appear to be anomalous, they should be flagged for follow up and the root cause investigated.

The free Data Analysis and Reporting Tool (DART) software was developed with EPA funding and incorporates preparation of the graphical displays mentioned above. DART is available at airnowtech.org at the following URL: http://airnowtech.org/dart/dartwelcome.cfm (all users must have an account with username and password).

3.3.1.3.15 Reporting of Results to AQS. Each monitoring organization must prescribe procedures and policies for the reporting of all applicable information generated in the conduct of the NATTS Program to the EPA AQS database. AQS is a repository of data from state, local, and tribal agencies as well as federal organizations. The stored data consist of descriptions of monitoring sites and associated monitoring equipment, reported concentrations of air pollutants, data flags, and calculated summary and statistical information.

This section discusses reporting of data to AQS and provides details on the following monitoring agency requirements. Monitoring agencies must:

- Report NATTS data to AQS within 180 days from the end of the calendar quarter in which samples were collected
- Report concentration data for all Tier I NATTS required HAPs
- Verify and validate data according to the monitoring agency policies
- Report QA data (field blanks, trip blanks, collocated, duplicate, replicate analysis, and lot blanks)
- Qualify data appropriately in relation to the MDL (EPA plans to implement automatic flagging for measured concentrations)
- Add other qualifiers as necessary when data do not meet acceptance criteria
- Report MDLs with the sample data
- Report data in appropriate units in standard conditions (except PM_{10} metals)
- Verify data were input to AQS properly

The concentrations of all HAPs measured during the execution of the NATTS Program must be input into AQS within 180 days from the end of the calendar quarter during which the applicable air samples were collected. All data uploaded to AQS must have been previously verified and validated per the requirements codified in the cognizant monitoring agency's quality system. Data preparation and entry are also the responsibility of each participating monitoring organization.

AQS permits entry of qualifier codes consisting of the following four different types: Informational Only, Null Data Qualifier, QA Qualifier, and Request Exclusion. Request Exclusion qualifiers do not apply to NATTS data. All uploaded data must be appropriately qualified, as necessary, in AQS. More than one qualifier may be reported with a concentration value to provide additional information regarding the applicable concentration result. However, the null data qualifier flag must not be entered with other flags, as such a flag indicates that no concentration data are reported. Invalidation of concentration results and the subsequent assignment of a null qualifier code in AQS require careful consideration and should be consistent with data review and reporting procedures in the monitoring agency QAPP. Data which do not meet method QC requirements may still be of use and should be entered with the appropriate QA qualifier code. AQS qualifier codes appropriate for qualification of NATTS data are listed in Table 3.3-2 (excludes Null Data Qualifier codes).

Table 3.3-2. AQS Qualifier Codes Appropriate for NATTS Data Qualification

Qualifier Code	Qualifier Description	Qualifier Type Code
1	Deviation from a CFR/Critical Criteria Requirement	QA
2	Operational Deviation	QA
3	Field Issue	QA
4	Lab Issue	QA
5	Outlier	QA
6	QAPP Issue	QA
7	Below Lowest Calibration Level	QA
CC	Clean Canister Residue	QA
CL	Surrogate Recoveries Outside Control Limits	QA
DI	Sample was diluted for analysis	QA
EH	Estimated; Exceeds Upper Range	QA
FB	Field Blank Value Above Acceptable Limit	QA
FX	Filter Integrity Issue	QA
HT	Sample pick-up hold time exceeded	QA
IC	Chem. Spills & Indust Accidents	INFORM
ID	Cleanup After a Major Disaster	INFORM
IE	Demolition	INFORM
IH	Fireworks	INFORM
II	High Pollen Count	INFORM
IJ	High Winds	INFORM
IK	Infrequent Large Gatherings	INFORM
IM	Prescribed Fire	INFORM
IP	Structural Fire	INFORM
IQ	Terrorist Act	INFORM
IR	Unique Traffic Disruption	INFORM
IS	Volcanic Eruptions	INFORM
IT	Wildfire-U. S.	INFORM
J	Construction	INFORM
LB	Lab blank value above acceptable limit	QA
LJ	Identification Of Analyte Is Acceptable; Reported Value Is An Estimate	QA
LK	Analyte Identified; Reported Value May Be Biased High	QA
LL	Analyte Identified; Reported Value May Be Biased Low	QA
MD	Value less than MDL	QA
MX	Matrix Effect	QA
ND	No Value Detected	QA
NS	Influenced by nearby source	QA
QX	Does not meet QC criteria	QA
SQ	Values Between SQL and MDL	QA
SS	Value substituted from secondary monitor	QA
SX	Does Not Meet Siting Criteria	QA
TB	Trip Blank Value Above Acceptable Limit	QA
TT	Transport Temperature is Out of Specs	QA
V	Validated Value	QA
VB	Value below normal; no reason to invalidate	QA
W	Flow Rate Average out of Spec.	QA

The most up-to-date AQS codes and descriptions, including qualifier codes and definitions, are available at the following URL:

https://www.epa.gov/aqs/aqs-code-list

Concentrations of HAPs uploaded to AQS must be flagged according to whether they are above or below the sample quantitation limit (SQL) or method detection limit (MDL) thresholds. Concentration data less than the laboratory MDL must be flagged with the QA qualifier code MD, data greater than or equal to the MDL but less than the SQL (3.18-fold the MDL) must be flagged using the QA qualifier code SQ. All concentration values for qualitatively identified analytes, even those less than MDL, must be reported to AQS and must not be censored by substitution of one half the MDL, by replacement with 0, or by any other method. Negative concentrations must not be translated to zero for reporting purposes. Where qualitative identification acceptance criteria are not met for a given HAP, its concentration must be reported as zero and flagged as ND. The convention for reporting concentration data and the associated QA flags are shown in Table 3.3-3.

Table 3.3-3. Required AQS Quality Assurance Qualifier Flags for Various Concentrations Compared to a Laboratory's MDL and SQL

Concentration Level	Reported Value	Associated QA Flag
≥ SQL	measured concentration	no flag
≥ MDL but < SQL	measured concentration	SQ
< MDL	measured concentration	MD
HAP not qualitatively identified	0	ND

The MDL for a given HAP must be reported to AQS along with the HAP's concentration or AQS will reject the submission. The reported MDL should ideally be normalized to the collected air volume for the respective air sample. Normalization of the MDL to the collected air volume is required when the collected air volume for the sample is greater than 10% different from the target collected air volume. If the total collected air volume is not within 10% of the target collected air volume, the monitoring organization should take corrective action which may involve troubleshooting the sampling unit and verifying calculations. For example, the target collected air volume for carbonyls sampling at 0.75 L/min is 1.08 m^3 and the formaldehyde MDL is 0.052 $\mu g/m^3$ for this target volume. For a total collected sample volume of 0.95 m^3, the collected volume is ~12% lower than the target, and requires normalization of the formaldehyde MDL as follows (MDL increases by the ~12% to account of the reduced sample volume):

$$\frac{0.052\ \mu g/m^3 \cdot 1.08\ m^3}{0.95\ m^3} = 0.059\ \mu g/m^3$$

Reporting units must be consistent across the NATTS network to ensure that data may be statistically combined with minimal manipulation. HAPs must be reported in the following unit conventions:

- VOCs – parts per billion by volume (ppbv)
- Carbonyls – mass per unit volume (e.g. $\mu g/m^3$ or ng/m^3)
- PAHs – mass per unit volume (e.g. $\mu g/m^3$ or ng/m^3)
- Metals – mass per unit volume (e.g. $\mu g/m^3$ or ng/m^3)

All concentrations, with the exception of those for PM_{10} metals, must be reported to AQS corrected to the standard conditions of 760 mm Hg and 25°C. PM_{10} metals data must minimally

be reported in local conditions but may also be reported in standard conditions at the discretion of the monitoring organization. Except for PM_{10} metals, this requires that sites calibrate sampling unit instruments in standard conditions or that conversion to standard conditions is performed with average temperature and barometric pressure readings taken during sample collection.

Sample collection must be performed from midnight to midnight local standard time (no correction for daylight savings time) which may require adjustment of recorded collection times generated by sampling unit clocks to ensure values are accurately input into AQS. Clock timers controlling sampling unit operation must be adjusted so that digital timers are within ±5 minutes of the reference time (cellular phone, GPS, or similar accurate clock) and mechanical timers within ±15 minutes.

NATTS agencies are required to report data for each of the Tier I analytes listed in Table 1.2-1 and are also encouraged to report data collected for Tier II analytes. Careful attention must be paid to coding of data uploaded to AQS to ensure that the five-digit parameter code is accurate and that the associated units comply with those listed above.

NATTS sites may have numerous monitors collecting data for programs besides NATTS. Each individual monitor of a given type (VOCs, carbonyls, PM_{10} metals, and PAHs) and duplicate samples collected from a single monitor are to be assigned a parameter occurrence code (POC) by the state, local, or tribal agency (SLT). There is no guidance on how POCs are assigned by SLTs and a survey of NATTS sites indicates that several monitors can be assigned the same POC. Data uploaded to AQS indicate the assigned POC, but the POC does not indicate whether the associated data are from a primary monitor, duplicate sample from the primary monitor, duplicate sample from a duplicate monitor, or collocated sample. Due to the ambiguous nature of POC assignment, each NATTS agency must prescribe and maintain a legend of POCs for minimally each of the four monitor types required for NATTS in the annual network plan (ANP) or other controlled document. The recommended convention is to assign a lower POC to the primary monitor and a higher POC to the duplicate and/or collocated monitor.

QA data including, but not limited to, field QA samples such as field and trip blanks and collocated and duplicate test samples, laboratory QA results from replicate analyses (as required by the workplan), and lot blanks must be reported to AQS. AQS also accepts laboratory blanks and laboratories are not required to, but may, report method blank data to AQS. Guidance for reporting QA samples (blanks and precision samples – collocated, duplicate, and replicate samples) is included in Appendix B.

Prior to submission of data to AQS, all data must be reviewed to ensure the parameter code, POC, unit code, method code, and any associated qualifier or null codes are properly assigned. In addition, the reported parameters should specify the NATTS network affiliation.

AQS instructions for data upload are described in the AQS User Guide and additional AQS manuals and guides available at the following URL:

http://www3.epa.gov/ttn/airs/airsaqs/manuals/

Additional assistance is available by calling the AQS help line at (866) 411-4372.

3.3.1.3.15.1 Corrections to Data Uploaded to AQS

If it discovered during data validation, as a result of corrective action, or through other means that erroneous data have been reported to AQS, the erroneous data must be deleted, and the corrected data uploaded to AQS. EPA Region staff must be notified when the erroneous data are discovered and SLTs must notify the EPA Region to correct the records in AQS when changes are needed to large swaths of data (e.g. a calendar quarter) or data from previous calendar years are to be altered. Monitoring agencies should also notify data users which may have provided notification of data query (as is done for AQS data pulls for conducting the NATTS assessments and data analysis for preparing the NATA), as the updated data may impact the data user's analysis outcomes.

3.3.1.3.16 Records Retention and Archival, and Data Backup. All records required to reconstruct activities to generate the concentration data for NATTS Program samples must be retained for a minimum of six years. The basis for the six-year retention period is that this covers the two successive three-year periods over which trends in HAP concentrations are determined. If problematic or anomalous data are observed during trends analysis, the archived records will be available for review to investigate the suspicious data. Quality system documents such as QMPs, QAPPs, and SOPs, sample collection and analysis records, maintenance logs, reagent logs, etc. must also be retained for at least six years. Requirements for records retention, including electronic records, must be prescribed in the QMP, agency NATTS QAPP, or similar controlled policy document.

Electronic data must also be retained for a minimum of six years. Data generated by sampling and analysis instruments, including all QA/QC data, as well as data stored in databases and/or in a LIMS must be backed up on a periodic basis as defined in an applicable quality system document such as the QAPP. Archived electronic data must be stored in a manner such that they are protected from inadvertent alteration. Additionally, monitoring agencies must maintain accessibility to the archived data which may include maintaining legacy software systems or computers or may involve conversion of the data to a format which is compatible with current computers and software systems. Monitoring agencies should consider the compatibility of the archived data when upgrading or replacing computer systems and software to ensure the archived data remain accessible.

3.3.1.3.17 Safety. While not strictly a quality system element, safety is integral in ensuring the continued collection of quality data. Each monitoring organization must codify appropriate safety requirements and procedures within the NATTS QAPP or similar controlled policy document. For monitoring organizations with existing safety plans or programs, these may be referenced within the QAPP. Safety plans should include information regarding safety equipment, inspection frequency of safety equipment, and safety training frequency.

3.3.2 Standard Operating Procedures. Each monitoring organization conducting NATTS Program work must develop and maintain SOPs, however named, which must describe in detail the procedures for performing various activities needed to execute air sampling, sample

analysis, data reduction, and data reporting, among others, for the NATTS program. It is not acceptable to simply cite a method document (e.g., EPA Compendium Method TO-11A) or instrument manual as the SOP, although these documents may serve as the basis for an SOP and may be referenced in the SOP. Instrument manuals and the compendium methods do not include sufficient detail on the specific procedures and/or equipment information necessary to perform the procedures and generally offer several different procedures or conventions for performing activities or operating equipment. SOPs must reflect current practice and the work performed must be in accordance with SOPs. SOPs must be written with sufficient detail to enable an individual with limited experience with or knowledge of the procedure, but with basic understanding of the procedure, to successfully perform the procedure when unsupervised. Production, review, revision, distribution, and retirement of SOPs must conform to the requirements prescribed by the monitoring organization's document control system as discussed in Section 3.3.1.3.5.

SOPs can be developed in many formats but should minimally contain information regarding the following, where applicable:

- Title (e.g., Collection of Ambient VOCs Samples in Stainless Steel Canisters)
- Scope and Objectives (e.g., covers sample collection but not analysis)
- References (e.g., EPA Compendium Method TO-11A)
- Definitions and Abbreviations
- Procedures – instructions (usually step-by-step) for performing activities within the scope of the SOP including information on required materials, reagents, standards, and instruments; sample preparation; instrument calibration and analysis, and data analysis and reporting procedures, among other information, as required
- Interferences
- Calculations
- Quality control acceptance criteria with associated corrective actions
- Safety information
- Revision history

The author of each SOP must be an individual knowledgeable with the activity and the organization's internal structure who has the responsibility for the veracity and defensibility of the document's technical content. A team approach may be followed to develop the SOP, especially for multi-tasked processes where experience of a number of individuals is critical to the procedure. SOPs must be approved in accordance with Section 3.3.1.3.5 of this TAD and must be revised when they no longer reflect current practices. At a minimum, SOPs are to be reviewed by the author and a member of QA to determine if revisions are needed and these reviews and revisions must be documented. The frequency for review is recommended to be annually, but must not exceed three years, and the period must be prescribed in the monitoring agency's NATTS QAPP, QMP, or similar controlled document. Once a new version is effective, the previous version must be retired and may not be referenced for conducting procedures.

3.4 References

1. Environmental Protection Agency. (September 2005). *Quality Assurance Guidance Document. Quality Management Plan for the National Air Toxics Trends Stations.* (EPA Publication No. EPA/454/R-02-006). Office of Air Quality Planning and Standards. Emission, Monitoring, and Analysis Division. Research Triangle Park, North Carolina. Available at (accessed October 19, 2016): https://www3.epa.gov/ttnamti1/files/ambient/airtox/nattsqmp.pdf

2. Environmental Protection Agency. (March 2001). *EPA Requirements for Quality Assurance Project Plans. EPA QA/R-5* (EPA Publication No. EPA/240/B-01-003). Office of Environmental Information, Washington, DC. Available at (accessed October 19, 2016): https://www.epa.gov/sites/production/files/2016-06/documents/r5-final_0.pdf

3. Environmental Protection Agency. (December 2002). *Guidance for Quality Assurance Project Plans. EPA QA/G-5* (EPA Publication No. EPA/240/R-02-009). Office of Environmental Information, Washington, DC. Available at (accessed October 19, 2016): https://www.epa.gov/sites/production/files/2015-06/documents/g5-final.pdf

4. Environmental Protection Agency. (May 2013). *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II.* (EPA Publication No. EPA-454/B-13-003). Office of Air Quality Planning and Standards, RTP, NC. Available at (accessed October 19, 2016): https://www3.epa.gov/ttnamti1/files/ambient/pm25/qa/QA-Handbook-Vol-II.pdf

5. Environmental Protection Agency. (April 20, 2016). *Technical Note – Use of Electronic Logbooks for Ambient Air Monitoring*. Office of Air Quality Planning and Standards, RTP, NC. Available at (accessed October 19, 2016): https://www3.epa.gov/ttnamti1/files/policy/Electronic__Logbook_Final_%204_20_16.pdf

6. Environmental Protection Agency. (November 2002). *Guidance on Environmental Data Verification and Data Validation. EPA QA/G-8* (EPA Publication No. EPA/240/R-02-004). Office of Environmental Information, Washington, DC. Available at (accessed October 19, 2016): https://www.epa.gov/sites/production/files/2015-06/documents/g8-final.pdf

4.0: COLLECTION AND ANALYSIS METHODS

4.1 Method Detection Limits

The MDL as prescribed in 40 CFR Part 136 Appendix B was initially developed and applied to wastewater analyses.[1] Since then, this procedure has been applied to a variety of other matrices and analysis methods to approximate the lowest concentration (or amount) of analyte that can be reported with 99% confidence that the actual concentration (or amount) is greater than zero. As can be seen below in Figure 4.1-1, the Gaussian curve represents analysis of contamination-free method (matrix) blanks and the distribution of their concentration values around zero. The small area of the blank values to the right of the MDL value (indicated by the vertical dashed line) represent the 1% of values which would be considered false positives.

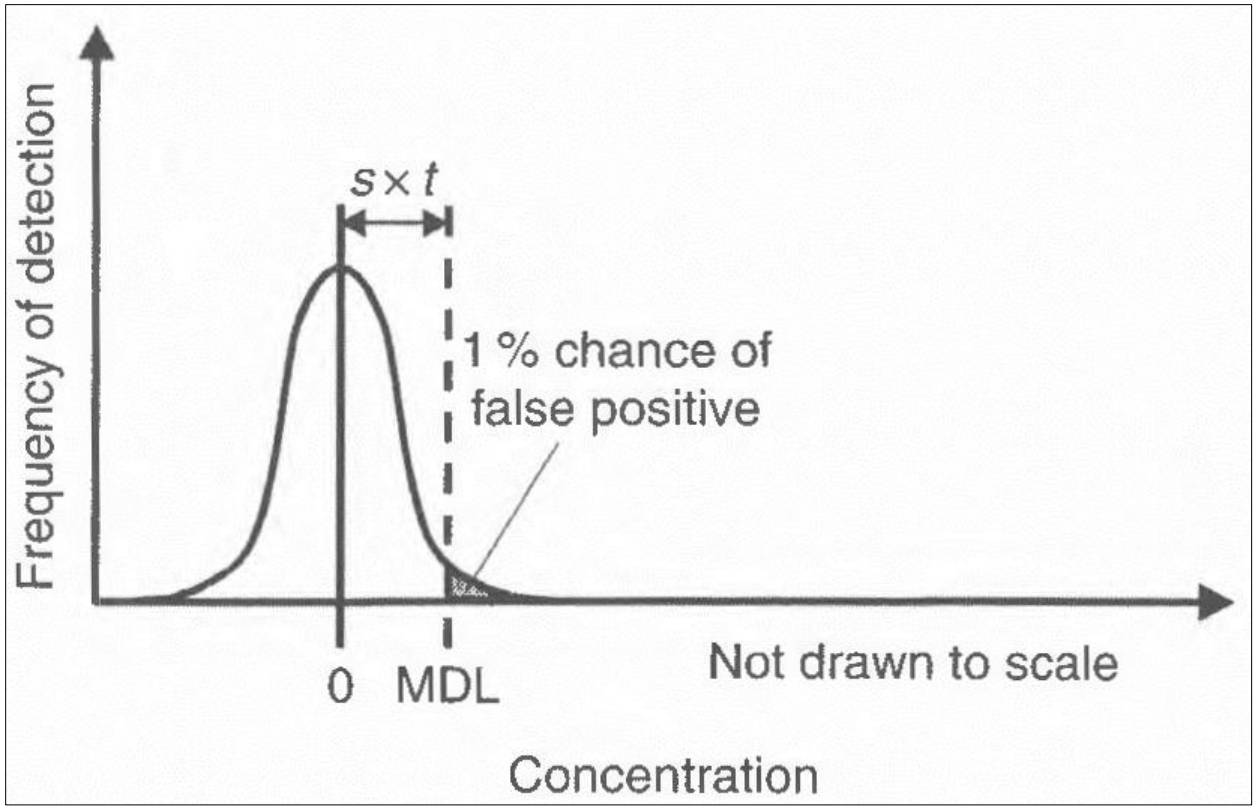

Figure 4.1-1. Graphical Representation of the MDL and Relationship to a Series of Blank Measurements in the Absence of Background Contamination
(Credit: Reference 2 as adapted from Reference 3)

In practical terms, this MDL procedure provides a conservative detectability estimate and aims to ensure that there is a 1% false positive rate – incorrectly reporting the presence of an analyte when it is in fact absent – at the determined MDL concentration. In many cases the analyte will be qualitatively identified (per, for example, the criteria given for the various analytical methods in Section 4.2) at concentrations below the MDL with a signal distinguishable from instrumental

noise. That is to say, the MDL procedure is not protective of false negatives, which is incorrectly concluding that the analyte is absent when it is in fact present; in fact, 50% of the time the analyte present at the MDL concentration will be measured at less than the MDL (the compound will not be 'detected').[4] This can be seen in Figure 4.1-2 – the solid Gaussian curve represents a series of measurements at the MDL concentration. The measurements in the shaded portion of the curve to the left of the MDL value are false negatives or values measured at less than the MDL. Such values may be properly qualitatively identified despite being less than the MDL value. Therefore, if an analyte is measured at the MDL concentration, the analyte is present 99% of the time; however, for analytes measured at or less than the MDL concentration, 50% of the time the analyte may also be present.

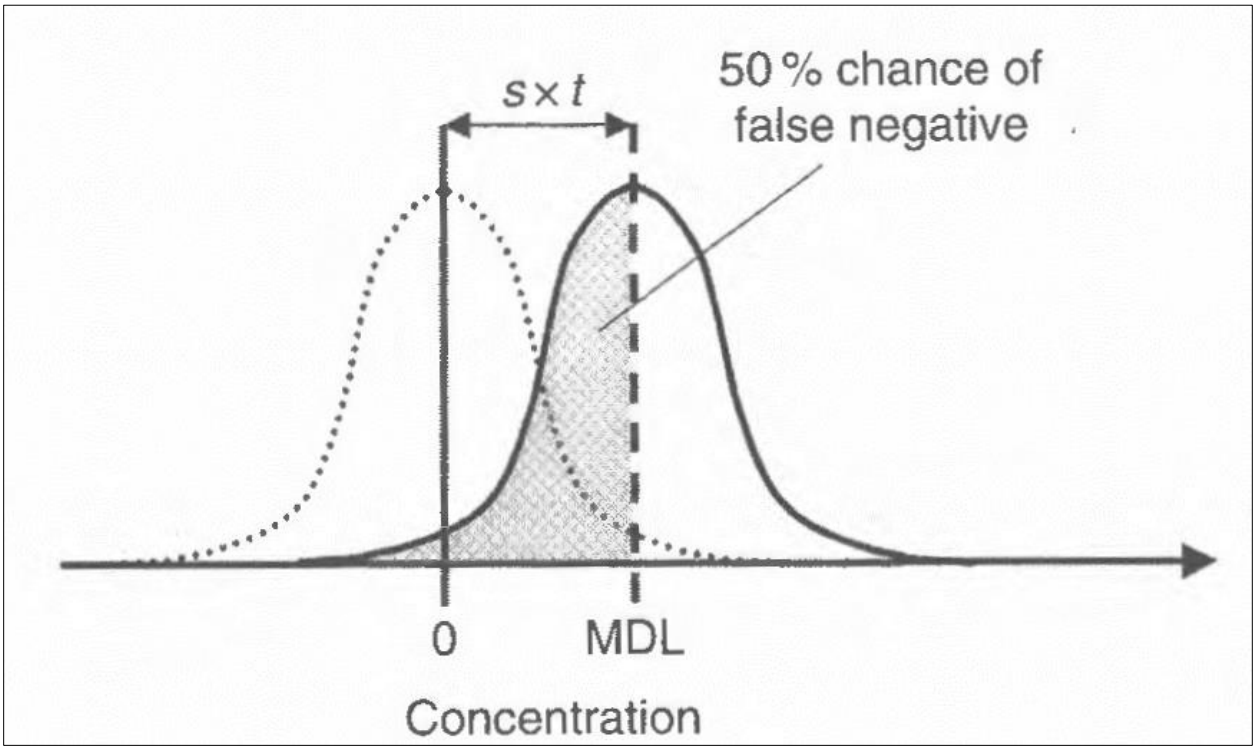

Figure 4.1-2. Graphical Representation of the MDL and Relationship to a Series of Measurements at the MDL Value
(Credit: Reference 2 as adapted from Reference 3)

In summary:

- 99% of the results measured ≥ MDL are in fact greater than zero (there is a 1% false positive rate, or chance that such measurements are not actually greater than zero)
- 50% of actual concentrations at the MDL will be reported as ≥ MDL
- 50% of actual concentrations at the MDL will be reported as < MDL (they will be false negatives) even though they may still be qualitatively identified and may still in fact be valid identifications

The MDL as described in 40 CFR Part 136 App B and in Reference 1 is a statistical *estimate* of the lowest concentration at which there is a 99% chance that the concentration is greater than zero. The MDL procedure is not simply a characterization of the noise of the instrument nor is it a known level of accuracy ensured at the MDL concentration. The MDL is also not an estimate of the precision or variability of the method. Moreover, the MDL is not simply a representation of the analysis instrument sensitivity, also known as the instrument detection limit (IDL), as the latter does not incorporate the potential effect of the matrix for samples taken through the preparation process (such as extraction or digestion). The IDL establishes the lowest concentration that may be measured with a defined confidence by the instrument, and knowing the IDL is particularly helpful when troubleshooting the MDL process; however, the IDL does not, and must not, replace the MDL.

There are known limitations to the 40 CFR Part 136 Appendix B MDL procedure, not the least of which is that it is a "compromise between statistical respectability and requirements of cost and time."[2,3] More specifically for the NATTS program, the MDL procedure prescribed in this TAD of spiking sample collection media in the laboratory does not explicitly take into account the functionality of all portions of the method from collection through analysis. In particular, conducting an MDL study through the probe is impractical for gases and not currently possible for PM_{10} metals and PAHs. To the extent feasible the impact of the sampling process on detectability is minimized by strongly recommending that bias checks (zero and known standard checks) are performed for carbonyls and VOCs field samplers.

The MDL concentration, as defined in 40 CFR Part 136 Appendix B, is determined statistically by preparing and analyzing minimally seven separate aliquots of a standard spike prepared in the method matrix. All portions of the method and matrix are to be included in the preparation and analysis such that any matrix effects and preparation variability are taken into account. The MDL procedure is an iterative process and, to be meaningful, the MDL procedure must be performed as prescribed.

The MDL procedure adopted for the NATTSs program, which is described in detail in Section 4.1.3.1, builds upon the 40 CFR Part 136 Appendix B by adding some aspects of the proposed method update rule (MUR).[5] The MUR recognizes that the CFR procedure assumes that blank values are centered around a concentration of zero and does not take into account the potential for background contamination to be present in the sample collection media. If there is a consistent background level of contamination on the sample collection media, as is typical for carbonyls on DNPH cartridge media and metals elements on QFF media, measured blank values will not be centered around zero; rather, they will be centered on the mean blank value. In such cases the MDL must be defined as the value that is statistically significantly greater than the blank value and the 40 CFR Part 136 Appendix B procedure will underestimate the MDL. This occurs since the resulting standard deviation of the MDL replicates (and thus the calculated MDL concentration) prepared in the presence of background contamination will not be different than if there was no discernable background (standard deviation simply evaluates the difference in the spread of the values, not the magnitude of the individual values). The MUR takes into account the media background and adjusts for matrix blanks levels that are not centered around zero.

The MDL procedure prescribed in Section 4.1.3.1 adds few additional steps than those required in the 40 CFR Part 136 Appendix B procedure. The net effect is that if there is little or no contribution of background contamination on the sampling media, the MDL will be no different than that determined previously by 40 CFR Part 136 Appendix B. If the sampling media (or other aspects of the standard preparation of instrumental analysis procedures) contributes blank contamination, the determined MDL will incorporate this average blank background concentration. In all cases, the new MDL will be the concentration at which there is a 99% chance that the actual reported concentration is statistically greater than the mean levels found in blanks.

The DQ FAC Single Laboratory Procedure v 2.4 described in Section 4.1.3.2 is a similar procedure to determine the MDL which takes into account the media background and other potential background contributions. This procedure is more involved and is better suited to laboratories with high sample throughput; however, laboratories may opt to determine MDLs via this procedure.

The MUR-modified 40 CFR Part 136 Appendix B method still has a 50% false negative rate, which is generally recognized as unacceptable for the purposes of environmental monitoring.[2,3] As a result, concentrations measured at less than the MDL, so long as the qualitative identification criteria have been met, are valid and necessary for trends analysis and substituting or censoring concentrations measured at less than MDL is not permitted. EPA recognizes that many laboratories are not comfortable reporting concentrations measured less than the MDL as these concentrations are outside of the calibrated range of the instrument and are associated with an unknown and potentially large uncertainty. However, actual values reported at less than the MDL are more valuable from a data analyst's standpoint and far superior than censored or substituted values. Addition of qualifiers as prescribed in Section 3.3.1.3.15 and in Table 3.3-1 indicates when values are near, at, and below detection limits and are therefore associated with larger uncertainties.

4.1.1 Frequency of Method Detection Limit Determination. MDLs must be determined minimally annually or when changes to the instrument or preparation procedure result in significant changes to the sensitivity of the instrument and/or procedure. Examples of situations where redetermination of the MDL is required include, but are not limited to:

- Detector replacement
- Replacement of the entire analytical instrument
- Replacement of a large (e.g. > 50%) portion of an agency's canister fleet
- Changing the cleaning procedure for sample collection media or labware which results in a marked reduction in contamination levels

4.1.2 MDL Measurement Quality Objectives. In order to ensure that measurements of air toxics in ambient air are sufficiently sensitive to assess trends in concentrations which may result in health effects due to chronic exposures, a minimum required method sensitivity, or MDL MQO, has been established for each of the core NATTS analytes. Though few changes have been made to MDL MQOs since the beginning of the NATTS Program, as new toxicology data are available, MDL MQOs may be adjusted. The annual NATTS network workplan

template includes the most up-to-date MDL MQO for each core analyte. Laboratories must meet (be equal to or less than) the MDL MQO listed in the most recent NATTS workplan.

The NATTS MDL MQOs are based on concentrations to which chronic exposures may result in unacceptable health risks. While analytical methods prescribed in this TAD are capable of meeting the MDL MQOs, MDLs may be elevated above the MDL MQOs due to background contamination. The convention listed in 40 CFR Part 136 Appendix B accounted for instrumental limitations during the determination of MDLs but did not consider the background or interferences, which, in certain instances, may be several-fold higher than the MDL MQO. As a result, the MUR MDL procedure has been adopted by the NATTS program to provide a more realistic threshold of detection given the limitations of the method and background concentrations attributable to the collection media and analytical instrumentation. The decision to include portions of the MUR for MDL determination for the NATTS Program was carefully weighed by examining historical data from the NATTS network and comparing typical media background levels to evaluate the percentage of data which would additionally be coded as less than the laboratory MDL. The results of the examination indicated that a minimum additional amount of concentration data would be marked as less than the MDL when reported to AQS.[6]

NATTS Tier I core analytes and the concentrations as of March 2015 that correspond to 10^{-6} cancer risk levels, to noncancer risk hazard quotients (HQs) of 0.1, and to MDL MQOs are listed in Table 4.1-1. Refer to the latest NATTS workplan template for the most up-to-date values.

Table 4.1-1. Concentrations of the NATTS Core Analytes Corresponding to a 10^{-6} Cancer Risk, a Noncancer Risk at a HQ of 0.1, and to the MDL MQO

Core Analyte	Cancer Risk 10^{-6} ($\mu g/m^3$)	Noncancer Risk at HQ = 0.1 ($\mu g/m^3$)	MDL MQO	
			($\mu g/m^3$)	(ppbv)
Acrolein	-	0.0020	0.090	0.039
Benzene	0.13	3.0	0.13	0.041
1,3-Butadiene	0.030	0.20	0.10	0.050
Carbon tetrachloride	0.170	19	0.17	0.027
Chloroform	-	9.8	0.50	0.10
Tetrachloroethylene	3.8	4.0	0.17	0.025
Trichloroethylene	0.21	0.20	0.20	0.037
Vinyl chloride	0.11	10	0.11	0.043
Acetaldehyde	0.45	0.90	0.45	0.25
Formaldehyde	0.080	0.080	0.080	0.065
Benzo(a)pyrene	0.00091	0.30	0.00091	NA
Naphthalene	0.029	0.029	0.029	NA
Arsenic (PM_{10})	0.00023	0.0030	0.00023	NA
Beryllium (PM_{10})	0.00042	0.0020	0.00042	NA
Cadmium (PM_{10})	0.00056	0.0020	0.00056	NA
Lead (PM_{10})	-	0.015	0.015	NA
Manganese (PM_{10})	-	0.0050	0.0050	NA
Nickel (PM_{10})	0.0021	0.00081	0.0021	NA

4.1.3 Determining MDLs. MDLs may be determined via one of two procedures. The first procedure in Section 4.1.3.1 is adopted from updates pending at the time this document was revised, an update to the MDL procedure described in 40 CFR Part 136 Appendix B, the MUR. [5]

The second procedure in Section 4.1.3.2 is to determine MDLs via the procedure described in the December 2007 Report of the Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs.[1] Both methods incorporate media blank background levels in the determination of analyte-specific MDLs.

MDL studies must be determined for each instrument employed to analyze samples for the NATTS Program. For laboratories utilizing multiple instruments for a given method, MDL studies must be performed for each instrument (the same samples or extracts may be used for all instruments). In instances where multiple instruments are employed for reporting NATTS Program results for the same analyte class (e.g., two or more HPLC-ultraviolet [UV] instruments), there are two conventions for how to report the MDLs. The preferred convention is to maintain an MDL for each instrument and report the respective MDL from the instrument on which a given sample was analyzed. Alternatively, the most conservative (highest) MDL from the multiple instruments can be reported – though this may not reflect the MDL associated with the sample analysis. It is not appropriate to average the MDL values for reporting.

4.1.3.1 MDLs via 40 CFR Part 136 Appendix B – Method Update Rule. The MDL procedure described in this section is adopted from the procedure as given in 40 CFR Part 136 Appendix B with several changes, based on those proposed in the CFR on February 19, 2015, to explicitly include in the MDL the background (i.e. contamination) contribution of the sample collection media and to incorporate temporal variability in laboratory preparation and instrument performance.[5] The preliminary work on the MUR identified measuring metals on air filters as an example of where the 40 CFR Part 136 Appendix B method did not generate a realistic concentrations level for the MDL value due to the elevated background contamination on the filter media.

A minimum of seven spiked samples and seven method blanks must be prepared in matrix over the course of a minimum of three different preparation batches. A batch is defined as a group of samples prepared on one day, therefore three different preparation batches would require preparation on three separate days. To properly characterize the variability in preparation, the dates of preparation should be spread out such that they are not consecutive. Analysis of these blanks and spikes must similarly be conducted over the course of three different analysis batches where each sample is only analyzed once. Again, a batch is defined as a group of samples analyzed on one day. Spreading the preparation and analysis over multiple preparation batches and across analysis days is intended to incorporate the variability of both sample preparation and analytical instrumentation that occurs over time. It is preferable to determine an MDL that is representative of the laboratory's capability than to have an unrealistically low MDL determined by selecting the best sampling media (i.e. canisters) and attempting to generate the lowest MDL value possible. Two MDL values are calculated, one MDL for the spiked samples according to the convention in 40 CFR Part 136 Appendix B (MDL_{sp}) and one MDL for the method blanks which includes the media background contribution (MDL_b).

The first step is to select a spiking level for preparing the MDL spiked samples. If too low of a spiking level is chosen, the analyte may not be reliably detected. If too high of a spiking level is chosen, the variability of the method near the actual limits of detection may not be properly

characterized. An appropriate spiking level may be selected by considering the following (in order of importance):

1. The concentration at which the instrument signal to noise ratio is three- to five-fold for the analyte.
2. The concentration at which qualitative identification criteria for the analyte are lost (note that this will be approximately the concentration determined from the MDL process absent of blank contamination).
3. Analysis of a suite of blank samples - calculate the standard deviation of the measured concentration and multiply by 3.
4. Previously acceptable MDL studies and related experience.

Note that the MDL spiking level should not be within the calibration curve; rather, the MDL spiking level should be less than the lowest calibration standard in order to best approximate the MDL. Concentrations within the calibration curve are required to meet precision and bias acceptance criteria and are of a high enough concentration that qualitative identification is certain.

The second step is to prepare the seven or more separate spiked samples (at the level determined in the first step) and seven or more method blank samples. In order to best mimic field-collected samples, each spiked and blank sample must include, to the extent feasible, all portions of the sample matrix and be subjected to the same procedures performed to process field samples in preparation for analysis. Prepare method blanks and spiked samples over the course of three different preparation batches preferably on non-consecutive days.

An efficient method to determine the MDL following this convention is to prepare and analyze an MDL sample on a continuous basis with typical sample batches prepared over the course of several weeks or months. In this scenario, one (or up to three) spikes would be prepared at the time of sample batch preparation and after seven or more data points have been collected for the MDL spikes and for the associated method blanks (which are already required with each analytical batch), the MDL could be calculated. This would alleviate the need to dedicate a significant contiguous block of time to preparing and analyzing MDL samples and method blanks. The following must be taken into consideration during preparation of the MDL samples:

1. Spiked samples must be prepared in matrix (DNPH cartridge, canister, PAH cartridge with quartz fiber filter, or metals Teflon® filter or QFF strip).
2. Selection of media should include as much variety as possible (e.g., different canister manufacturers or individual DNPH cartridges selected from different boxes or lots) to best characterize the variability of the method attributable to the use of media representative of field-collected samples.
3. Blank media which do not meet cleanliness criteria for a given analyte should trigger root cause analysis to determine the source of the contamination and should not be used to determine the method blank portion of the MDL. Cleanliness criteria are given in Tables 4.2-3, 4.3-4, 4.4-2, and 4.5-3 for VOCs, carbonyls, metals, and PAHs

collection media, respectively. Of particular concern are background levels of contaminants in canisters and on PUF/XAD cartridges resulting from insufficient cleaning. For DNPH cartridges, media background levels should meet the criteria specified in Method TO-11A (duplicated in Table 4.3-2). Metals quartz fiber filter media typically show elevated background levels of certain elements such as chromium, nickel, manganese, and lead. It is not possible to decrease the background levels of these three elements on QFFs, though EPA is working with manufacturers to reduce the amount of background contamination on the filter media.

The third step is to analyze the samples against a valid calibration curve. QC criteria for the analytical sequences must be met (blanks, laboratory control sample [LCS], calibration checks, etc.). Analyze the samples over the course of minimally three different analytical batches.

1. Perform all MDL calculations in the final units applicable to the method.
2. Calculate the MDL of the spiked samples, MDL_{sp}:
    a. Following acquisition of the concentration data for each of the seven or more spiked samples, calculate the standard deviation of the calculated concentrations for the spiked samples (s_{sp}). Include all replicates unless a technically justified reason can be cited (faulty injection, unacceptably low internal standard response, etc.), or if a result can be statistically excluded as an outlier.
    b. Calculate the MDL for the spiked samples (MDL_{sp}) by multiplying s_{sp} by the one-sided student's T value at 99% confidence corresponding to the number of spikes analyzed according to Table 4.1-2. Other values of T for additional samples (n > 13) may be found in standard statistical tables.

$$MDL_{sp} = s_{sp} \cdot T$$

Table 4.1-2. One-sided Student's T Values at 99% Confidence Interval

number of MDL samples (n)	degrees of freedom ν (n-1)	student's T value
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
12	11	2.718
13	12	2.681

    c. Compare the resulting calculated MDL_{sp} value to the nominal spiked amount. The nominal spiked level must be greater than MDL_{sp} and less than 10-fold MDL_{sp}, otherwise the determination of MDL_{sp} must be repeated with an adjusted spiking concentration. For MDL_{sp} values greater than the nominal spike level, the MDL spiking level should be adjusted higher by

approximately two or three-fold. For nominal spike levels which are greater than the 10-fold the MDL_{sp}, the MDL spiking level should be adjusted lower by approximately two or three-fold.

3. Calculate the MDL of the method blanks, MDL_b:

    a. If none of the method blanks provide a numerical result for the analyte, the MDL_b does not apply. A numerical result includes both positive and negative results for analytes which are positively identified. Non-numeric values such as "ND" would result when the analyte is not positively identified. Only method blanks that meet the specified qualitative criteria for identification (signal to noise, qualifier ion presence, etc.) are to be given a numerical result.

    b. If the method blank pool includes a combination of non-numeric (ND) and numeric values, set the MDL_b to equal the highest of the method blank results. If more than 100 method blank results are available for the analyte, set the MDL_b to the level that is no less than the 99th percentile of the method blanks. In other words, for n method blanks where $n \geq 100$, rank order the concentrations. The value of the 99th percentile concentration ($n \cdot 0.99$) is the MDL_b. For example, to determine MDLb from a set of 129 method blanks where the highest ranked method blank concentrations are … 1.10, 1.15, 1.62, 1.63, and 2.16, the 99th percentile concentration is the 128th value ($129 \cdot 0.99 = 127.7$, which rounds to 128), or 1.63. Alternatively, spreadsheet programs may be employed to interpolate the MDL_b more precisely.

    c. If all concentration values for the method blank pool are numeric values, calculate the MDLb as follows:

        i. Calculate the average concentration of the method blanks ($\bar{x}_b$).

        ii. Calculate the standard deviation of the method blank concentrations, s_b.

        iii. Multiply s_b by the one-sided student's T value at 99% confidence corresponding to the number of blanks analyzed according to Table 4.1-2. Other values of T for additional samples (n > 13) may be found in standard statistical tables.

        iv. Calculate MDL_b as the sum of $\bar{x}_b$ and the product of s_b and the associated student's T value:

$$MDL_b = \bar{x}_b + s_b \cdot T$$

4. Compare MDL_{sp} and MDL_b. The higher of the two values is reported as the laboratory MDL for the given analyte.

5. If the MDL is determined as the MDL_{sp}, laboratories should perform verification of the determined MDL by:

    a. Preparing one or more spiked samples at one to five-fold the determined MDL and analyze the sample per the method to ensure the determined MDL is reasonable. Recall that at the MDL_{sp} concentration there is a 50% chance that the

analyte will not be detected; however, the analyte should be detected at two- to five-fold the determined MDL.

b. Developing reasonable acceptance criteria for the MDL verification. For example, an MDL verification that recovers 2% of the nominal amount is not realistic, nor is one that recovers 300%. An appropriate starting point for acceptance limits is to double or triple the acceptance window prescribed by the method for the given analyte. For example, TO-15 normally permits benzene LCS recoveries to be 70 to 130% (± 30% error), therefore doubling the MDL verification acceptance limits would permit 40 to 160% recovery. Note that for collection media with a significant background contamination, blank subtraction may be necessary to evaluate the recovery of the MDL verification sample.

c. Examining the MDL procedure for reasonableness if the verification sample is outside of the laboratory-defined acceptance criteria. Such an examination might include investigating the signal-to-noise ratio of the analyte response in the spiked samples, comparing the MDL to existing instrument detection limits (if known – discussed below), and relying on analyst experience and expertise to evaluate the MDL procedure and select a different spiking level. The MDL study should then be repeated with a different spiking level.

   Troubleshooting may include determination of the instrument detection limit (IDL) to evaluate whether the poor or elevated recovery is due to the instrument. The IDL is determined by analyzing seven or more aliquots of a standard, calculating the standard deviation of the measurements, and multiplying the standard deviation by the appropriate student's T value. IDL samples are to be prepared in the same matrix as calibration standards and are not processed through sample collection media as is done for MDL spiked samples (e.g. for TO-11A and TO-13A, the standard would be in solvent, for TO-15 the standard would be typically in a single canister, and for IO3.5 metals analysis the standard would be prepared in the aqueous acid matrix).

Example calculation:

A laboratory is determining the MDL for formaldehyde by TO-11A by spiking commercially-prepared DNPH cartridges. The analyst spiked eight cartridges with formaldehyde-DNPH at 0.030 µg/cartridge (in terms of the amount of the free formaldehyde) over three separate preparation batches. These eight spiked cartridges and eight additional method blank cartridges were extracted over three different dates. Results were analyzed over three different analysis batches per Method TO-11A yielding the following results:

Cartridge Number	Preparation Batch and Date	Analysis Batch and Date	Spikes (µg/cartridge)	Method Blanks (µg/cartridge)
1	A - September 12, 2015	QR9 - September 13	0.1685	0.1412
2	A - September 12, 2015	QR9 - September 13	0.1651	0.1399
3	A - September 12, 2015	QR9 - September 13	0.1701	0.1402
4	B - September 19, 2015	QR12 - September 21	0.1673	0.1405
5	B - September 19, 2015	QR12 - September 21	0.1692	0.1408
6	C - September 28, 2015	QR16 - September 29	0.1686	0.1403
7	C - September 28, 2015	QR16 - September 29	0.1705	0.1402
8	C - September 28, 2015	QR16 - September 29	0.1696	0.1410

The average ($\bar{x}$) and standard deviation (s) of measured formaldehyde mass were determined for both the spikes and the method blanks (all in units of µg/cartridge):

$\bar{x}_{sp}$ = 0.1686
$\bar{x}_{b}$ = 0.1405
s_{sp} = 0.0017
s_{b} = 0.0004

To calculate the MDL_{sp}, the standard deviation of the spiked aliquots is multiplied by the associated student's T. The student's T value for eight aliquots is 2.998, corresponding to seven degrees of freedom (8 - 1 = 7):

$$MDL_{sp} = 0.0017 \text{ µg/cartridge} \cdot 2.998$$

$$= 0.0051 \text{ µg/cartridge}$$

The MDL_{sp} is subsequently verified to be less than the spike level, and the spike level is confirmed to be less than 10-fold the MDL_{sp}:

MDL_{sp} < spike level < 10-fold MDL_{sp}
0.0051 µg/cartridge < 0.030 µg/cartridge < 0.051 µg/cartridge

Observe that the determined MDL_{sp} is less than the background level of formaldehyde ($\bar{x}_b$ = 0.1405 µg/cartridge) on the DNPH cartridge media; such indicates that the MDL_{sp} is biased low and that background levels must be taken into account.

To calculate the MDL_b, the standard deviation of the blank measurements is multiplied by the associated student's T and this product is added to the average blank value, $\bar{x}_b$:

$$MDL_b = 0.0004 \text{ µg/cartridge} \cdot 2.998 + 0.1405 \text{ µg/cartridge}$$

$$= 0.1417 \text{ µg/cartridge}$$

The MDL_{sp} and MDL_b are compared to determine which is greater, and the greater of the two values is reported as the laboratory MDL for the specific analyte.

0.1417 µg/cartridge > 0.0051 µg/cartridge

In this case, the formaldehyde MDL_b of 0.1417 µg/cartridge is greater than the MDL_{sp} of 0.0051 µg/cartridge, and is reported as the laboratory MDL for formaldehyde as measured by Method TO-11A.

4.1.3.2 MDLs via DQ FAC Single Laboratory Procedure v 2.4.[7] The MDL procedure described in this section involves examination and manipulation of historical method blank data to derive the MDL. This procedure must be performed only with method blanks that include all media contributions and processing procedure elements. Also, method blank analyses which were the result of laboratory preparation or analysis errors must not be included.

The DQ FAC procedure requires that historical method blank data be examined to verify that at least 50% of the results are a numerical value (zero, positive concentration, or negative concentration). If fewer than 50% of the method blank values are numerical, or, stated another way, if 50% or more of the values are reported as nondetects, use the procedure described above in Section 4.1.3.1. Once it is determined that the DQ FAC method is applicable, assign method blanks without a numerical value (i.e., non-detect) as zero. Calculate the standard deviation of the included method blanks. A minimum of seven method blanks meeting these criteria is required within the calendar year. If results of more than seven method blanks within the year meet these criteria, all such method blank data should be included in the evaluation.

Calculate the MDL as follows:

$$MDL = \bar{x}_{mb} + s \cdot K$$

where:

$\bar{x}_{mb}$ = mean result of the method blanks
s = standard deviation of the method blanks
K = is a multiplier for a tolerance limit based on the 99th percentile for n-1 degrees of freedom according to Table 4.1-3.

Note that if $\bar{x}_{mb}$ is a negative value, substitute zero for this value.

If 5% or more of the blank results are greater than the MDL, raise the MDL as follows:

1. To the highest method blank result if less than 30 method blank results are available.
2. To the next to highest method blank result if 30 to 100 method blank results are available.
3. To the 99th percentile, or the level exceeded by 1% of all method blank results, if there are more than 100 method blank results available.

Only method blanks that meet the specified qualitative criteria for identification (signal to noise, qualifier ion presence, etc.) are to be given a numerical result.

Table 4.1-3. K-values for n Replicates

n	K	n	K	n	K	n	K
7	6.101	30	3.317	53	2.993	76	2.855
8	5.529	31	3.295	54	2.977	77	2.851
9	5.127	32	3.273	55	2.970	78	2.847
10	4.829	33	3.253	56	2.963	79	2.843
11	4.599	34	3.234	57	2.956	80	2.839
12	4.415	35	3.216	58	2.949	81	2.836
13	4.264	36	3.199	59	2.943	82	2.832
14	4.138	37	3.182	60	2.936	83	2.828
15	4.031	38	3.167	61	2.930	84	2.825
16	3.939	39	3.152	62	2.924	85	2.821
17	3.859	40	3.138	63	2.919	86	2.818
18	3.789	41	3.125	64	2.913	87	2.815
19	3.726	42	3.112	65	2.907	88	2.811
20	3.670	43	3.100	66	2.902	89	2.808
21	3.619	44	3.088	67	2.897	90	2.805
22	3.573	45	3.066	68	2.892	91	2.802
23	3.532	46	3.055	69	2.887	92	2.799
24	3.494	47	3.045	70	2.882	93	2.796
25	3.458	48	3.036	71	2.877	94	2.793
26	3.426	49	3.027	72	2.873	95	2.790
27	3.396	50	3.018	73	2.868	96	2.787
28	3.368	51	3.009	74	2.864	97	2.784
29	3.342	52	3.001	75	2.860	98	2.782

4.1.4 References

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7. *Report of the Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs, Submitted to the US Environmental Protection Agency*, Final Report 12/28/07. Appendix D, pages D-1 through D-9.

4.2 VOCs – Overview of EPA Compendium Method TO-15

Each agency must codify in an appropriate quality systems document, such as an SOP, or equivalent, its procedures for performing VOC sampling, canister cleaning, and analysis. Various requirements and best practices for such are given in this section. Note that regardless of the specific procedures adopted, the method performance specifications as given in Section 4.2.12 must be met.

Of the 188 HAPs listed in Title III of the CAA Amendments of 1990, 97 of these are VOCs. VOCs are defined as organic compounds having a vapor pressure greater than 10^{-1} Torr at 25°C.[1] VOC air toxics ambient air concentrations are typically measured at the single part per trillion (ppt) to single ppb level. Measurement of these VOCs is based on the techniques described in EPA Compendium Method TO-15[1, 2], which describe collection of whole air samples into evacuated stainless steel canisters followed by preconcentration of the volatiles for analysis via GC/MS. When initially released, TO-15 indicated the lower limit for concentration measurement was approximately 0.5 ppbv. However, with newer more sensitive mass spectrometer detectors, much lower detection limits are achievable such that the MDL MQOs listed in Table 4.1-1 can be attained. Due to the lack of current and specific guidance for measuring low (sub-ppbv) levels of VOCs in ambient air, at the time of this TAD's release, EPA was collecting public comments to revise TO-15 to include techniques and instrumentation that permit sub-ppbv measurements of VOCs in ambient air. Much of the guidance listed in this section are anticipated to be included in EPA's update of TO-15.

4.2.1 General Description of Sampling and Analytical Methods. An MFC and/or critical orifice regulates the flow of ambient atmosphere into an evacuated passivated stainless steel canister at a known, constant rate over the course of 24 hours. Following completion of collection, the canister is transported to a laboratory for analysis within 30 days of collection. Previous studies suggest that most compounds analyzed via TO-15 are stable for up to 30 days in passivated stainless steel canisters;[3,4] however, the condition of the wetted surfaces of each individual canister is likely to influence the stability of the VOCs. Analysis of the sample as soon as possible after collection is strongly recommended to minimize changes of the collected sample, especially for HAPs such as acrolein, 1,3-butadiene, and carbon tetrachloride, among others.

VOCs are identified and quantified via cryogenic preconcentration GC/MS and a typical analysis scheme is as follows. A known volume of the whole air (an air parcel from which gases have not been removed and are completely captured for sample collection) is passed through and the VOCs are cryogenically trapped onto a sorbent bed while N_2, O_2, Ar, CO_2, and to the extent possible, H_2O are selectively removed. The volume trapped is measured via MFC or by the change in pressure of a known volume downstream of the sorbent trap. The sample introduction pathway and sorbent bed are then swept with dry inert gas (such as helium) to remove water, while the VOCs are retained on the cold sorbent. After the preconcentration and dehydration, the sorbent is heated to desorb the VOCs and the VOCs entrained in a carrier gas stream where they are refocused and subsequently introduced onto the GC column for separation. After separation on the column, VOCs are ionized in a quadrupole, ion trap, or time of flight (TOF) MS which detects the ion fragments according to their mass to charge (m/z) ratio. The responses

of the ion fragments are plotted against the retention time and compared to the standard chromatogram to identify the compounds in the sample based on retention times and ion fragments of standards analyzed under the same chromatographic and MS conditions.

Method TO-15 addresses sampling of VOCs such that integration of the sample results in a final canister pressure is subambient (< 14.7 psia, or less than the typical ambient atmospheric pressure at the field location) or above ambient (> 14.7 psia, or above the typical ambient atmospheric pressure at the field location). Previous versions of this TAD have disallowed superambient sampling since such is thought to result in depressed recoveries of hydrophilic polar VOCs due to their dissolution into condensed water. However, many of the sites in the NATTS network collect canisters at superambient pressures. Due to a lack of definitive studies demonstrating one method to be superior, this revision of the TAD permits pressurized sampling but *strongly recommends* that collected canister pressures remain less than or equal to 3 psig (~17.7 psia) to minimize the potential for water condensation. Regardless of the chosen final canister pressure, each agency is responsible for ensuring that method performance specifications are met, and specifically that method precision and bias are acceptable for their selected combination of sampling instrument; final canister pressure; canister type; and preconcentration, water management, and analysis techniques.

A previous study by McClenny et al.[5] indicates that ambient air samples collected above atmospheric pressure may exhibit condensation on the interior canister surfaces. Liquid water inside the canister decreases precision from canister reanalysis since the amount of condensation decreases as air is removed from the canister, and the pressure decreases, which changes the equilibrium of analytes between the liquid and gas phases. For monitoring agencies collecting samples to superambient pressure, samples should not be pressurized above 3 psig to minimize the condensation of liquid water inside the canister.

The calibration and tuning of the MS must be monitored and compensated for by the analysis of internal standards (IS) with each injection and analysis of continuing calibration standards minimally every 24 hours of analysis (recommended every 10 sample injections and concluding each sequence).

The VOCs including, but not limited to, those in Table 4.2-1 may be determined by this method.

Table 4.2-1. VOC Target Compounds and Associated Chemical Abstract Service (CAS) Number via Method TO-15

Target Compound	CAS #
acetone	67-64-1
acrolein [a b]	107-02-8
acrylonitrile	107-13-1
benzene [a b]	71-43-2
benzyl chloride	100-44-7
bromodichloromethane	75-27-4
bromoform (tribromomethane)	75-25-2
1,3-butadiene [a b]	106-99-0
2-butanone (methyl ethyl ketone)	78-93-3
carbon disulfide	75-15-0
carbon tetrachloride (tetrachloromethane) [a b]	56-23-5
chlorobenzene	108-90-7
chloroform (trichloromethane) [a b]	67-66-3
cyclohexane	110-82-7
dibromochloromethane	124-48-1
1,2-dibromoethane [b]	106-93-4
1,2-dichlorobenzene	95-50-1
1,3-dichlorobenzene	541-73-1
1,4-dichlorobenzene	106-46-7
dichlorodifluoromethane (Freon-12)	75-71-8
1,1-dichloroethane	75-34-3
1,2-dichloroethane [b]	107-06-2
1,1-dichloroethene	75-35-4
cis-1,2-dichloroethene	156-59-2
trans-1,2-dichloroethene	156-60-5
1,2-dichloropropane [b]	78-87-5
cis-1,3-dichloropropene [b]	10061-01-5
trans-1,3-dichloropropene [b]	10061-02-6
1,2-dichlorotetrafluoroethane (Freon-114)	76-14-2
1,4-dioxane	123-91-1
ethanol	64-17-5
ethyl acetate	141-78-6
ethyl chloride (chloroethane)	75-00-3
ethylbenzene	100-41-4
4-ethyl toluene	622-96-8
heptane	142-82-5
hexachloro-1,3-butadiene	87-68-3
hexane	110-54-3
2-hexanone (methyl butyl ketone)	591-78-6
isoprene	78-79-5
isopropyl alcohol	67-63-0
methanol	67-56-1
methyl bromide (bromomethane)	74-83-9
methyl chloride (chloromethane)	74-87-3
methyl isobutyl ketone (4-methyl-2-pentanone)	108-10-1
methyl methacrylate	80-62-6
methyl tert-butyl ether	1634-04-4
methylene chloride (dichloromethane) [b]	75-09-2
propene	115-07-1

Table 4.2-1. VOC Target Compounds and Associated Chemical Abstract Service (CAS) Number via Method TO-15 (Continued)

Target Compound	CAS #
styrene	100-42-5
1,1,1,2-tetrachloroethane	630-20-6
1,1,2,2-tetrachloroethane [b]	79-34-5
tetrachloroethene [a b]	127-18-4
tetrahydrofuran	109-99-9
toluene	108-88-3
1,2,4-trichlorobenzene	120-82-1
1,1,1-trichloroethane	71-55-6
1,1,2-trichloroethane	79-00-5
trichlorofluoromethane (Freon 11)	75-69-4
1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113)	76-13-1
1,2,4-trimethylbenzene	95-63-6
1,3,5-trimethylbenzene	108-67-8
trichloroethene [a b]	79-01-6
vinyl acetate	108-05-4
vinyl bromide	593-60-2
vinyl chloride (chloroethene) [a b]	75-01-4
m&p-xylene	108-38-3 (m)/106-42-3 (p)
o-xylene	95-47-6

[a] NATTS Tier I core analyte
[b] NATTS PT target analyte

4.2.1.1 Sampling Pathway. All wetted sampling surfaces that contact the sampled atmosphere, including the inlet probe, must be of chromatographic grade stainless steel or borosilicate glass. Stainless steel tubing may be additionally fused silica lined which increases the inertness of the flow path. While PTFE Teflon is permitted, its use is not recommended as high molecular weight compounds may adsorb to the surface. Use of other materials such as copper, FEP Teflon®, or rubber is not permitted, as they have active sites or provide opportunities for VOCs to adsorb and later desorb.

4.2.1.2 Particulate Filtration. A 2-µm pore size sintered stainless steel particulate filter must be installed on the sampling unit inlet for all VOC collection. If employing a standalone VOC inlet probe, a particulate filter placed further upstream in the sampling pathway may permit a longer period between sampling inlet pathway cleaning. Failure to install a particulate filter allows particulate residue such as dust and pollen to adhere to the interior of the sampling unit (to valves, MFC, etc.) and to be pulled into the evacuated canister during sample collection. Once inside the canister, particulate matter can form active sites, adsorb analytes, and/or provide reactants which may degrade and form target analytes or interferants, potentially rendering the canister irreversibly contaminated. The particulate filter must be replaced minimally annually or more frequently if in areas with high airborne PM levels which may result in decreased flows or decreased collected pressures.

4.2.2 Precision – Sample Collection and Laboratory Processing. Each agency must prescribe procedures that it will follow to assess VOCs precision in the NATTS QAPP, SOP, or similar controlled document. Given below are the various types of precision and associated frequency requirements for VOCs.

Precision between duplicate, collocated, and replicate analysis samples must be ≤ 25% relative percent difference (RPD) for target compound concentrations ≥ five-fold the laboratory MDL. Both sample results must be qualified when entered into AQS for instances in which collocated or duplicate samples fail this precision specification. For precision criteria failures of replicate analyses, the value reported as the RD transaction must be qualified. Root cause analysis must be performed to investigate and correct the failure. If a root cause cannot be identified, results should be qualified as estimated. Please refer to the list of qualifiers in Table 3.1-1.

4.2.2.1 Sample Collection and Analysis Precision. Collocated and duplicate samples are compared to the primary sample to determine the precision inclusive of all sample collection and analysis procedures.

For samples to be collocated, each sampling unit must have its own pathway to the ambient atmosphere. If collected from a manifold, each sampling unit must have a dedicated manifold for it to be collocated; otherwise this configuration is defined as duplicate. The rationale behind this distinction is that there is potential non-homogeneity of the sampled atmosphere in the manifold when compared to the ambient atmosphere. Any effect of the manifold impacts both sampling units and they are not sampling truly independently from the ambient atmosphere. If both sampling unit inlets connect to the same inlet manifold, the samples are duplicate, not collocated, as shown in Figure 4.2-1. To summarize,

- Collocated samplers must have two separate flow control devices and two separate discrete inlet probes to the ambient atmosphere. If applicable, each sampling unit must connect to a separate manifold. Collocated sampling inlet probes must be within 1 to 4 meters of the primary sampling inlet probe.
- Duplicate sampling is performed in situations where two canisters are collected through a single inlet probe, which includes a common inlet manifold.

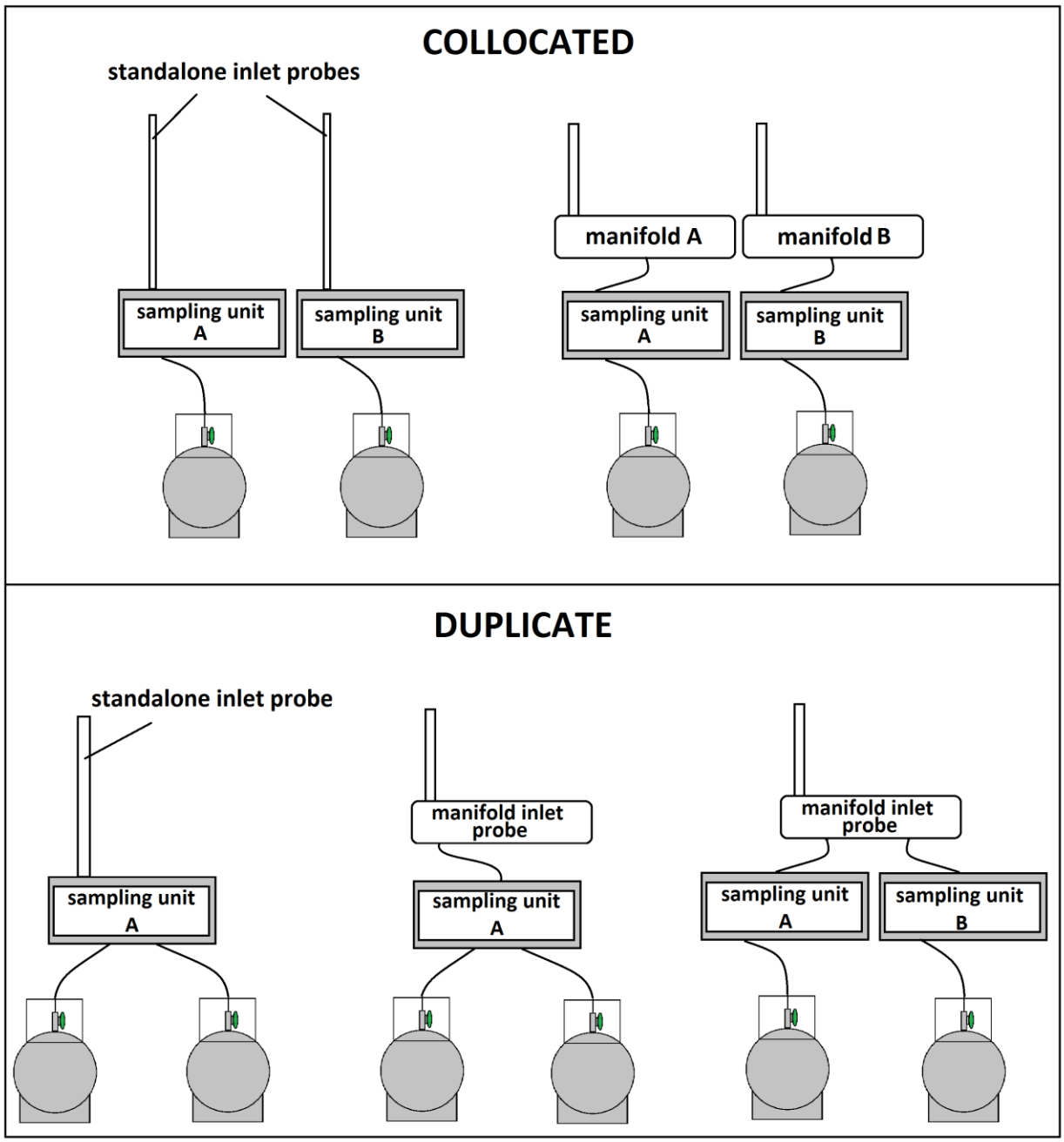

Figure 4.2-1. Collocated and Duplicate VOC Canister Sample Collection

Collocated or duplicate VOC sampling, if performed (as detailed in the workplan), must be conducted at a minimum frequency of 10%. This is equivalent to a minimum of six collocated samples per year, or roughly one every other month, for sites conducting one-in-six days sampling for a total of 61 primary samples annually. More frequent collocated sample collection provides additional sample collection precision and is encouraged where feasible.

4.2.2.2 Laboratory Analytical Precision. Several analysis aliquots can be removed from a collected canister which affords replicate analysis to evaluate analytical precision. The same

sample is injected twice and the results are evaluated for precision as RPD. The required frequency for replicate analyses reported to AQS is prescribed in the workplan, but is recommended to be performed on a one-per-batch frequency or one-in-20 sample injections, whichever is more frequent. Monitoring organizations are encouraged to report all replicate analysis results to AQS.

4.2.3 Sample Collection Procedures

4.2.3.1 Sampling Equipment Specification. Various sampling instruments are commercially available. Such systems may permit simultaneous collection of VOCs canisters and carbonyl cartridges or include secondary channels for collection of duplicate VOCs canister samples. Regardless of the additional features, each sampling unit must minimally include the following options:

- Elapsed time indicator
- Multi-day event control device (timer)
- Latching solenoid valve with a low temperature rise coil
- Pressure gauge or pressure transducer to perform leak checking of canister connection
- MFC (preferred) or critical orifice to control sampling flow

All wetted surfaces of the flow path in the sampling unit must be constructed of chromatographic grade stainless steel or borosilicate glass. Stainless steel may be additionally deactivated with fused silica linings. Use of PTFE Teflon is discouraged as it can behave as a sorbent for high molecular weight VOCs. Inclusion of glass-lined stainless steel is discouraged as it is prone to breakage which can cause flow restrictions.

4.2.3.2 Sample Collection, Setup, and Retrieval

4.2.3.2.1 Sample Setup. It is strongly recommended that the initial canister pressure be checked prior to sample collection by measurement of the canister vacuum with a calibrated pressure gauge or pressure transducer. If a built-in gauge on the sampling unit cannot be calibrated, a standalone gauge should be employed for this measurement. This initial pressure should be documented on the sample collection form. Canisters must show > 28 inches Hg vacuum to conduct sampling.

Once vacuum is verified, the canister is connected to the sampling unit and a leak check is performed. A leak check may be performed by quickly opening and closing the valve of the canister to generate a vacuum in the sampling unit. The vacuum/pressure gauge in the sampling unit should be observed for a minimum of 5 minutes to ensure that the vacuum does not change by more than 0.2 psi. Commercially-available canister sampling units may include a leak check routine. For onboard leak check routines, the leak check criteria should be equivalent or better than those listed above. If a leak is detected, fittings should be tightened to locate the source of

the leak. Sample collection must not commence until a successful leak check is attained. Leak check pressure change and duration is documented on the field collection form.

Following successful leak check, the sample collection program is verified and the canister valve is opened.

4.2.3.2.2 Subambient Sample Collection. Subambient pressure sample collection results in a canister pressure that is approximately 10 to 13 psia (2 to 10 inches Hg vacuum). Sample collection must be performed at a constant flow rate over the 24-hour collection period. Flow rates are typically 2.5 to 3.5 mL/minute for 6-L canisters.

As discussed earlier in Section 4.2.1, the management of water in sample collection is important to the ability to remove air from the canister that is representative of the atmosphere initially collected. At subambient pressures, the partial pressure of water vapor does not typically exceed the equilibrium vapor pressure at the typical analysis temperature, thus water generally will not condense on the interior surfaces of the canister.

Subambient sample collection does not include a pump in the sampling pathway. With fewer components, moving parts, seals, and surfaces, there is generally less risk of contaminating a collected sample. A less complex sampling system has fewer parts to wear out and break, simplifying maintenance.

Two disadvantages with subambient sample collection relate to contamination due to leaking and a smaller overall volume of collected gas for analysis. A canister leak on a subambient pressure sample will cause ambient air to enter the canister and contaminate the sample, invalidating the sample. Moreover, a canister at subambient pressure contains less air than an equivalent superambient sample, which limits the number of aliquots that may be effectively removed from the canister before there is insufficient gas remaining for analysis.

4.2.3.2.3 Superambient (Positive) Pressure Sampling. Superambient pressure sampling (positively pressurized sampling) involves collection of samples above atmospheric pressure utilizing a pump to push air into the canister. As discussed earlier in Section 4.2.1, sample collection at pressures above ambient pressure may result in water condensation on the interior walls of the canister.[5] It is theorized that this condensation may lead to poor representation of hydrophilic polar compounds in the aliquot of gas removed from the canister for analysis. An advantage of superambient pressure sample collection is that if the canister leaks slightly, the sample will not become contaminated so long as the canister pressure remains greater than atmospheric pressure.

A disadvantage of superambient sample collection is that it requires incorporation of a pump and additional valves in the sampling pathway, which provide additional opportunities for contamination over time when compared to subambient sampling methods which do not require the additional pumps and valves.

Some sampling systems are susceptible to condensation in the flow pathway during high-dewpoint conditions. This condensation manifests in the high pressure area between the pump

and the bypass valve and is evidenced by rough pressure responses when the bypass valve is operating. To alleviate this condensation, the bypass valve should be kept as open as possible to maximize the air flow through the sampler and minimize the condensation.

4.2.3.2.4 Sample Retrieval. Following completion of sample collection, it is strongly recommended that the final canister pressure be measured with a calibrated pressure gauge and recorded on the sample collection form. If an on-board gauge on the sampling unit cannot be calibrated, a standalone calibrated gauge should be used. The sample start and stop times as well as the elapsed collection time must also be recorded on the sample collection form. The sample custody form must be completed and accompany the collected sample at all times until relinquished to the laboratory. COC documentation must comply with Section 3.3.1.3.7.

Sampling units which incorporate computer control of the sampling event with associated data logging may provide the above information which should be printed and attached to the sample collection form or transcribed. If transcribed, the transcription must be verified by another individual. For such sampling units, the data logged should be reviewed to ensure the sample collected appropriately and there are no flags or other collection problems that may invalidate the collected sample. Collected data should be downloaded and provided to the analysis laboratory.

4.2.3.3 Sampling Schedule and Duration. VOC sample collection must be performed according to the national sampling schedule at one-in-six days for 24 ± 1 hours beginning at midnight and concluding on midnight of the following day, standard local time, unadjusted for daylight savings time. For missed or invalidated samples, a make-up sample should be scheduled and collected per Section 2.1.2.1. Clock timers controlling sampling unit operation must be adjusted so that digital timers are within ±5 minutes of the reference time (cellular phone, GPS, or similar accurate clock) and mechanical timers within ±15 minutes.

4.2.3.4 Sampling Train Configuration and Presample Purge. Sampling unit inlets may be connected to a standalone inlet probe or may be connected to a sampling inlet manifold with a single inlet probe. If connected to a manifold inlet, the VOC sampling line must be connected to the port closest to the manifold inlet probe. Inlet manifolds must incorporate a blower to pull ambient air through the manifold; the manifold flow rate should be minimally two times greater than the total demand of the systems connected to the manifold. An exit flow meter should be installed to ensure excess air flow which reduces residence time and ensures that a fresh supply of ambient air is available for sampling. Refer to Section 2.4 for sampler siting requirements.

For either inlet system listed above, the inlet line to the sampling unit must be purged with ambient air such that the equivalent of a minimum of 10 air changes is completed just prior to commencing sample collection. This purge eliminates stagnant air and flushes the inlet line.

4.2.3.5 Sampling Unit Non-Biasing Certification. Prior to field deployment and annually thereafter, each VOC sampling unit must be certified as non-biasing by collection over 24 hours of both a sample of hydrocarbon-free (HCF) zero air (or equivalent VOC- and oxidant-free air) or zero grade nitrogen and known concentration VOC standard in air.

This certification may be performed as part of an internal audit, however, this certification is best performed following annual maintenance which includes calibration (or calibration checks) of MFCs and pressure gauges and other preventive maintenance, as needed, to ensure the sampling unit is non-biasing prior to field deployment. Equipment such as dynamic dilution systems, connecting tubing, and MFCs should be purged with humidified zero air or nitrogen for sufficient time (typically one hour) to ensure the challenge delivery system is clean.

A best practice is to perform this procedure through the probe (TTP) where the entire sampling train is assessed for bias. Conducting the TTP procedure requires equipment such as portable zero air generators and portable gas-phase dynamic dilution systems and staff familiar with their operation. While the TTP procedure is the best practice, each sampling unit must minimally be bench tested. Suitable test procedures are described below.

Recommended certification check procedures are described below. For agencies which cannot perform the annual maintenance and challenge in-house, manufacturers, the national contract lab, or third party vendors may offer certification services. Regardless of the exact procedure adopted, the performance specifications listed below must be met.

4.2.3.5.1 Zero Check. The zero check is performed by simultaneously providing humidified (50 to 70% RH) hydrocarbon- and oxidant-free zero air (must meet the cleanliness criterion of < 0.2 ppbv or < 3x MDL, whichever is lower) or UHP nitrogen to the sampling unit for collection into a canister and to a separate reference canister connected directly to the supplied HCF zero air gas source. The reference canister collects the challenge gas directly and is the baseline for comparison of the challenge sample. Compounds which show increased concentrations in the challenge sample compared to the reference sample indicate contamination attributable to the sampling unit.

The humidified zero gas flow is provided to a challenge manifold constructed of chromatographic stainless steel. The manifold should include three additional ports for connections to the sampling unit inlet, reference MFC, and a rotameter which acts as a vent to ensure that the manifold remains at ambient pressure. The reference MFC flow is set to approximately the same flow rate as the sampling unit. Zero gas is to be supplied such that there is excess flow to the manifold as indicated by the rotameter on the vent port. Sampling is performed over 24 hours, to simulate real world conditions, into the reference canister and through the sampling unit into the zero challenge canister. Sampling for 24 hours best replicates conditions in the field, however, shorter sampling durations for these challenges are also acceptable.

Analysis by GC/MS for target compounds must show all Tier I core compounds in the zero challenge canister are not greater than 0.2 ppbv or 3x MDL (whichever is lower) higher than the reference canister and the remaining core compounds should also meet these criteria. Where exceedances are noted in the zero challenge canister for Tier I core compounds, corrective action must be taken to remove the contamination attributable to the sampling unit and the sampling unit zero challenge repeated to ensure criteria are met before sampling can be conducted. Subsequent collected field sample results for non-Tier I compounds that fail this criterion must be qualified when input to AQS.

4.2.3.5.2 Known Standard Challenge. The known standard challenge is performed by simultaneously providing a humidified (50 to 70% RH) known concentration standard of target VOCs (at approximately 0.3 to 2 ppb each) in air or UHP nitrogen to the sampling unit for collection into a canister and to a separate reference canister connected directly to the supplied standard gas stream. The reference canister collects the challenge gas directly and is the baseline for comparison of the challenge sample. Compounds which show enhanced or decreased concentrations in the challenge sample compared to the reference sample indicate bias attributable to the sampling unit.

It is recommended that the challenge gas contain all target VOCs, however, a smaller subset of compounds is sufficient provided that each target compound type is represented in the gas mixture (e.g. low molecular weight, fluorinated, chlorinated, brominated, high molecular weight, etc.).

The standard challenge gas is supplied to the challenge manifold by dilution of a gas mixture of VOCs via dynamic dilution with humidified HCF zero air. The manifold should be constructed of chromatographic stainless steel and should include three additional ports for connections to the sampling unit inlet, reference canister, and a rotameter acting as a vent to ensure that the manifold remains at ambient pressure. The reference canister may be collected via MFC, other constant flow device, or a grab sample to characterize the plenum manifold concentrations. Challenge gas is to be supplied such that there is excess flow supplied to the challenge manifold as indicated by the rotameter on the vent port. Samples are collected simultaneously for 24 hours to simulate real world conditions. Sampling for 24 hours best replicates conditions in the field, however, shorter sampling durations for these challenges are also acceptable.

Analysis by GC/MS for target compounds must demonstrate that each VOC in the challenge sample is within 15% of the concentration in the reference sample. All Tier I core compounds in the challenge gas must meet this criterion. For Tier I core compounds exceeding these criteria, corrective action must be taken to address the bias in recovery attributable to the sampling unit. Subsequent collected field sample results for non-Tier I compounds that fail this criterion must be qualified when input to AQS.

Following completion of the known standard challenge, the sampling unit should be flushed with humidified HCF zero air or ultra-high purity (UHP) nitrogen for a minimum of 24 hours.

Once shown as non-biasing, a best practice to assess ongoing bias is to compare fingerprint plots (discussed in Section 3.3.1.3.14.2) of each sample from the site.

4.2.4 Canister Hygiene. At the time of this TAD revision, measuring VOCs in ambient air using passivated stainless steel canisters is approximately a 40-year old technology. While measurement systems have become more sensitive with the advent of selected ion monitoring (SIM) and TOF detection, many agencies are unable to achieve sufficient sensitivity to measure VOCs at ambient concentrations in collected air samples due to the inability to properly clean and maintain canisters. The following sections present requirements and best practices for assessing background levels in canister media and maintaining sufficiently low background levels to the measurement of VOCs in ambient air.

4.2.4.1 Qualification of Canisters. When new canisters are received, it is *strongly recommended* that they be qualified appropriately prior to use for sample collection or for preparation of standards and blanks. New canisters may contain residues such as cutting oils, pump oils, or coating byproducts from the manufacturing process and/or residual contamination from compounds added by manufacturers to perform QC checks on the canisters prior to release to customers. Additionally, new canisters may have defects making them unsuitable for use even after the canisters have been cleaned and treated for the residual contaminants. Such defects may relate to poor valve sealing, active sites from incomplete coating or surface deactivation, or poor canister integrity due to inadequate welds.

Following new canister receipt and before use and annually thereafter, it is *strongly recommended* that canisters be properly cleaned, tested for leaks, and evaluated for bias such that the requisite canister performance specifications are met. As with new canisters, existing canisters in agency fleets may exhibit some of the same problems over time and it is *strongly recommended* that they be qualified on an annual basis to verify they are non-biasing. All canisters in a given fleet need not be qualified at the same time, rather a subset can be qualified on a rolling basis such that all canisters are qualified within the period of a year. For monitoring agencies with large canister fleets, it may not be feasible to assess each canister within a year. In such cases, the monitoring agency should prepare a schedule to assess canisters in a reasonable timeframe (e.g. every 18 months). Suitable procedures are described in the following sections.

4.2.4.1.1 Canister Bias. It is *strongly recommended* that all canisters be evaluated for bias when newly purchased (prior to use for field sample collection or use for laboratory QC sample preparation) and annually thereafter. Assessment for bias of newly purchased canisters or canisters from an existing fleet is performed identically. Canisters which exhibit a positive or negative bias exceeding the criteria below should be segregated and reconditioned before reuse or discarded. Some commercial canister manufacturers offer reconditioning services for their canisters. Consult the manufacturer for methods to clean or recondition cans which fail these bias criteria.

4.2.4.1.1.1 Canister Integrity and Zero Air Check

Within two days following cleaning, preferably the same day, canisters should be pressurized with humidified HCF zero grade air (or UHP N_2). This short duration following cleaning is intended to characterize the canister condition before analytes have a chance to "grow" in the canister. In order to assess leak tightness of the canisters and to best represent the contamination potential from collected field samples, pressurization should be performed so that the final canister pressure closely matches that of the typical pressure of field sample canisters. Subambient pressurization provides less diluent and may provide more measurable target compound mass per injection aliquot. Pressurization above ambient pressure permits removal of larger aliquots of sample gas, and as such affords more opportunities for reanalysis. In either case, canisters must be approximately 2 psi above or below ambient pressure to permit assessment of canister leaks. The leak check process given here is one example for a method to determine canister leak tightness. Other equivalent methods can be performed provided they meet the leak criteria of < 0.1 psi/day. Leak checks are recommended to be performed annually,

however the frequency of performing leak checks must be prescribed in the NATTS QAPP, SOP, or similar controlled document.

Immediately upon pressurization, each canister's pressure is measured with a calibrated gauge for establishment of a baseline. After a minimum of 7 days and after as long as 30 days, each canister's pressure is again measured. Canisters with leak rates > 0.1 psi/day must be removed from service and repaired. This leak rate permits 5% of the sample volume to leak over 7 days and a 20% sample volume leak over 30 days.

The canister should be analyzed within two days of initial pressurization and all Tier I core analytes must be < 3x MDL or < 0.2 ppb, whichever is lower, and non-Tier I compounds should meet this criterion. Note that following this analysis, the canister pressure must be remeasured to accurately assess the canister leak rate as the aliquot removed for analysis changes the canister pressure. Subsequent analysis may be performed minimally at 14 days after pressurization and is highly recommended to be performed at 30 days after initial pressurization. Laboratories may tailor this later timepoint to be representative of the maximum holding time experienced by the laboratory (e.g. 21 days if all samples are analyzed within this time frame from sample collection). Analyses at these later timepoints must show all Tier I core analytes < 3x MDL or < 0.2 ppb, whichever is lower, and non-Tier I compounds should meet this criterion. Intermediate timepoints less than 30 days will likely indicate if there is a problem with a particular canister. Canisters which meet criteria at intermediate timepoints should be analyzed at the 30-day timepoint to verify they are bias free for the 30-day period. If analysis can be performed at only one timepoint after initial pressurization, it is recommended to be at 30 days.

Laboratories have reported growth of oxygenated compounds (e.g. ketones, alcohols, aldehydes) in canisters. Of particular concern in the canister zero air checks is acrolein, which evidence suggests may "grow" in canisters that are stored for extended periods. The mechanism for acrolein growth is not well understood; however, such is widely regarded as problematic in performing ambient concentration analysis. Suggested pathways of acrolein growth are decomposition of particulate residue, slow time-release of acrolein from interstitial spaces within the canister, breakdown of cutting oil residues in valves, or decomposition of other volatile constituents within the canister. Concentrations of target compounds above twice the laboratory MDL should be closely scrutinized as they indicate the presence of canister background concentrations which may cause issues with future sample collection measurements.

4.2.4.1.1.2 Known Standard Gas Check

Following the canister zero air check in Section 4.2.6.1.1.1, it is *strongly recommended* that canister bias be assessed by filling a cleaned canister with a low-level (0.3 to 2 ppb) humidified standard gas and analyzed 30 days following the initial pressurization. Intermediate timepoints minimally 14 days after pressurization may be added and may indicate a bias problem, eliminating the need to perform the 30-day timepoint analysis. Canisters which meet criteria at intermediate timepoints should be analyzed at the 30-day timepoint to verify they are bias free for the 30-day period. Laboratories may tailor this later timepoint to be representative of the maximum holding time experienced by the laboratory (e.g. 21 days if all samples are analyzed within this time frame from sample collection). The initial analysis should show that target

analytes are within 30% of nominal and not show significant degradation beyond 30% of nominal for subsequent timepoints over the 30-day evaluation period.

While not a substitute for performing canister bias checks, an additional method to assess canister bias is to collect an ambient air sample, analyze it immediately, and analyze it again following an extended period (e.g. 30 days) and look for changes in analyte concentration which exceed 30% from the initial analysis.

4.2.4.2 Canister Cleaning. Cleaning of canisters for ambient sample collection may be performed in a variety of ways which may result in acceptably low background levels in the canister. Systems are commercially available from a variety of manufacturers or may be custom-built. Many incorporate the following elements:

1. Manifold for connection of several canisters (typically 4 to 8)
2. Rough vacuum pump to achieve vacuum of approximately 1 inch Hg
3. High vacuum pump (such as a molecular drag pump) to achieve a final canister vacuum of approximately 50 mTorr or less
4. Heating oven, heating bands, or heating jackets
5. Humidification system
6. Automated switching between evacuation and pressurization
7. A pressure release valve to minimize the likelihood of system overpressurization
8. Trap (cryogenic or molecular sieve) to eliminate backstreaming of contaminants into canisters (only necessary for systems with a non-oil free vacuum pump – note use of such pumps is not recommended)
9. Chromatographic grade stainless steel tubing and connections – recommend minimizing system dead volume to minimize pressurization/evacuation time and provide less surface area for contaminants
10. Source of clean purge gas such as zero air or UHP nitrogen
11. Absence of butyl rubber, Teflon®, or other materials that may adsorb and/or offgas compounds of interest or other potential interferences

Regardless of how canisters are cleaned, canister cleanliness criteria must be met.

Monitoring agencies must prescribe a policy for holding time for cleaned canisters, which must not exceed 30 days unless objective evidence indicates that the additional time does not negatively impact measured sample concentrations.

4.2.4.2.1 Heated Canister Cleaning. Heating of canisters during cleaning is *strongly recommended*. Various methods of heating canisters during cleaning may be employed. The temperature applied to the canister should depend on whether the canister is silica-lined or electropolished, the temperature rating of the valve and vacuum gauge (if so equipped), and the heating method employed.

Heating bands often cause hot spots on the canister, do not evenly heat canister surfaces further from the bands, and may not adequately heat the valve. Heating jackets and ovens heat the canister evenly, but may not be able to isolate the valve from the heat source, which may cause damage to the valve if cleaning is performed at high heat (> 80ºC). Some heating jackets or ovens allow the valve to protrude from the jacket or oven and allow the valve to only be exposed to radiant heat.

If employing humidified HCF zero grade air during canister cleaning (specifically the canister pressurization steps), silica-lined canisters should not be heated above 80°C as oxidation of the surface may occur which leads to active sites within the canister.[6]

Heating is recommended for cleaning of ambient concentration canisters, however higher temperatures are not always better. For canisters of known history used for ambient sample collection, heating to approximately 75°C during cleaning is generally sufficient. Canisters used for collection of source level (part per million) samples or samples with matrices including high molecular weight compounds with high boiling points should be heated to a higher temperature (100°C or higher), if permitted by the canister and valve. Typically such canisters cannot be sufficiently cleaned and should be sequestered from use for collecting ambient samples.

4.2.4.2.2 Cycles of Evacuation and Pressurization. Canisters containing standards or unknown contents with pressures above ambient pressure should be vented into a fume hood or other exhaust outlet prior to connection to the canister cleaning manifold. In general, the greater the number of evacuation and pressurization cycles, the more effective the cleaning. Also, longer holds of vacuum generally result in more effective cleaning. Canisters should be evacuated to > 28 inches Hg vacuum during each evacuation cycle.

While TO-15 recommends three cycles of evacuation and pressurization, minimally five cycles of evacuation and pressurization are recommended and ten or more have been shown to be effective in removing stubborn oxygenated compounds (e.g. acetone, methyl ethyl ketone, and isopropanol). [7] Following the principle of extraction efficiency where each cycle recovers a specific percentage of each compound (i.e. 85%), additional evacuation and pressurization cycles (up to 20) are highly recommended to achieve sufficiently clean canisters. Vacuum of > 28 inches Hg should be maintained for minimally 5 minutes before the pressurization step. Final evacuation to ≤ 50 mTorr and maintaining this vacuum for minimally 5 minutes is recommended. Longer final vacuum holds up to approximately an hour are recommended if feasible. Automated canister cleaning systems may be advantageous as including additional cycles or extending vacuum hold times can easily be programmed.

An alternative to performing the final evacuation at the end of the cleaning cycles, canisters may be stored pressurized with humidified zero air or other clean purge gas. When stored pressurized, canisters are evacuated to ≤ 50 mTorr just prior to field deployment.

4.2.4.2.3 Gas Source for Canister Cleaning Pressurization. If canisters are heated during cleaning, pressurization of canisters to approximately 5 psig is recommended to avoid rupture of the canister when heat is applied. For canisters which are not heated during cleaning, pressurization up to approximately 30 psia is recommended. The purge gas for canister cleaning

should be high purity zero air or nitrogen. Scrubbing of purge gas with additional hydrocarbon traps, moisture traps, and/or catalytic oxidation may be necessary to obtain sufficiently clean purge gas which should be < 0.2 ppbv or < 3x MDL, whichever is lower. When using zero air as the purge gas, lower temperatures should be maintained during the cleaning process (as compared to temperatures possible with UHP N_2) in order to avoid oxidation of interior canister surfaces. UHP nitrogen may be sourced from cylinders or may be the headspace gas from a liquid nitrogen dewar. Regardless of the purge gas selected, its cleanliness should be verified by analysis to ensure that contaminants are not introduced into the canisters during the cleaning process.

The source gas should be humidified to approximately 30 to 70% as practical, generally higher humidity levels are considered to be more effective. The water assists in removal of polar compounds which may otherwise remain adsorbed to interior canister surfaces. Most commercial canister cleaning systems incorporate a type of humidifier, however these typically do not provide a sufficient level of humidity. Humidification systems may be constructed which incorporate a diptube in deionized water which humidifies by bubbling the purge gas through the deionized water or via an impinger placed above the surface of the water in the humidifying chamber. If a bubbler type humidifier is employed, care should be taken to ensure the downstream pressure is lower than the humidifier upstream pressure to avoid backflow of the water. It is recommended that the RH of the purge gas be measured with a calibrated hygrometer to ensure the desired RH is attained.

4.2.4.2.4 Verification of Canister Cleanliness. Following completion of canister cleaning activities, minimally one canister per batch cleaned must be pressurized to approximately the pressure of field collected samples with humidified purge gas, held minimally overnight, and analyzed to ensure all target compounds are < 3x MDL or < 0.2 ppbv, whichever is lower. Cleanliness criteria must be lowered for agencies which dilute field samples such that the cleanliness criteria are met for undiluted samples. For instance, if a laboratory dilutes all samples by two-fold by addition of gas to the collected sample canister, the cleanliness criteria are not doubled, but are cut in half. A detected concentration of benzene at 0.15 ppbv (assuming 3x MDL is higher) at the instrument would not pass criteria, as the concentration adjusted for dilution is 0.30 ppbv which exceeds the 0.2 ppbv criterion.

Analysis of more than one canister from each batch is highly recommended and should be no less than one out of every ten canisters. A best practice is to survey every canister in a cleaning batch. Following analysis, canisters are re-evacuated to ≤ 50 mTorr. If only a subset of the canisters in the batch is able to be analyzed, the selected canisters should be those which indicated the highest total VOC concentration or the highest single target compound concentration in the previous sample. Other conventions for selecting the batch blank canister include random selection or evaluating high molecular weight compounds or oxygenated compounds which are more difficult to completely remove from canisters.

A composite batch blank sample may be prepared by closing the valve of a chosen canister (which is still under vacuum). The manifold is then pressurized with clean purge gas such that the other connected canisters are pressurized. The chosen batch blank canister is then opened to fill the canister with the composite gas from all of the canisters connected to the manifold.

Actions must be taken to further investigate failure of batch blanks to meet the cleanliness criteria. If each cleaned canister from the batch is surveyed, only those canisters which fail the criteria must be recleaned. If one canister representing the batch fails, either the entire batch can be recleaned (recommended) or two canisters from the batch can be selected and analyzed to confirm the batch does not pass criteria. If both of these canisters pass, only the failing canister must be recleaned, otherwise, the batch must be recleaned. Continued failure of batch blanks may indicate that the manifold or other parts of the system has become contaminated.

4.2.4.3 Canister Maintenance and Preventive Maintenance. Maintenance of canisters involves a combination of preventive actions and best practices related to initial canister qualification, sample collection, cleaning, and general handling.

4.2.4.3.1 Collection of Whole Air Samples into Canisters. Whole air sampling into canisters must be performed with a particulate filter as discussed in Section 4.2.3.3 as once particulates have been drawn into a canister, they are difficult to remove. Particulate residue inside of a canister creates active sites and adsorption sites which may have a detrimental effect on sample compound recovery. Particulates may deposit into canister valves, potentially leading to the damage of the threads and seals, resulting in leaks. Furthermore, general cleaning of canisters does little to remove particulate residue interferences which may be indistinguishable from degradation of the interior surface of the canister. For canisters which cannot be remediated successfully, the canister may require retirement. Alternatively, canister manufacturers offer canister reconditioning services which can restore canisters to brand new condition.

When not connected to a system for cleaning, sample collection or analysis, the canister opening should always be capped with a brass cap to ensure particulates do not deposit into the valve opening. To avoid galling the threads of the connection, the brass cap should be installed finger tight then snugged gently, no more than 1/8 turn with a wrench.

4.2.4.3.2 Overtightening of Valves. The amount of torque required to close a valve depends on the particular type of valve and overtightening will likely damage the valve. Canister valves should never be closed with excessive force or by using a wrench. Damaged valves may not seal appropriately resulting in leaks. Valves with damaged threads or seals should be replaced.

4.2.4.3.3 General Canister Handling. Canisters should be handled with care to ensure that weld integrity is maintained, that the interior canister surface is not compromised, and that the valve-to-canister connection remains intact. Shocks to the surface of the canister may damage welds or create small cracks in the interior canister surface which may expose active sites. Excessive pressure on the canister valve may cause leaks in the seal between the canister valve and canister stem.

Shipment of canisters in protective hard-shell boxes and/or sturdy cardboard boxes is recommended to ensure canister longevity. Care should be taken to replace any boxes which have lost integrity or rigidity.

4.2.5 Method Detection Limits. MDLs for VOCs must be determined minimally annually by following the procedures in Section 4.1. To ensure that the variability of the media is characterized in the MDL procedure, separate spiked canisters (it does not suffice to simply analyze a low-concentration level standard) and method blanks must be prepared, carried out with canisters in use for field collection. It is recommended that canisters are chosen randomly and that each type of canister employed for field sample collection be represented. It is not acceptable to "cherry pick" the best performing canisters for determining MDLs. For example, laboratories determining the MDL following Section 4.1.2.1 must prepare a minimum of seven method blank canisters and a minimum of seven spiked canisters over the course of three different batches (different calendar dates – preferably non-consecutive). These samples must be analyzed in three separate analytical batches (different calendar dates – preferably non-consecutive). The MDL is then determined by calculating the MDL_{sp} and MDL_b and selecting the higher of the two concentrations as the laboratory MDL. Please refer to section 4.1.2 for specific details on selecting a spiking concentration, procedures, and calculations for determining MDLs.

While the MDL capabilities of each laboratory may vary due to a number of factors (canister hygiene, condition of equipment, cleanliness of diluent gases, etc.), spiking concentrations for VOCs MDLs of approximately 0.05 to 0.125 ppbv are typical to achieve the required MDL MQOs.

All steps performed in the preparation and analysis of field sample canisters (such as dilution) must be included in the MDL procedure. Canisters must be prepared at the selected spiking concentration with humidified diluent gas. It is not appropriate to prepare a higher concentration spike and analyze a smaller aliquot than analyzed for field collected samples. For example, for laboratories which analyze 500 mL of field collected sample, a spike concentration of 0.06 ppbv was chosen. The spiked canisters should be prepared at 0.06 ppbv with humidified diluent gas and 500 mL analyzed. It would not be acceptable for the laboratory to prepare spikes at 0.30 ppbv and analyze only 100 mL of the sample as this would not be representative of the procedure for field collected samples.

Note that at very low levels approximating the MDL, the qualitative identification criteria related to qualifier ion abundance ratio and/or signal-to-noise ratio listed in Section 4.2.10.5.3 may not be strictly met when determining the MDL. As the MDL spikes are prepared in a clean matrix with standard materials, the presence of the analyte is expected.

Determined MDLs for Tier I core analytes must meet (be equal to or lower than) those listed in the most current workplan template.

4.2.6 Canister Receipt. When received at the laboratory, canister samples must be accompanied by a COC form. The sample custodian must sign and date the custody form indicating transfer of custody and examine the sample collection documentation. Sample custody is further described in Section 3.3.1.3.7.

Canister pressure for canisters collected to subambient pressure must be measured with a calibrated gauge or pressure transducer when received at the laboratory to ensure that the sample

has not leaked. This is a best practice for canisters collected to pressures above ambient pressure. An acceptable pressure change for subambient pressure samples between the measured pressure at sample retrieval in the field and the pressure upon receipt in the laboratory must be defined in an SOP or similar quality systems document. The recommended tolerance is a pressure change of ≤ 0.5 psia (ensure the measurement is in absolute pressure to account for differences in altitude which contribute to error when measured in psig). Pressurized samples must be measured prior to analysis to ensure that they have not leaked down to atmospheric pressure. Subambient pressure samples which demonstrate pressure changes exceeding criteria should be invalidated.

4.2.7 Dilution of Canisters. Canister samples collected at subambient pressures may require pressurization with HCF zero air or UHP nitrogen to provide sufficient pressure for analysis. When such dilution is performed, the diluent gas must be collected in a separate certified clean canister as a dilution blank (DB) and analyzed to ensure that the dilution process does not contaminate collected samples.

The canister pressure must be measured with a calibrated pressure gauge or pressure transducer just prior to dilution and immediately following dilution. A canister dilution correction factor (CDCF) is calculated from the two absolute pressure readings as follows:

$$\mathrm{CDCF} = \frac{P_d}{P_i}$$

where:
P_d = The pressure of the canister following dilution (psia)
P_i = The pressure of the canister immediately preceding dilution (psia)

Diluted canisters should be allowed to equilibrate minimally overnight, and preferably 24 hours before analysis.

4.2.8 GC/MS Tuning, Calibration, and Analysis

4.2.8.1 Interferences. Moisture in the sample gas may interfere with VOC analysis by GC/MS. Poor water management can cause peak broadening and retention time shifts resulting in peak misidentification, particularly for hydrophilic polar compounds. Carbon dioxide in the collected sample can coelute with more volatile VOCs and interfere with their quantitation. A properly configured moisture management system (as discussed below) can reduce or eliminate the interference of water and carbon dioxide.

Preconcentration systems employ moisture management techniques to eliminate most of the water in the concentrated sample. Instrument manufacturers utilize different methods to manage water removal as well as carbon dioxide such as extended cold trap dehydration (ECTD) or microscale purge and trap (MPT) techniques.

ECTD removes most of the water in the sampled gas by passing the sample gas through an empty first trap cooled to approximately -50°C. This low temperature immediately freezes the

water and allows the VOCs to pass through to a second trap consisting of a weak adsorbent where the VOCs are then trapped. To ensure complete transfer of the VOCs, the first trap is warmed to just above the freezing point of water and a small volume of dry inert gas is employed to sweep any higher boiling point VOCs to the second trap while retaining the water on the first trap.[8]

MPT typically permits a larger amount of water to pass through to the second trap and ultimately to the analytical column than ECTD, potentially resulting in peak broadening and retention time shifts. For MPT, the first trap containing sorbent and/or deactivated glass beads is cooled to approximately -160 to -110°C where all the water and VOCs are retained. The first trap is then heated to several degrees above the freezing point of water and purged with dry inert gas to sweep the VOCs to the second sorbent trap.[8] The purge of the first trap at a higher temperature may permit more water onto the column compared to ECTD.

Artifacts in chromatograms such as silanol compounds formed from the breakdown of fused silica linings of canisters and siloxane compounds from the breakdown of the stationary phase in an analytical column can interfere with quantitation of less volatile VOCs.

4.2.8.2 Specifications for the Preconcentrator and GC/MS. The analysis instrument must employ detection via mass spectrometer (MS). The MS may be a quadrupole, ion trap, TOF detector. Detection via flame ionization detector (FID) does not permit positive compound identification. Flame ionization detection may be performed by way of splitting the column effluent with the MS and quantitation can be performed from the FID signal. However due to the non-specific nature of FID detectors, analytes must be qualitatively identified via the MS.

Sample introduction and concentration should be handled by an automated cryogenic preconcentration system capable of cooling to as low as -190°C and capable of quantitatively transferring target analytes to the GC column. For cryogenic systems, the target VOCs are isolated from the whole air matrix by passage of the matrix onto a series of traps packed with deactivated glass beads or with a polymer or graphitized sorbent; in some systems, water management is performed by passage of the gas stream through a cryocooled, empty trap. Typically the final step in the cryogenic preconcentration routine is to refocus the VOCs onto another low-volume trap for introduction as a tight band onto the head of the GC column.

The GC should be temperature programmable with cryogenic cooling capabilities. VOCs should be separated with a 60 m by 0.32 mm capillary column with 1 µm lining of 100% dimethylpolysiloxane (e.g., DB-1), or with a column capable of separating the target analytes and ISs so that method performance specifications are attained. The transfer line to the MS should be capable of maintaining 200°C.

The MS detector is operated in electron ionization mode at 70 electron volt (eV) in full scan, SIM, or SIM/scan mode. If operated in full scan or SIM/scan mode, the MS must be capable of completing an entire scan in ≤ 1 second. The MS must be capable of scanning from 45 to 250 atomic mass unit (amu) and producing a mass spectrum of BFB compliant with the ion abundances listed in Table 4.2-2 (for instruments operating in SCAN or SIM/SCAN mode). For laboratories performing analysis of lower molecular weight analytes such as acetonitrile (ACN),

methanol, acetylene, etc., a lower MS scan range capable of 25 to 250 amu may be necessary. Note that the lower scan range often increases the presence of low mass interferences in the chromatogram.

Sample and standard introduction to the preconcentrator is preferably performed via autosampler which allows connection of many canisters that permits unattended analysis of anywhere from four to 16 or more canisters and permits unattended operation. Ports are also typically available on the preconcentrator for internal standard and/or standard introduction.

4.2.8.3 Standards and Reagents

4.2.8.3.1 Calibration Standards. Stock calibration gases may be procured at concentrations ranging from approximately 50 to 1000 ppb of each target VOC in UHP nitrogen. Target VOCs in this concentration range are generally stable in high pressure passivated cylinders for at least one year, although some vendors certify their mixtures for longer time periods. Calibration gases should be recertified by the supplier or third party annually unless a longer expiration period is assigned by the supplier. Alternatively, a new stock standard or set of stock standard gases may be procured; however, this is typically several-fold more expensive than recertification. Dilution of the stock calibration gas by approximately 400-fold permits preparation of working range calibration standards in canisters at single digit ppb concentrations.

Off-the-shelf stock mixes are available containing approximately 65 target VOCs including the NATTS core VOCs at 1 ppm, and gas mixtures with tailored compound lists and concentrations are available as custom orders from certain suppliers. It may be necessary to procure multiple stock gases to acquire all desired VOCs.

Calibration stock gases must be purchased from a supplier that provides a COA stating each target VOC's concentration with associated uncertainty. An expiration must be assigned to each standard gas mixture. Uncertainty of the certified concentrations must be specified as within no more than ± 10%.

4.2.8.3.2 Secondary Source Calibration Standards. Secondary source stock calibration gases must be procured from a separate supplier and meet the criteria listed above in Section 4.2.10.3.1. A standard prepared with a different lot of source material from the same supplier as the primary calibration stock is only acceptable if it is unavailable from another supplier. As with the calibration stock gases, the secondary source stock must be recertified annually.

4.2.8.3.3 Internal Standards. IS gases should be procured including a minimum of three VOCs covering the early, middle, and late elution range of the target VOC elution order. At minimum a single IS compound must be used. ISs must either be deuterated VOCs or VOCs which behave chromatographically similarly to, but are not, target VOCs. Three typical VOCs internal standards are 1,4-difluorobenzene, chlorobenzene-d_5, and bromochloromethane.

IS stock gases are commercially available at 100 ppb in UHP nitrogen, or may be purchased with a custom suite of compounds at desired concentrations. IS stock gases should be evaluated upon

receipt for the presence of contaminants. Compounds whose response increases with an increasing volume of IS analyzed are present in the IS mixture. IS gas standards which contribute unacceptable levels of target VOCs, such that, for instance, system blanks fail acceptance criteria, must not be employed for analysis and must be replaced. Typical contaminants in IS mixtures include methylene chloride and carbon disulfide.

The IS must be added to and analyzed with each injection at the same concentration in order to monitor instrument sensitivity and assess potential matrix effects. ISs are not added directly to the sample canister, rather they are introduced through a different dedicated non-sample port in the preconcentrator and trapped along with the sample aliquot on the first trapping module in the preconcentrator. The concentration of IS added to each injection should be chosen such that the IS compounds provide a peak which is onscale and approximates the area response of the highest calibration standard.

4.2.8.3.4 Diluent Gases. Diluent gases may consist of zero air or UHP nitrogen. Zero air is typically sourced from a zero air generator and may be further scrubbed by treatment with activated carbon scrubbers or oxidizers. Zero air is also commercially available in cylinders, however may be cost prohibitive to procure meeting cleanliness specifications or may require further cleanup to remove impurities which affect analysis. Nitrogen gas must be from an UHP source (purity ≥ 99.999%) or from the headspace of a liquid nitrogen dewar. Regardless of which gas is chosen as a diluent, it must be analyzed to demonstrate to verify that levels of target VOCs are acceptably low (≤ 3x MDL or 0.2 ppb, whichever is lower). For diluent gas contained within a cylinder or from discrete liquid nitrogen tanks, the gas must be analyzed prior to preparing dilutions with the gas. For zero air generators or replenished onsite fixed liquid nitrogen Dewars, the diluent gas must be analyzed monthly.

4.2.8.3.5 MS Tuning Standard – BFB. 4-bromofluorobenzene (BFB) may be purchased as a standalone gas at approximately 30 to 100 ppb in UHP nitrogen or may be purchased as a component in the IS mixture.

4.2.8.3.6 Reagent Water for Humidification of Gases. Reagent water for humidification of gases must be ASTM Type I (≥ 18 MΩ·cm). Additional purifying steps, such as sonication, helium sparging, or boiling may be necessary to reduce or eliminate dissolved gases potentially present in the water.

Humidification is most efficiently performed by bubbling the gas to be humidified through a bubbler via a diptube submerged in the reagent water or passing the gas across the surface of the reagent water via an impinger. Analysts should be aware of the potential for water to enter the bubbler tube and be sucked into the gas supply tubing if the pressure downstream of the bubbler becomes greater than the upstream pressure. Passing of the gas to be humidified through the headspace of a vessel containing water typically achieves a RH of 20 to 30%, which is insufficient to maintain the desired RH level of approximately 50% for serving as a diluent gas in standards preparation or as a humidified blank. Laboratories should measure the RH of the resulting humidified gas stream to ensure it reaches approximately 50%. If this RH level cannot be reached with an inline humidification system, liquid water should be added to the canister. Approximately 75 µL of deionized water can be added to the canister to increase the RH to

approximately 40-50% at room temperature and 30 psia. Adding water to canisters with a syringe via rubber septum is not recommended, as the syringe needle can core the septum resulting in deposits of rubber into the canister and valve, leading to later bias problems with the canister. For direct injection of water into a canister with a syringe, a high pressure Teflon sealed septum (such as a Merlin Microseal®) should be installed on the canister. For canisters which are connected to a gas source for pressurization via a dynamic or static dilution system, the water can be added to the valve opening prior to connecting the outlet tubing. Once the tubing is connected, the valve is opened and the water is pulled into the canister along with the diluted standard gas.

4.2.8.4 Preparation of Calibration Standards and Quality Control Samples

4.2.8.4.1 Calibration Standards. Working calibration standards are typically prepared by diluting the calibration stock gas with humidified zero air by dynamic dilution or calibrated automated static dilution. In these types of dilution, flows of the stock gas(es) and diluent gas are carefully metered and the gases may be blended in a mixing chamber to ensure complete mixing. Such systems are commercially available which permit the mixing of multiple standard gases with a diluent gas. The homogenous, diluted gas mixture is then collected into a cleaned canister. Working level concentrations are tailored to provide standards covering approximately 0.1 to 5 ppb.

Calibration standard canisters may be prepared according to two conventions for calibrating the GC/MS. The first convention consists of preparing a separate canister for each calibration concentration level such that a total of five different calibration standard canisters are prepared to establish the calibration curve with the required minimum five points. For this procedure, the same volume is analyzed from each canister to establish the calibration curve. The second convention consists of preparing two separate canisters at a low and high concentration. Different volumes of each of the two canisters are analyzed to prepare the five-point calibration curve. It is also acceptable to prepare the calibration curve by injecting different volumes from a single canister provided the calibration curve is verified with an independent second source quality control standard.

MFCs in dynamic dilution systems must be calibrated initially and the calibration verified minimally quarterly. Mass flow controllers which fail the calibration check criterion of 2% must be calibrated. Removal of the MFC from the dynamic dilution system to be calibrated by the manufacturer is inconvenient and expensive. Instead, a regression calibration can be generated by challenging the MFC with gas and recording the MFC setting and measuring the flow with a flow calibrator for a minimum of five points covering the 10% to 100% of the flow range of the MFC. The resulting regression slope and intercept is then employed to provide the MFC setting for a given desired flow.

Dynamic dilution systems should be powered on and diluent and stock gases flowing through the MFCs for minimally one hour prior to use. Warm-up flows should be the desired settings necessary to prepare the working calibration standards. This warm-up period allows passivation and equilibration of gases to ensure the concentration of the blended gas is stable prior to transferring to the canister. When changing stock gas flow rate to prepare a different

concentration, calibration gas should flow through the system for a minimum of 30 minutes prior to preparation of the working calibration canister. These warm-up and equilibration times are particularly important for laboratories analyzing compounds with higher boiling points such as hexachlorobutadiene and 1,2,4-trichlorobenzene. Extended equilibration times may be necessary to fully passivate the flow path and mixing chamber of the dynamic dilution system when these compounds are desired.

Note that final pressures of calibration standard canisters must not exceed the maximum pressure permitted by the preconcentrator unit. Closely matching the pressure of the calibration standard canisters to the expected pressure of the collected field samples is recommended when analysis is performed with preconcentrators that measure volumes with MFCs. Consult the preconcentrator instrument manual for further guidance on matching canister pressures.

The preferred procedure for preparing calibration standards is dynamic dilution; however, static dilution by way of syringe injection of calibration stock gases may also be employed. Syringe dilution requires excellent technique to accurately and reproducibly prepare calibration standards.

Calibration standard canisters must be humidified to approximately 50% RH by either humidifying the diluent or by addition of liquid water to the canister. For diluent gases which are humidified to approximately 25% RH, approximately 100 µL of reagent water should be added to the canister prior to pressurization with standard gas to approximately 30 psia. For standard canisters prepared at lower pressures, a smaller volume of water should be added. Standard canisters must be allowed to equilibrate minimally overnight (recommended 24 hours) before analysis.

4.2.8.4.2 Second Source Calibration Verification Sample. A second source calibration verification (SSCV) is prepared in a canister at approximately the mid-range of the calibration curve by dilution of the secondary source stock standard. The SSCV verifies the accuracy of the calibration curve. The SSCV must minimally contain all Tier I core compounds and it is recommended that the SSCV also contain at least one compound representative of each type of compound in the calibration (e.g. low molecular weight, chlorinated, fluorinated, brominated, high molecular weight, etc.). It is strongly recommended that the SSCV contain all compounds in the calibration mix.

4.2.8.4.3 Method Blank. The MB canister is prepared by filling a cleaned canister with humidified diluent gas. For laboratories using a dilution system (dynamic or automated static), the method blank should be pressurized with the dilution system. The MB verifies the diluent gas is sufficiently clean. To best represent canisters which are sent to the field for sample collection, the MB should be prepared in a clean canister which was verified by batch blank analysis. Analysis of a canister cleaning batch blank as the MB complicates the corrective action process to locate the source if the MB canister analysis indicates contamination.

4.2.8.4.4 Laboratory Control Sample. The LCS is prepared at approximately the lower third of the calibration range by dilution of the calibration stock gas. While not required, preparation and analysis of the LCS is recommended. The LCS may serve as the CCV and the

volume of LCS analyzed should be the same volume as that taken from sample canisters for routine analysis. The LCS serves to both verify that calibration standards were prepared correctly and that the instrument remains in calibration.

4.2.8.5 Analysis via GC/MS

4.2.8.5.1 Tuning of the MS. Prior to initial calibration and every 24 hours of analysis thereafter, the MS tune of quadrupole MS detectors must be verified to meet the abundance criteria in Table 4.2-2 by injection and analysis of approximately 50 ng of BFB when operating in SCAN or simultaneous SIM/SCAN mode.

Failure to meet the BFB tuning criteria requires corrective action which may include adjusting MS tune parameters or cleaning of the ion source. The instrument must be recalibrated following adjustments or maintenance which impacts the MS tune.

To the extent possible for ion trap and TOF MS detectors, tune the MS such that the m/z abundance sensitivities are maximized for the lower mass range, m/z < 150. TOF and ion traps should be tuned per the manufacturer specifications.

Table 4.2-2. Required BFB Key Ions and Ion Abundance Criteria

Mass (m/z)	Ion Abundance Criteria *
50	8.0 to 40.0% of m/z 95
75	30.0 to 66.0% of m/z 95
95	Base peak, 100% relative abundance
96	5.0 to 9.0% of m/z 95 (see note)
173	Less than 2.0% of m/z 174
174	50.0 to 120.0% of m/z 95
175	4.0 to 9.0% of m/z 174
176	93.0 to 101.0 of m/z 174
177	5.0 to 9.0% of m/z 176

* All abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120% of m/z 95.

4.2.8.5.2 Leak Check and Calibration of the GC/MS

4.2.8.5.2.1 Leak Check

Prior to beginning an analytical sequence, including an initial calibration (ICAL) sequence, each canister connection must be verified as leak-free through the preconcentrator. During the leak check, canisters are connected to the autosampler or sample introduction lines and the canister valves are kept closed. Each port of the autosampler or sample introduction line is evacuated and the pressure monitored over 30 seconds or 1 minute for a change in pressure. Connections

which show a pressure change of > 0.2 psi/minute or exceed manufacturer criteria must be corrected by tightening the fittings. Leak check criteria in automated leak check routines should be equivalent to or better than those listed above and should be prescribed in the analysis SOP. Analysis must not be performed on any canister connection which does not pass the leak check. Canisters which do not pass leak check may leak to atmospheric pressure allowing laboratory air into the analyzed sample stream. Many preconcentration control software systems include a leak check function which provides standard QC reports. Following the leak check all autosampler ports or sample introduction lines are evacuated and the canister valves are opened. Leak checks must be documented in the analysis records.

4.2.8.5.2.2 Initial Calibration of the GC/MS

The GC/MS instrument must be calibrated initially, following failure of CCV checks, and following adjustments or maintenance which impact the performance of the GC/MS system including, but not limited to: cleaning of the ion source, trimming or replacing the capillary column, or adjustment of MS tune parameters.

The MS must meet BFB tune criteria listed in Section 4.2.10.5.1 before calibration may begin. An instrument blank (IB) is recommended to be analyzed prior to analysis of calibration standards to demonstrate the instrument is free of target VOCs and potential interferences. The IB is an injection of carrier gas taken through the preconcentration steps without introduction of sample gas into the preconcentrator. Analysis of the IB must show all target compounds are < 3x MDL or < 0.2 ppb, whichever is lower.

The ICAL curve is prepared by analysis of different concentration levels covering approximately 0.03 to 5 ppbv. At minimum five levels must be included in the ICAL and more are recommended, especially in the lower end of the calibration curve if the lowest standard concentration is in the tens of pptv. Calibration curves may be established on the instrument by two conventions. The first convention is to prepare a separate canister for each level of the calibration curve and inject the same volume from each canister. The second convention involves preparation of one to three canisters at different concentrations from which different volumes are analyzed to establish the calibration curve. An example of this second convention with two separate canisters follows:

> For a typical analysis volume of 400 mL, an eight-point calibration curve is constructed utilizing two standard canisters prepared at 0.25 ppbv and 5.0 ppbv. The curve is established at 0.03, 0.05, 0.075, 0.1, 0.25, 0.75, 1.5, and 5.0 ppb by analysis of 48, 80, 120, 160, and 400 mL from the 0.25 ppb canister and analysis of 60, 120 and 400 mL from the 5.0 ppb canister.

For measuring low (tens of pptv) levels of VOCs as is needed for ambient air analysis, it is important to characterize the lower end of the calibration curve by loading the number of calibration points toward the bottom of the curve (as shown in the example above). Including more points in the lower end of the curve minimizes calibration error at the low end of the curve as the upper end of the curve has an outsized influence on the curve model when calibration levels are evenly distributed across the calibration range.

When the second calibration convention is utilized (analyzing different volumes out of one to three canisters), checking the calibration of the MFC quarterly is recommended to ensure accurate volumes are metered for analysis.

Following analysis of all calibration standards, a calibration curve is prepared for each target analyte by determining the relative response factor of each concentration level. Following data acquisition for the calibration standards, the relative response factor (RRF) of each target compound in each calibration level is determined as follows:

$$RRF = \frac{A_s \cdot C_{IS}}{A_{IS} \cdot C_s}$$

where:

A_s = peak area for quantitation ion of the target compound
A_{IS} = peak area for quantitation ion of the assigned internal standard compound
C_s = concentration of the target compound
C_{IS} = concentration of the assigned internal standard compound

If the method of RRFs is selected for construction of the calibration curve, the relative standard deviation (RSD) of the RRFs for each Tier I Core target VOC must be ≤ 30% and all other compounds should meet this specification. For Tier II compounds which do not meet this criterion, results should be qualified when reported to AQS. Alternatively, a calibration curve may be prepared by linear or quadratic regression of the ratios A_S/A_{IS} as the dependent variables and the ratios C_S/C_{IS} as the independent variables. The correlation coefficient for linear or quadratic curves must be ≥ 0.995 for target VOCs. Irrespective of the curve fit method selected, the calculated concentration for each VOC at each calibration level must be within 30% of the nominal concentration when quantitated against the resulting calibration curve. Exclusion of calibration standard levels is not permitted unless justifiable (for example, a known error in standard preparation). Sample analysis must not be performed, and if performed, results must not be reported when calibration acceptance criteria are not met for Tier I core analytes. Rather, corrective action, possibly including recalibration, must be taken.

Relative retention times (RRTs) are calculated for each concentration level of each target compound by dividing the target compound retention time (RT) by the associated IS compound RT. The RRTs of each target compound are then averaged to determine the mean RRT ($\overline{RRT}$) of the ICAL. RRT at each concentration level must be within ± 0.06 RRT units of $\overline{RRT}$.

4.2.8.5.2.3 Secondary Source Calibration Verification

Following each successful initial calibration, a SSCV standard must be analyzed to verify the ICAL. Each target VOC in the SSCV must recover within ± 30% of nominal or the RRF must be within ± 30% of the mean ICAL RRF. Periodic reanalysis of the SSCV is recommended once the ICAL has been established.

4.2.8.5.2.4 Continuing Calibration Verification

Once the GC/MS instrument has met tuning and calibration criteria, a CCV must be analyzed after every 24 hours of analysis immediately following the BFB tune check and is recommended to be analyzed after every ten sample injections and at the end of each analytical sequence. Each target VOC's concentration in the CCV must be within ± 30% of nominal or the RRF must be within 30% of the average RRF from the ICAL. Corrective action must be taken to address CCV failures, including, but not limited to, preparing and analyzing a new CCV, trimming or replacing the column, retuning the MS, or preparing a new ICAL.

4.2.8.5.2.5 Analysis of Laboratory QC Samples and Field Samples

The following laboratory QC samples are required with each analysis batch containing 20 or fewer field-collected canisters:

- MB
- Replicate sample analysis

Each target VOC's concentration in the MBs must be < 3x MDL or < 0.2 ppb, whichever is lower. The precision of the replicate analysis must be such that ≤ 25% RPD is achieved for each target VOC having a concentration > 5x MDL. Samples should be reanalyzed to confirm the out of criteria result(s) and if confirmed, should be a trigger for corrective action. Sample data associated with these failures must be qualified appropriately when reported to AQS.

An LCS is recommended to be analyzed with each analysis batch, and must recover within 70 to 130%.

4.2.8.5.3 Compound Identification. Four criteria must be met in order to positively qualitatively identify a target compound:

1. The signal-to-noise ratio of the target and qualifier ions must be > 3:1, preferably > 5:1.
2. The target and qualifier ion peaks must be co-maximized (peak apexes within one scan of each other).[9]
3. The RT of the compound must be within the RT window as determined from the ICAL average.
4. The abundance ratio of the qualifier ion response to target ion response for at least one qualifier ion must be within ± 30% of the average ratio from the ICAL.

Please refer to Figure 4.2-2 for an example of the qualitative identification criteria listed above and the following discussion. The RT is within the retention time window defined by the method (red box A), and the abundance ratios of the qualifier ions are within 30% of the ICAL average ratio (red box B). The signal-to-noise ratio of the peak is shown to be greater than 5:1 (red oval C) and the target and qualifier ion peaks are co-maximized (dotted purple line D).

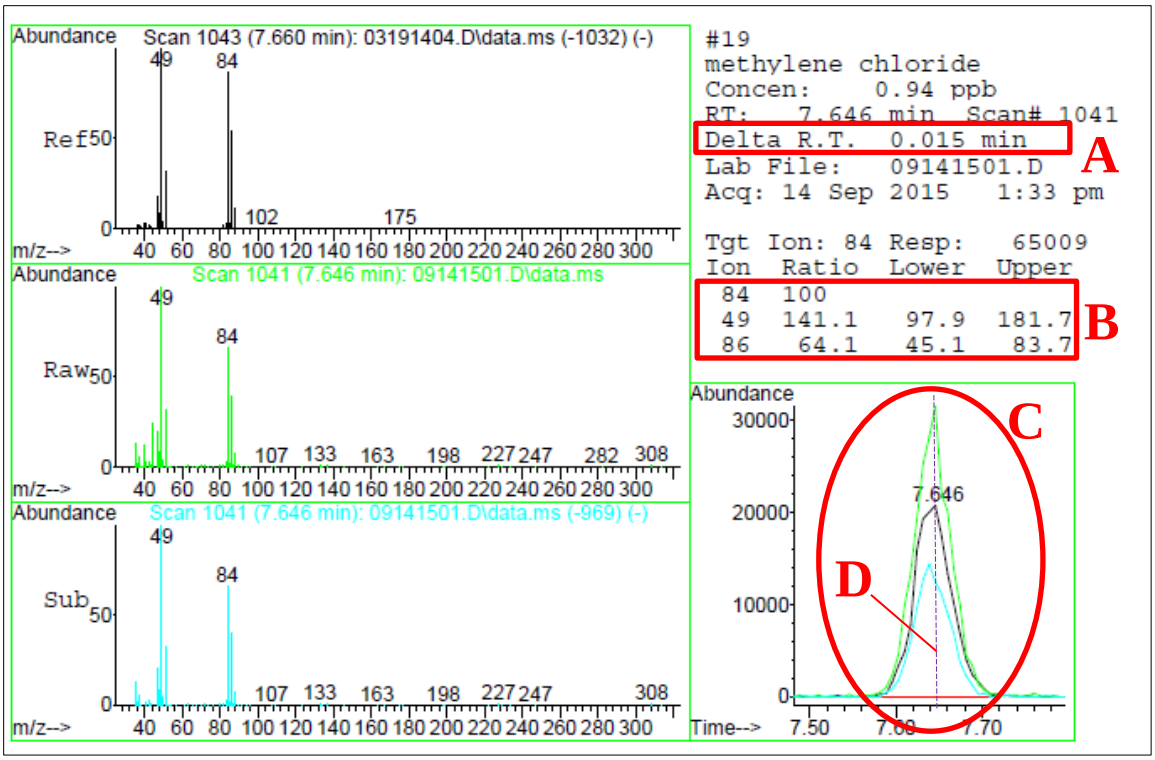

Figure 4.2-2. Qualitative Identification of GC/MS Target Analytes

Please refer to Figure 4.2-3 for the following example for determining the signal-to-noise ratio. To determine signal-to-noise, the characteristic height of the noise of the baseline (A) just before the peak and the height of the analyte peak (B) are measured. The ratio of the analyte peak height (B) is divided by the noise height (A) to calculate the S:N ratio. In the example below, the peak at 17.0 minutes is discernable from the noise, but is not well-resolved and is very close to a S:N of 3. In the example, the peak heights of the noise and analyte peak (at approximately 17.0 minutes) are approximately 700 units and 1700 units, respectively, for a S:N of 2.4.

Determination of the S:N is somewhat subjective based on the individual analyst and their characterization of the noise and analyte peak. Some chromatography systems include S:N functions which require the analyst to assign the noise and target peak. For well-resolved peaks, the S:N will greatly exceed 5:1, and does not need to be measured. For peaks with low S:N that are questionable as to whether they meet the criteria in item #1 above, the 3:1 S:N criterion is a guideline; it is unnecessary to measure each peak, rather the experienced analyst's opinion should weigh heavily on whether the peak meets the S:N criterion.

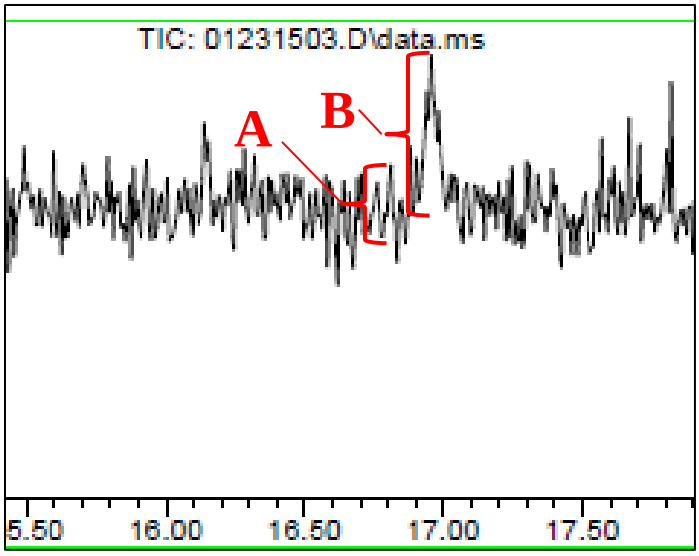

Figure 4.2-3. Determination of Chromatographic Peak Signal-to-Noise Ratio

As with the S:N determination, evaluation of whether target and qualifier ion peaks are co-maximized does not need to be rigorously evaluated with each peak. Rather the interpretation of the experienced analyst should weigh heavily on whether the qualifier ion peaks are co-maximized with the target ion. Items 3 (retention time) and 4 (relative ion abundances) above may be automated by the analysis software such that they are automatically flagged. It is important that the RT windows and ion abundances be updated with each new ICAL.

If any of these criteria are not met, the compound may not be positively identified. The only exception to this is when in the opinion of an experienced analyst the compound is positively identified. The rationale for such an exception must be documented.

4.2.8.5.4 Internal Standards Response. The response of the ISs must be monitored for each injection (except for the instrument blank immediately preceding the ICAL or daily CCV). Area responses of each IS must be within ± 40% of its mean area response in the five-point ICAL. Each IS must elute within 0.33 minutes of its average RT from the five-point ICAL.

Note: Comparing the IS response to the most recent CCV is not appropriate as this permits the IS response to drift by as much as 64% from the five-point ICAL before corrective action is necessary. For example, if the average IS response in the ICAL is 10000 area counts, the CCV IS response may decrease to as low as 6000 area counts (a decrease of -40% from the five-point ICAL average) and still meet criteria. Comparing sample IS response to this CCV permits the IS to drift as low as 3600 area counts (a decrease of -40% from the CCV response), a drift of -64% from the five-point ICAL average IS response.

The IS response tends to decrease over time as the MS ion optics age and become dirty. If an IS response is nonconformant and appears to be isolated to a specific sample, the possibility of a matrix interference should be investigated by analysis of a smaller volume of the air sample. If an IS response in the dilution remains nonconformant, corrective action should be taken which

may include investigating problems with the preconcentrator, autosampler, or other parts of the sample introduction path. The MS tune should also be evaluated for a degradation or enhancement of sensitivity.

4.2.9 Data Review and Concentration Calculations. Each chromatogram must be closely examined to ensure chromatographic peaks are appropriately resolved and integration does not include peak shoulders or inflections indicative of a coelution.

The concentrations of target compounds detected in the analyzed aliquot are quantitated by relating the area response ratio of the target compound and assigned IS in the unknown sample to the average RRF ($\overline{RRF}$) of the initial calibration curve as follows:

$$C_D = \frac{A_t \cdot C_{IS}}{A_{IS} \cdot \overline{RRF}}$$

where:

C_D = instrument detected analyte concentration (ppb)
A_t = area response of the target compound quantitation ion
C_{IS} = concentration of assigned internal standard (ppb)
A_{IS} = area response of the assigned internal standard quantitation ion
$\overline{RRF}$ = average relative response factor from the initial calibration

If a smaller aliquot was analyzed from the sample canister than the typical analysis volume, an instrument dilution correction factor (IDCF) must be calculated:

$$IDCF = \frac{V_{nom}}{V_{inj}}$$

where:

V_{nom} = nominal volume of sample injected (typical volume analyzed)
V_{inj} = reduced volume of the sample injected

The final in air concentration (C_F) of each target compound is determined by multiplying the instrument detected concentration by the canister dilution correction factor and the instrument dilution correction factor:

$$C_F = C_D \cdot CDCF \cdot IDCF$$

where:

C_F = concentration of the target compound in air (ppb)
CDCF = canister dilution correction factor
IDCF = instrument dilution correction factor

MDLs reported with the final concentration data must be corrected by multiplying the MDL by the canister and instrument dilution correction factors applied to the sample concentrations. For example, if the benzene MDL is 0.0091 ppbv for an undiluted sample and the sample was diluted by 2.5, the MDL becomes 0.023 ppbv.

4.2.10 Summary of Quality Control Parameters. A summary of QC parameters is shown in Table 4.2-3.

Table 4.2-3. Summary of Quality Control Parameters for NATTS VOCs Analysis

Parameter	Description and Details	Required Frequency	Acceptance Criteria
Instrument Blank (IB)	Analysis of swept carrier gas through the preconcentrator to demonstrate the instrument is sufficiently clean to begin analysis	Prior to ICAL and daily beginning CCV	Each target VOC's concentration < 3x MDL or 0.2 ppb, whichever is lower
BFB Tune Check	50 ng injection of BFB for tune verification of quadrupole MS detector	Prior to initial calibration and every 24 hours of analysis thereafter	Abundance criteria listed in Table 4.2-2
Initial Calibration (ICAL)	Analysis of a minimum of five calibration levels covering approximately 0.1 to 5 ppb	Initially, following failed BFB tune check, failed CCV, or when changes/maintenance to the instrument affect calibration response	Average RRF ≤ 30% RSD and each calibration level must be within ± 30% of nominal For quadratic or linear curves, r ≥ 0.995, each calibration level must be within ± 30% of nominal
Secondary Source Calibration Verification (SSCV)	Analysis of a secondary source standard at the mid-range of the calibration curve to verify ICAL accuracy	Immediately after each ICAL	Recovery within ± 30% of nominal or RRF within ±30% of the mean ICAL RRF
Continuing Calibration Verification (CCV)	Analysis of a known standard at the mid-range of the calibration curve to verify ongoing instrument calibration	Following each daily BFB tune check and every 24 hours of analysis; recommended after each ten sample injections and to conclude each sequence	Recovery within ± 30% of nominal or RRF within ±30% of the mean ICAL RRF
Canister Cleaning Batch Blank	A canister selected for analysis from a given batch of clean canisters to ensure acceptable background levels in the batch of cleaned canisters	One canister from each batch of cleaned canisters – Canister chosen must represent no more than 10 total canisters.	Each target VOC's concentration < 3x MDL or 0.2 ppb, whichever is lower (All Tier I Core analytes must meet this criterion)
Internal Standards (IS)	Deuterated or not naturally occurring compounds co-analyzed with samples to monitor instrument response and assess matrix effects	Added to all calibration standards, QC samples, and field-collected samples	Area response for each IS compound within ± 40% of the average response of the ICAL
Preconcentrator Leak Check	Pressurizing or evacuating the canister connection to verify as leak-free	Each standard and sample canister connected to the instrument	< 0.2 psi change/minute or manufacturer recommendations

Table 4.2-3. Summary of Quality Control Parameters for NATTS VOCs Analysis (Continued)

Parameter	Description and Details	Required Frequency	Acceptance Criteria
Method Blank (MB)	Canister filled with clean diluent gas	One with every analysis batch of 20 or fewer field-collected samples	Each target VOC's concentration < 3x MDL or 0.2 ppb, whichever is lower
Laboratory Control Sample (LCS)	Canister spiked with known amount of target analyte at approximately the lower third of the calibration curve	(Recommended) One with every analysis batch of 20 or fewer field-collected samples	Each target VOC's recovery must be 70 to 130% of its nominal spiked amount
Duplicate Sample	Field sample collected through the same inlet probe as the primary sample	10% of primary samples for sites performing duplicate sample collection (as prescribed in workplan)	Precision ≤ 25% RPD of primary sample for concentrations ≥ 5x MDL
Collocated Sample	Field sample collected through a separate inlet probe from the primary sample	10% of primary samples for sites performing collocated sample collection (as prescribed in workplan)	Precision ≤ 25% RPD of primary sample for concentrations ≥ 5x MDL
Replicate Analysis	Replicate analysis of a field-collected sample (chosen by analyst)	Once with every analysis sequence (as prescribed in workplan)	Precision ≤ 25% RPD for target VOCs with concentrations ≥ 5x MDL
Retention Time (RT)	RT of each target compound and internal standard	All qualitatively identified compounds and internal standards	Target VOCs within ± 0.06 RRT units of mean ICAL RRT IS compounds within ± 0.33 minutes of the mean ICAL RT

4.2.11 References

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4.3 Carbonyl Compounds via EPA Compendium Method TO-11A

Each agency must codify in an appropriate quality systems document, such as an SOP, or equivalent, its procedures for collection of airborne carbonyls onto cartridges, extraction of the cartridges, and analysis of the extracts. Various requirements and best practices for such are given in this section. Note that regardless of the specific procedures adopted, method performance specifications as given in Section 4.3.10 must be met.

4.3.1 General Description of Sampling Method and Analytical Method. Carbonyl compounds such as aldehydes and ketones may be collected and analyzed via EPA Compendium Method TO-11A. The atmosphere to be characterized is drawn at a known flow rate for a known duration of time through an ozone denuder and through a sorbent cartridge coated with DNPH, where the carbonyl compounds react with the DNPH and are derivatized to form carbonyl-hydrazones. These carbonyl-hydrazones are solids at typical ambient temperatures and are retained on the cartridge sorbent bed until eluted with acetonitrile (ACN). Eluted extracts are analyzed by HPLC with a UV detector at a wavelength 360 nm.[1]

The carbonyls including, but not limited to, those in Table 4.3-1 may be determined by this method.

Table 4.3-1. Carbonyl Target Compounds and Associated Chemical Abstract Service (CAS) Number via Method TO-11A

Target Carbonyl	CAS #
acetaldehyde [a b]	75-07-0
acetone	67-64-1
benzaldehyde [b]	100-52-7
butyraldehyde	123-72-8
crotonaldehyde	4170-30-3
2,5-dimethylbenzaldehyde	5779-94-2
formaldehyde [a b]	50-00-0
heptaldehyde	111-71-7
hexaldehyde	66-25-1
isovaleraldehyde	590-86-3
m&p-tolualdehyde	(m) 620-23-5/(p) 104-87-0
methyl ethyl ketone	78-93-3
methyl isobutyl ketone	108-10-1
o-tolualdehyde	529-20-4
propionaldehyde [b]	123-38-6
valeraldehyde	110-62-3

[a] NATTS required core analytes
[b] NATTS PT analytes

4.3.2 Minimizing Bias. The sampling of airborne carbonyls onto DNPH cartridges is potentially affected by a variety of interferences. For example, nitrogen oxides react with the DNPH derivative to form compounds which may coleute with carbonyl-hydrazone derivatives. Moreover, ozone reacts with DNPH to form possible coeluting interferences and also reacts with and causes negative bias in the measurement of various carbonyl-hydrazones. (More information on ozone management is given in Section 4.3.4.) To minimize introduction of

contamination and to keep bias to a minimum, manage ozone per Section 4.3.4 and handle cartridges as in Section 4.3.5.2. Clean labware and select high-purity reagents as in Section 4.3.9.

The cartridge inlet and outlet caps must be installed when the cartridge is not in use so as to isolate it from the ambient atmosphere where carbonyl compounds and interfering compounds may be passively sampled. Further, cartridges must be stored sealed in the foil pouch or similar opaque container, as light may degrade the DNPH derivatives. Finally, DNPH cartridges must be stored at ≤ 4°C after sampling as such slows the reaction of contaminants. Cartridges should only be handled while wearing powder-free nitrile or vinyl gloves.

4.3.3 Carbonyls Precision

4.3.3.1 Sampling Precision. Depending on the configuration of the sampling unit or units at the monitoring site, sampling precision may be assessed by way of the collection and analysis of collocated or duplicate cartridges. Sampling precision is a measure of the reproducibility in the sampling, handling, extraction, and analysis procedures. Monitoring agencies are encouraged to collect collocated and duplicate samples. For monitoring agencies collecting collocated and/or duplicate samples (as detailed in each site's workplan), they must be collected at a minimum frequency of 10% of primary samples.

4.3.3.1.1 Collocated Sample Collection. A collocated sample is a sample for which air is drawn through a co-collected cartridge from an independent inlet probe via a separate discrete sampling unit. If two cartridges are collected together with a single sampling instrument, to be collocated the air passing onto each cartridge must flow through wholly separate channels, where each channel must have a discrete inlet probe, plumbing, pump, and flow controller such as an MFC or rotameter. For sites which employ a manifold inlet to which one or more carbonyl sampling unit inlets is connected, samples co-collected with the primary sample will be designated as duplicate, as shown in Figure 4.3-1.

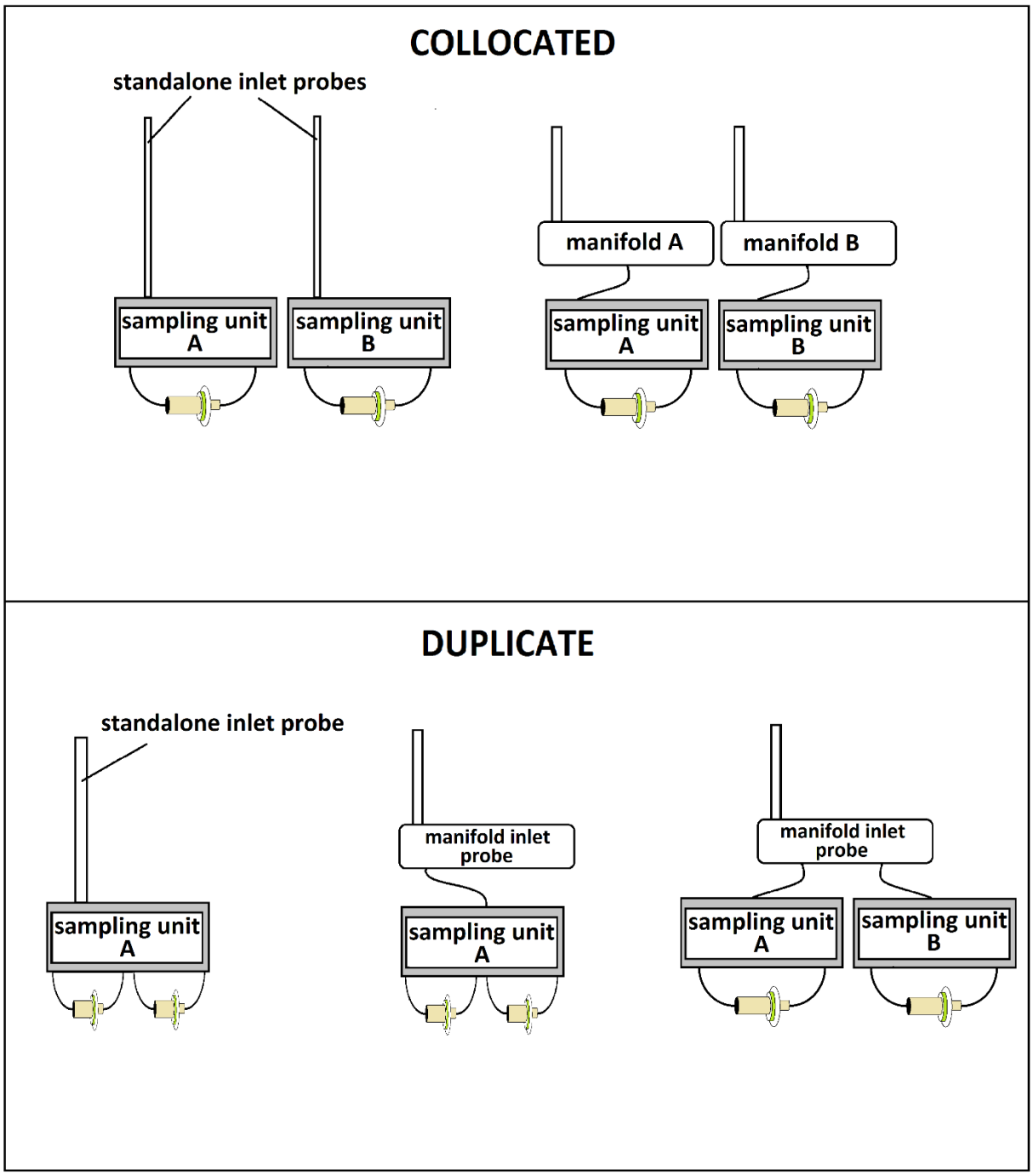

Figure 4.3-1. Collocated and Duplicate Carbonyls Sample Collection

More information on collocated samples is given in Section 4.3.8.2.3.

4.3.3.1.2 Duplicate Sample Collection. Duplicate sampling assumes that both the primary and duplicate sampling inlets are connected to the same inlet probe to the atmosphere whether connected to a manifold or a standalone inlet probe.

A duplicate sample may be collected, for example, by splitting (with a tee, or similar) the primary sample flow path onto two separate cartridges, where each cartridge has its own discrete and separate flow channel and/or flow control device (MFC, orifice, or rotameter) located within a single sampling unit.

More information on duplicate samples is given in Section 4.3.8.2.4.

4.3.3.2 Laboratory Precision. Laboratory precision for field-collected carbonyls cartridges is limited to replicate analysis of a single extract. Each DNPH cartridge is extracted as a discrete sample which does not permit assessing precision through the extraction process. Replicate analysis of a given extract is required with each analysis sequence and must show ≤ 10% RPD for concentrations ≥ 0.5 µg/cartridge.

Precision incorporating both the extraction and analysis procedures may be assessed by preparation, extraction, and analysis of duplicate LCSs. An LCS and LCS duplicate (LCSD) must be prepared minimally quarter, and are recommended with each extraction batch at a concentration in the lower third of the calibration range. The LCS/LCSD pair must show precision of ≤ 20% RPD.

4.3.4 Managing Ozone. Ozone is present in the atmosphere at various concentrations ranging from approximately 20 ppb at rural sites to as much as 150 ppb at peak times in urban environments. Ozone is a strong oxidant and may impact the sampling and analysis in various ways. Ozone which is not removed from the sampled air stream may react directly with the DNPH reagent thereby making the DNPH unavailable for derivatizing carbonyl compounds. Ozone may also react with carbonyl-hydrazones on the sampled cartridge to degrade these compounds, leading to underestimation of carbonyl concentrations. These degradation byproducts may also be difficult or impossible to separate chromatographically from desired target compounds, resulting in overestimation or false positive detection of target compounds.

In order to mitigate the impact of ozone on carbonyl measurements, an ozone denuder/scrubber must be installed in the sampling unit flow path upstream of the DNPH cartridge(s). Typically, the removal of ozone by potassium iodide (KI) is effected by the oxidation of the iodide ion to iodine in the presence of water, as follows:

$$\begin{array}{r} O_3 \rightarrow O_2 + O \\ +\ 2KI + \ H_2O + O \ \rightarrow 2KOH + \ I_2 \\ \hline O_3 + 2KI + \ H_2O \ \rightarrow \ I_2 + O_2 + 2KOH \end{array}$$

Several different KI ozone scrubbers are described in the following sections. For the NATTS program, ozone must be removed during the collection of carbonyls with the denuder in Section 4.3.4.1.

4.3.4.1 Copper Tubing Denuder/Scrubber. Method TO-11A describes an ozone denuder/scrubber and this is the preferred ozone removal method for the NATTS program. The scrubber is fashioned from coiled copper tubing whose interior has been coated with a saturated KI solution and which is heated to approximately 50°C or above to eliminate condensation.

Heating prevents the deposition of liquid water to the denuder walls which may both dissolve the KI coating and may clog the silica gel pores in the DNPH cartridge with KI as it recrystallizes. As this type of scrubber/denuder operates via titration, its efficacy over time is related to the amount of deposited KI, the total volume of sampled air, and the average ozone concentration of the sampled air. In general, it is presumed that this type of denuder/scrubber should be effective for up to 100,000 ppb-hours at flow rates of less than 1 L/minute.[1] A study not yet published at the time of this TAD's release has found that such copper tubing ozone scrubbers are effective for the 100,000 ppb-hours cited in TO-11A; they were able to efficiently remove 150 ppb O_3 over 30 consecutive days when operated at a flow rate of 1 L/min at relative humidities ranging from 10 to 85% at a nominal temperature of 25°C.[2] Given an average ozone concentration of approximately 70 ppb, this type of denuder/scrubber should effectively scrub ozone from the sampled air stream for all 61 annual 24-hour samples required by the NATTS Program without depleting the KI reagent. If the average concentration of ozone is greater than 70 ppb over the course of the year or the sampling frequency is increased from one-in-six days, or if duplicate sampling is performed more frequently than every other month such that the flow rate through the denuder is doubled during most sampling events (thereby exposing the scrubber to twice the burden of ozone), the life span of the KI denuder/scrubber will be proportionately reduced.

The denuder/scrubber must be replaced or recharged with KI minimally annually to ensure there is sufficient KI substrate to eliminate co-sampled ozone; they should also be recharged if ozone breakthrough is observed as decomposition products of O_3 attacking the DNPH and the formaldehyde hydrazone derivative (see reference 1 for more information). Denuders are commercially available or they may be recharged by recoating the copper tubing with a saturated solution of KI in deionized water (144 grams KI in 100 mL deionized water). The solution is maintained inside the copper tubing for minimally 15 minutes (some agencies suggest 24 hours or more), then the solution drained. The emptied tubing is then dried by a gentle stream of dry UHP nitrogen for minimally one hour.

When a sampling instrument is removed from service for recharging the KI denuder/scrubber and/or for calibration/maintenance, a best practice is to challenge the denuder with ozone at 120% of the maximum measured ozone concentration for several hours and measure the resultant downstream concentration. Such will demonstrate the ozone scrubber's efficacy prior to removal from the field. For denuders shown to be less than fully effective upon removal from the field, defined as downstream ozone concentration > 10 ppb or a breakthrough > 5%, chromatograms from recent sampling events should be examined for indications of ozone interference. Following recharge/replacement of the KI denuder/scrubber, the 120% ozone concentration challenge should be repeated to demonstrate effective ozone removal prior to its deployment for field use. The zero challenge of the sampling unit prescribed in Section 4.3.7.1.1 must be performed following recharging of the denuder/scrubber.

4.3.4.2 Sorbent Cartridge Scrubbers. Sorbent cartridges, such as silica gel, coated with KI are commercially available, but their use is not permitted due to their sorption of water vapor. Sampling in humid environments results in the sorbent bed becoming saturated with water, resulting in clogging of the cartridge substrate which substantially reduces or eliminates sample flow. While inexpensive and convenient for use, sorbent bed KI cartridges must not be employed for the NATTS Program sampling.

4.3.4.3 Other Ozone Scrubbers. Agencies may opt to develop custom-made KI ozone scrubber/denuders. The efficiency of ozone removal must be demonstrated for such custom systems. To demonstrate efficiency of ozone removal, the homemade scrubber/denuder must be challenged over a contiguous 24-hour period with a minimum of 100 ppb ozone at the flow rate for the carbonyl instrument sampler (typically approximately 1 L/min) and demonstrate breakthrough of < 5%. Agencies must also quantify the capacity of such scrubbers (for example, in ppb-hours) and with such data they must determine and codify in their quality system the minimum required recharge/replacement frequency of the scrubbers.

4.3.4.3.1 Cellulose Filter Ozone Scrubbers. The California Air Resources Board (CARB) removes ozone with cellulose filters coated with KI on the RM Environmental Systems Incorporated 924 and Xonteck 924 sampling units. These samplers are standalone and not installed in a separate shelter, so do not allow the ready installation of a heated copper tubing ozone scrubber. The DNPH cartridge is installed in close proximity (several millimeters) from the inlet probe, which is open to the atmosphere. The KI-coated filter is installed at the inlet probe, just upstream of the DNPH cartridge.

4.3.4.3.2 Modified Dasibi^{TM} Ozone Scrubber. In the Dasibi^{TM} scrubber fifteen 2-inch diameter copper mesh screens are arranged in a stacked formation. The magnesium oxide coated screens provided with the unit are exchanged for copper screens which are coated with KI. To coat the screens, they are immersed in a saturated KI solution in deionized water and air dried. The coated screens are assembled in the Dasibi enclosure with a fiberglass particulate filter at each end, the O-rings installed, and the enclosure secured with the supplied screws. This procedure imparts approximately 4 mmoles or 700 mg of KI over the fifteen 2-inch diameter screens. With this mass of KI, the scrubber should effectively remove ozone for approximately 300 sampling dates assuming 24 hours of sampling at 1 L/minute with ozone concentrations of 100 ppb.

In order to ensure that condensation does not impact the scrubber's performance, it should be maintained at a minimum temperature of 50°C.

4.3.5 Collection Media. EPA Compendium Method TO-11A specifies DNPH-coated silica gel sorbent cartridges for the collection of carbonyl compounds from ambient air. These DNPH cartridges may be prepared in house or purchased from commercial suppliers. Most NATTS sites utilize one of two commercial brands of media, specifically the Waters WAT037500 or Supelco S-10 cartridges. These cartridges are specified to meet the background criteria of TO-11A and typically exhibit proper flow characteristics. Examination of background concentrations and proficiency test data do not indicate an obvious difference in the performance between the two brands of cartridges. Laboratories may prepare DNPH cartridges in house; however, preparation is a time- and labor-intensive process which requires meticulous detail to cleanliness to ensure the resulting media are contaminant-free. The expense and resources involved in preparation of DNPH media in house is generally greater than the cost of purchasing commercially-available DNPH cartridge media. Regardless of the type of cartridge selected, the method performance specifications in Section 4.3.10 must be met.

4.3.5.1 Lot Evaluation and Acceptance Criteria. For each lot or batch of purchased or prepared DNPH cartridge, a representative number of cartridges must be analyzed to demonstrate that the lot or batch is sufficiently free of contamination. Most commercially-available DNPH cartridges are accompanied by a COA indicating the lot or batch background of various carbonyls. While a COA provides a level of confidence that the lot or batch is sufficiently clean, laboratories must verify the background levels of carbonyls in each batch or lot of cartridges.

For commercially-purchased cartridges, a minimum of three cartridges, or 1% of the total lot, whichever is greater from each lot or batch, must be extracted and analyzed. For cartridges prepared in house, a minimum of three cartridges per each preparation batch must be extracted and analyzed. Each cartridge tested in the lot or batch must meet the criteria listed in Table 4.3-2. Ongoing analysis of method blanks permits continual assessment of the lot's contamination levels.

Additionally, agencies may elect to perform flow evaluations of the lot(s) to ensure cartridges do not overly restrict sampling flows.

Table 4.3-2. Maximum Background per Lot of DNPH Cartridge

Carbonyl Compound	Not-to-Exceed Limit (µg/cartridge)
Acetaldehyde	< 0.10
Formaldehyde	< 0.15
Acetone [a]	< 0.30
Other Individual Target Carbonyl Compounds	< 0.10

[a] Acetone is not a target compound and should not be grounds for lot disqualification unless it interferes with other target analytes in the chromatogram.

If any cartridge tested exceeds these criteria, an additional three cartridges, or 1% of the total lot, whichever is greater, must be tested to evaluate the lot. If the additional cartridges meet the criteria, the lot or batch is acceptable for sampling. If any of the additional cartridges fail criteria, the lot or batch must not be used for NATTS sampling and should be returned to the provider.

4.3.5.2 Cartridge Handling and Storage. DNPH sampling cartridge media are typically shipped unrefrigerated by the supplier. DNPH cartridges must be stored refrigerated at ≤ 4°C upon receipt. Unsampled cartridges must be maintained sealed in their original packaging and protected from light (foil pouch or similar opaque container) until installed for sample collection or prepared as QC samples as light may degrade the DNPH derivatives. Cartridges which are not stored appropriately may suffer from degradation of the DNPH reagent and may show increased levels of contaminants from passive sampling of target compounds and interferants.

DNPH cartridges should only be handled by staff wearing powder-free nitrile or vinyl gloves or equivalent. Measures must be taken to avoid exposure of DNPH cartridges (unsampled or collected samples) to exhaust fumes, sunlight, elevated temperatures, and laboratory environments where carbonyl compounds such as acetone may contaminate sampling media.

As soon as possible after sample collection, cartridges must be capped (if caps are provided), sealed in the foil pouch (to protect from light and the ambient atmosphere), and transported (shipped) and stored refrigerated at ≤ 4°C. Cartridges must be transported in coolers with ice, freezer packs, or equivalent method for providing refrigeration during transport to and from the laboratory. Monitoring the shipping temperature with a calibrated min-max type thermometer is a best practice.

4.3.5.3 Damaged Cartridges. DNPH cartridges are susceptible to water damage and to physical damage. Unused or sampled cartridges, including blanks, must not indicate clumping of the silica gel sorbent which is indicative of water condensation inside the cartridge sorbent bed. Physical damage to cartridges such as cracks, broken inlet or outlet fittings, or openings into the sorbent bed are pathways for the ingress of contamination. Cartridges which indicate such damage must not be used in the NATTS Program, or if already used for sample collection, must be voided and a make-up sample should be collected per Section 2.1.2.1, where possible.

4.3.5.4 Cartridge Shelf Life. DNPH cartridges that are commercially purchased typically are provided with an expiration from the manufacturer specifying storage conditions. Agencies must comply with the manufacturer expiration, if given. Degradation of the DNPH reagent or silica gel sorbent bed which may reduce collection efficiency to unacceptable levels may occur after the assigned expiration date. Additionally, as DNPH cartridge media age, their levels of background contamination are likely to have increased, perhaps to unacceptable levels, due to passive sampling and uptake from the ambient atmosphere. For cartridges which are not assigned an expiration date or are assigned an arbitrary expiration date (i.e. six months from time of receipt) by the manufacturer, agencies should work within this expiration period as practical. For such cartridges which have exceeded the arbitrary expiration period, they may be shown to be acceptable if levels of contaminants meet the criteria in Table 4.3-2 and there remains sufficient DNPH to conduct sampling and ensure excess DNPH levels remain following sample collection. This level of DNPH on unsampled cartridges is recommended to be a reduction of DNPH area counts of no more than ~15% from the original lot acceptance analysis.

4.3.6 Method Detection Limits. MDLs for carbonyls must be determined minimally annually by following the procedures in Section 4.1. To ensure that the variability of the media and the extraction process is characterized in the MDL procedure, separate cartridges must be spiked and extracted (it does not suffice to simply analyze a low-concentration solution of derivatized carbonyls). For example, laboratories determining the MDL following Section 4.1.2.1 must prepare a minimum of seven method blank cartridges and a minimum of seven spiked cartridges over the course of three different batches (different calendar dates – preferably non-consecutive). These samples must be analyzed in three separate analytical batches (different calendar dates – preferably non-consecutive). The MDL is then determined by calculating the MDL_{sp} and MDL_b and selecting the higher of the two concentrations as the laboratory MDL. Please refer to section 4.1.2 for specific details on selecting a spiking concentration, procedures, and calculations for determining MDLs.

All steps performed in the preparation and analysis of field sample cartridges (such as dilution of extracts) must be included in the MDL procedure. Cartridges should be spiked and the solvent permitted to dry prior to extraction.

Determined MDLs for Tier I core analytes must meet (be equal to or lower than) those listed in the most recent workplan.

4.3.7 Carbonyls Sample Collection Equipment, Certification, and Maintenance.

Carbonyls are collected by drawing the ambient atmosphere through a DNPH cartridge at a known flow rate of approximately 0.25 to 1.25 L/minute over the 24-hour collection period. An ongoing EPA funded study not yet published at the time of this TAD's release indicated that at 1.25 L/minute there was no breakthrough at aldehyde concentrations of 5 ppbv. Collection of samples with flow rates of approximately 1 L/minute represents an appropriate compromise between maximizing collection efficiency and sensitivity.

4.3.7.1 Sampling Equipment. The sampling unit may control flow rate by a MFC or by a combination critical orifice and flow rotameter. Advantages of MFCs include that they provide real-time control of a specified flow, adjusting for changes in backpressure and sampling conditions. Additionally, MFC flow data may be continuously captured and recorded so as to permit calculation of a total sampled volume. Such is in contrast with sampling units with rotameters for which only beginning and ending flow rate measurements are available for total volume calculations. Another limitation of rotameters is that their indicated flows must be manually corrected to standard conditions using the barometric pressure and temperature at the site on the day of sample collection. Rotameters are less complicated and expensive than MFCs.

A variety of commercial and custom-built sampling instruments is available. These range from simple flow pumps controlled via critical orifice and flow rotameter to multi-channel/multi-pump systems connected through multiple MFCs and operated by touch screen control. Some units are also able to simultaneously collect VOC canisters or allow remote computer login to monitor sampling events and download sample collection data. Note that such options are advantageous, but not required.

Regardless of the additional features, each sampling unit must minimally include the following options:

- Elapsed time indicator
- Multi-day event control device (timer)
- MFC (preferred) or critical orifice and flow rotameter to control sampling flow
- Ozone denuder

Each sampling unit must be flow calibrated annually and shown to be free of positive bias.

4.3.7.1.1 Sampling Unit Zero Check (Positive Bias Check). It is required that prior to field deployment and minimally annually thereafter each carbonyl sampling unit be certified to be free of positive bias by collection over 24 hours of a sample of humidified HCF zero air (or equivalent carbonyl- and oxidant-free air) or UHP nitrogen. Each channel of each carbonyl sampling instrument should be so verified. A best practice is to perform this procedure TTP where the entire in-situ sampling train is tested. As many agencies do not possess the resources to perform TTP procedures, the zero check may be performed in the laboratory where as much of the flow path as possible must be included. Minimally the portion of the flow path comprising

the ozone denuder/scrubber and sampling unit into which the DNPH cartridge is installed should be verified as non-biasing. The positive bias check should be performed following the recharge or replacement of the ozone scrubber/denuder, is ideally performed following the annual recalibration of the flow control device, and ideally includes the length of tubing that connects the instrument to the manifold or the entire new or cleaned inlet probe.

A recommended zero check procedure is described below. For agencies which cannot perform the annual maintenance (ozone scrubber/denuder recharge, flow control calibration) and challenge in house, manufacturers, the national contract laboratory, or third party laboratories may perform this service. Regardless of the exact procedure adopted, when performed, the performance specifications listed below must be met.

The zero check is performed by simultaneously providing humidified (50 to 70% RH) hydrocarbon- and oxidant-free zero air or UHP nitrogen to the sampling unit for collection onto a cartridge and to a separate reference cartridge connected directly to the supplied zero gas source. As closely as possible, sample collection parameters for the ozone scrubber/denuder, flow rate, etc., should mimic those for field sample collections.

The humidified zero gas flow is provided to a challenge manifold constructed of chromatographic stainless steel. The manifold should include three additional ports for connections to the sampling unit inlet, reference sample, and a rotameter to serve as a vent to ensure that the manifold remains at ambient pressure during sample collection. The reference sampling flow is set to approximate the flow rate of the sampling unit with an MFC, mechanical flow device, or needle valve downstream from the reference cartridge. Zero gas is supplied such that there is excess flow to the manifold as indicated by the rotameter on the vent port. Sampling is performed over 24 hours to simulate real world conditions, into the reference cartridge and through the sampling unit and into the zero challenge cartridge.

Another method to provide the sampling unit with carbonyl-free gas is to install a DNPH sampling cartridge on the inlet to sampling unit. This cartridge traps the carbonyl compounds and replaces the zero gas source. A zero challenge cartridge collected in this manner should be compared to a field blank as the reference cartridge.

Analysis for target compounds in the zero challenge cartridge must show that each compound is ≤ 0.2 ppbv greater than the reference cartridge. Comparison to the reference cartridge permits evaluating the contribution of the sampling unit irrespective of cartridge background contamination. Where exceedances are noted for the zero challenge cartridge, corrective action must be taken to remove the contamination attributable to the sampling unit and the sampling unit zero challenge repeated to ensure criteria are met before sampling may be conducted.

4.3.7.1.2 Carbonyls Sampling Unit Flow Calibration. Initially prior to field deployment and whenever independent flow verification indicates the flow tolerance has been exceeded, the flow control device (MFC or flow rotameter) must be calibrated against a calibrated flow transfer standard and the flow control device (or regression for a flow rotameter) adjusted to match the transfer standard (or the regression characterizing its response must be reset to match the transfer standard).

Note that manufacturer procedures for calibration may be followed if flows can be calibrated at standard conditions. A suitable calibration procedure for MFCs is as follows. The sampling unit pump(s) and MFC should be warmed up and run for approximately five minutes to ensure the MFC is stable. A blank DNPH cartridge should be installed into the air sampler to provide a pressure drop to the pump, and airflow through the cartridge commenced. The calibrated flow transfer standard should be connected at the upstream end of the sampling unit so as much of the flow path is included as possible in order to identify potential leaks in the flow path that may not otherwise be evident. MFC calibration should be performed at minimally three flow rates: the typical flow rate for sample collection, approximately 30% less than the typical flow of sample collection, and approximately 30% higher than the typical flow of sample collection. Particular attention should be paid to ensure that the correct calibration conditions are compared – that both the reading on the flow transfer standard and MFC are in standard (25°C and 760 mm Hg) conditions.

Calibration of flow rotameters is more complex than calibration of MFCs. The temperature and barometric pressure both at the time of calibration and during sample collection are needed to correct the indicated rotameter flow rate to the actual flow rate.[3] A suitable rotameter calibration procedure is given below.

The flow rotameter should be challenged with a flow of air which is simultaneously measured by a calibrated flow transfer standard. At each flow rate set point, the flow reading from the flow transfer standard and the corresponding reading from the flow rotameter are recorded. The challenged flow range should include a minimum of five flow rates that span the useful scale of the flow rotameter and include the expected indicated flow rate during field operation. A linear regression is then generated by plotting the flow transfer (known) readings on the x-axis and the flow rotameter readings (unknown) on the y-axis. The resulting linear regression equation allows the rotameter's indicated flow (on the y-axis) to be related to the known calibrated flow of the rotameter on the x-axis at the specific conditions of ambient temperature and barometric pressure at which the flow calibration is performed.

To calculate the actual flow rate during operation of the rotameter in the field, the rotameter flow rate during calibration is found by way of cross reference with the indicated flow from the rotameter calibration plot. Stated another way, the rotameter is read, and this indicated flow is found on the y-axis of the calibration plot and the corresponding flow rate during calibration is read from the x-axis (or the regression equation is solved for x). This flow rate during calibration, Q_c, along with the ambient temperature and pressure during calibration and during sample collection are input into the following equation to calculate the flow during sample collection:

$$Q_a = Q_c \sqrt{\frac{P_c T_a}{P_a T_c}}$$

where:

Q_a = volumetric flow rate at ambient (or local) conditions where the rotameter is operated
Q_c = volumetric flow rate at ambient (or local) conditions during rotameter calibration
P_c = barometric pressure during rotameter calibration

P_a = barometric pressure at ambient (or local) conditions where the rotameter is operated
T_a = absolute temperature at ambient (or local) conditions where the rotameter is operated
T_c = absolute temperature during rotameter calibration

For flow rotameters which are calibrated by delivery of a known flow measured at standard conditions, the calculation of the ambient flow at standard conditions is performed according to the following equation:

$$Q_{a,std} = Q_{c,std}\sqrt{\frac{P_a T_c}{P_c T_a}}$$

where:

$Q_{a,std}$ = flow rate where the rotameter is operated, in standard conditions (760 mm Hg, 25°C)
$Q_{c,std}$ = flow rate where the rotameter was calibrated, in standard conditions
T_c, P_c, T_a, and P_a are as above.

As an example, assume that a rotameter is calibrated – its indicated flow is cross-referenced to a calibrated flow – by delivery of known flows measured at standard conditions. Assume as well that the calibration is performed near sea level at a typical laboratory temperature such that P_c = 750 mm Hg and T_c = 20° C = 293.15 K, and that a field sample is collected in the summer in Grand Junction, Colorado, such that P_a = 650 mm Hg, T_a = 35° C = 308.15 K. Assume the indicated rotameter flow is 800 mL/min, which from the calibration plot corresponds to a known flow rate at standard conditions of 750 mL/min. The actual flow rate, in standard conditions, for this carbonyl sample in Grand Junction is equal to 750 mL/min · √ (650/750 · 293.15/308.15) = 681 mL/min.

To perform a flow calibration verification on the sampling unit flow, the sampling unit pump(s) should be warmed up and run for approximately five minutes to ensure flows are stable. A blank DNPH cartridge should be installed into the air sampler to provide a pressure drop to the pump, and airflow through the cartridge commenced. The calibrated flow transfer standard should be connected at the upstream end of the sampling unit so as much of the flow path is included as possible in order to identify potential leaks in the flow path that may not otherwise be evident. The sample flow is then set to the flow setting of typical sample collection and the flow compared to the transfer standard. Ensure that both the sampling unit and flow transfer standard are set to report flows at standard conditions of 25ºC and 760 mm Hg. Rotameter flows must be converted to standard conditions ($Q_{a, std}$) with the temperature and barometric pressure measured at the time of the calibration check via the equation above. The sampling unit flow in standard conditions must be within 10% of the flow indicated by the transfer standard. If outside of this range, the MFC must be recalibrated or the regression equation for the flow rotameter must be re-established.

4.3.7.1.3 Moisture Management. Humidity plays several roles with regard to sample collection. Water vapor can condense on interior portions of the sample flow path

potentially resulting in a low measurement bias due to carbonyls dissolving in the liquid water. To minimize the condensation of liquid water onto the interior surfaces of the flow path, the ozone scrubber is maintained at a minimum of 50°C. Additionally, connecting tubing may be insulated to maintain the elevated temperature and discourage condensation. High humidity in sampled atmospheres may also lead to somewhat lower carbonyl collection efficiencies due to the possible back reaction of the DNPH-carbonyl derivative with water to form the free carbonyl. The reverse reaction is less likely for aldehydes due to their higher reactivity, however can lead to lower collection efficiencies for ketones. [4]

4.3.7.2 Sampling Train Configuration and Presample Purge. The carbonyl sampling inlet probe may be standalone or connected to a manifold inlet. For either configuration, components comprising the wetted surfaces of the flow path must be constructed of borosilicate glass, PTFE Teflon, or chromatographic grade stainless steel. Due to the reactivity of materials such as copper or adsorptive/desorptive properties of materials such as FEP Teflon®, rubber, or plastic tubing, these materials must not be utilized within the flow path.

For sites having a common inlet manifold, it must be constructed of borosilicate glass. A bypass pump is connected to the manifold to continuously pull ambient air though the manifold. The flow rate of the bypass pump must be minimally double the total maximum sampling load for all sampling units connected to the manifold. Where the carbonyls sampling unit has its own inlet probe separate from the manifold, no additional bypass pump is necessary.

Regardless of how the ambient air is introduced into the sampling instrument, it is *strongly recommended* that the inlet line to the sampling unit be purged with ambient air such that the equivalent of a minimum of 10 air changes is completed just prior to commencing sample collection. This purge eliminates stagnant air and flushes the inlet line.

4.3.7.3 Carbonyl Sampling Inlet Maintenance. Over time, the carbonyl inlet probe and connecting tubing will become laden with particulate residue. This particulate residue may scrub target analytes from the gas stream and may act as sites for adsorption/desorption. Wetted surfaces of inlet probes and connecting tubing must be cleaned and/or replaced minimally annually, and preferably every six months, particularly if operated in an urban environment where there is a higher concentration of PM.

Only deionized water should be used to clean inlet lines. If the lines are short enough, a small brush can be employed in concert with the deionized water to effectively clean the interior of the tubing. It may be more effective to simply replace the tubing on a prescribed basis. Many carbonyl sampling units utilize Teflon® particulate filters upstream of the denuder to alleviate particulate loading of internal parts (valves and MFCs) of sampling units. Such particulate filters must be replaced periodically, recommended to be replaced after six months but must not exceed annually.

4.3.8 Sample Collection Procedures and Field Quality Control Samples

4.3.8.1 Sample Collection Procedures. Prior to beginning sample collection, all DNPH cartridge lot characterization must be completed as described in Section 4.3.5.1. The sampling

unit must have passed the zero check in the previous 12 months, the sampling inlet line cleaned or replaced in the previous 12 months, the flow control device calibrated within the past 12 months, and, if so equipped, the particulate filter must have been changed in the previous year.

In addition to the procedures described below, all cartridges must be handled as prescribed in Section 4.3.5.2.

4.3.8.1.1 Sample Setup. Blank DNPH cartridge media are transported to the site in a cooler on ice packs where they are either stored on site in a refrigerator or freezer (with calibrated temperature monitoring), or installed into the sampling unit for sample collection.

Appropriate blank, non-exposed DNPH cartridge(s) are installed into the sampling unit and the sample collection program verified to comply with Section 4.3.8.1.3. The flow rate of collection should be set to a known calibrated flow rate of approximately 0.7 to 1.5 L/minute (at standard conditions) for a total collection volume of 1.0 to 2.2 m^3 at standard conditions. Method sensitivity is linearly proportional to the total collection volume, and the latter should be adjusted within the specified range so that MDL MQOs are attained. An ongoing EPA funded study not yet published at the time of this TAD's release indicated that at these flow rates there was no breakthrough at aldehyde concentrations of 5 ppbv. Flow rates greater than 1.5 L/minute may result in decreased in collection efficiency.

For sampling units which permit a leak check function on the sample pathway, a leak check must be initiated prior to sample collection. A successful leak check indicates no flow through the sampling unit.

The initial flow rate, date and time of sample initiation, and cartridge identification information must be recorded on the sample collection form.

4.3.8.1.2 Sample Retrieval. The collected cartridges must be retrieved as soon as possible after the conclusion of sampling in order to minimize degradation of the carbonyl-DNPH derivatives, preferably within 72 hours of the end of sample collection. The ending flow rate, total flow (if given), and sample duration must be documented on the sample collection form. The cartridges are removed from the sampling unit, the caps installed on the inlet and outlet of each cartridge, each cartridge sealed in its separate foil pouch, and the pouches immediately placed in cold storage. The sample must be kept cold during shipment such that the temperature remains $\leq 4°C$, and the temperature of the shipment must be determined upon receipt at the laboratory. A best practice to minimize contamination is to transport the sealed foil pouch in an outer zipperlock bag containing activated carbon.

Sampling units which incorporate computer control of the sampling event with associated data logging may provide the above information which must be printed and attached to the sample collection form or transcribed. For such sampling units, the data logged should be reviewed to ensure the sample was collected appropriately and there are no flags or other collection problems that may invalidate the collected sample. Collected data should be downloaded and provided to the analytical laboratory. The sample custody form must be completed and accompany the

collected sample at all times until relinquished to the laboratory. COC documentation must comply with Section 3.3.1.3.7.

4.3.8.1.3 Sampling Schedule and Duration. Carbonyl sample collection must be performed on a one-in-six days schedule per the national sampling calendar for 24 ± 1 hours beginning at midnight and concluding on midnight of the following day, local time unadjusted for daylight savings time. For missed or invalidated samples, a make-up sample should be scheduled and collected per Section 2.1.2.1. Clock timers controlling sampling unit operation must be adjusted so that digital timers are within ±5 minutes of the reference time (cellular phone, GPS, or similar accurate clock) and mechanical timers within ±15 minutes.

4.3.8.2 Field Quality Control Samples. QC samples co-collected with field samples include field and trip blanks, collocated and duplicate samples, field matrix spikes, and breakthrough samples. Blank cartridges provide information on the potential for field-collected samples to be subjected to positive bias, whereas spiked cartridges assess the potential for the presence of both positive and negative bias.

4.3.8.2.1 Field Blanks. Field blanks must be minimally collected once per month; however, it is a best practice to increase this frequency, ideally to collect a field blank with each collection event. Field blanks must be handled in the same manner as all other field-collected samples, transported in the same cooler and stored in the same refrigerator/freezer storage units. Field blanks are exposed to the ambient atmosphere for approximately five to ten minutes by installation of the blank cartridge into the sampling position on the primary sampling unit with no air drawn through the cartridge. The field blank cartridge is then removed from the sampling unit and placed immediately into cold storage. Collection of the field blank in this manner characterizes the handling of the blank cartridge in the sampling position in the primary sampling unit and standardizes field blank collection across the NATTS network for carbonyls and with metals and PAHs field blank collection.

An exposure blank is similar to a field blank, but is not required, and may be collected via several protocols. The exposure blank includes opening the cartridge pouch, removing the caps exposing the cartridge to the ambient atmosphere briefly, and exposing it to the temperature conditions of the primary sampling cartridge for the same duration as the co-collected field samples. Like a field blank, air is not drawn through the exposure blank cartridge. Some sampling units have a dedicated "field blank" channel for installation of the exposure blank through which air is not permitted to flow. For multi-channel sampling units, the exposure blank may be installed in channel which is not activated for sample flow. For sampling units which have neither a dedicated blank channel nor unused channel available on the sampling unit, the exposure blank cartridge may be removed from the foil pouch, installed in the sampling unit for five to ten minutes, the cartridge uninstalled and the end caps reinstalled, and the cartridge placed near the sampling unit for the duration the primary sample is installed in the sampling unit.

Field blanks and exposure blanks may passively sample ambient air throughout the time of exposure, and as a result may have somewhat higher background levels as compared to lot

blanks, trip blanks, or laboratory method blanks. Field blanks must meet and exposure blanks should meet the following criteria listed in Table 4.3-3.

Table 4.3-3. Carbonyls Field Blank Acceptance Criteria

Carbonyl Compound	Not-to-Exceed Limit (µg/cartridge)
Acetaldehyde	< 0.40
Formaldehyde	< 0.30
Acetone [a]	< 0.75
Sum of Other Target Carbonyls	< 7.0

[a] Acetone is not a target compound and should not be grounds for field blank criteria failure unless it interferes with other target analytes in the chromatogram.

Failure to meet the field blank criteria indicates a source of contamination and corrective action must be taken as soon as possible. For agencies which collect associated trip blanks, comparison of the field blank to trip blank values may provide meaningful insight regarding the contamination source. Field-collected samples associated with field blanks which do not meet these criteria must be flagged/qualified when input to AQS. For field blanks which fail criteria and are collected with each sampling event, the co-collected field sample results must be flagged/qualified when input to AQS. For failing field blanks which are collected on a less frequent basis (i.e. monthly basis), field collected samples since the last acceptable field blank must be flagged/qualified when input to AQS.

Field samples must not be corrected for field blank values. Field blank values must be reported to AQS so that data users may estimate field and/or background contamination.

4.3.8.2.2 Trip Blanks. Trip blanks are a useful tool to diagnose potential contamination in the sample collection and transport of carbonyl samples. Trip blanks are not required, but are a best practice. A trip blank consists of a blank unopened cartridge which accompanies field sample cartridges at all times to and from the laboratory. The trip blank cartridge is stored in the same refrigerator/freezer, transported in the same cooler to and from the site, and kept at ambient conditions during sample collection. The cartridge must remain sealed in the foil pouch and not removed from its pouch until extracted in the laboratory.

Background levels on the trip blank should be comparable to the lot blank average determined as in Section 4.3.5.1 and must not exceed the values listed in Table 4.3-2. Exceedance of these thresholds must prompt corrective action and the results of the associated field-collected samples must be appropriately qualified when input to AQS.

4.3.8.2.3 Collocated Samples. Collocated sampling is described in detail in Section 4.3.3.1.1. Where such is performed, it must be done at a frequency of no less than 10%, meaning approximately one collocated sample every other month.

Following extraction and analysis the collocated cartridge results are compared to evaluate precision. Precision must be ≤ 20% RPD for results ≥ 0.5 µg/cartridge. Root cause analysis must be performed for instances in which collocated samples fail this precision specification and the results for both the primary and collocated samples must be qualified when entered into AQS.

4.3.8.2.4 Duplicate Samples. Duplicate sampling is described in detail in Sections 4.3.3.1.1 and 4.3.3.1.2. Where such is performed, it must be done at a frequency of no less than 10%, meaning approximately one duplicate sample every other month.

Following extraction and analysis the duplicate cartridge results are compared to evaluate precision. Precision must be ≤ 20% RPD for results ≥ 0.5 μg/cartridge. Root cause analysis must be performed for instances in which duplicate samples fail this precision specification and the primary and duplicate results must be qualified when entered into AQS.

4.3.8.2.5 Field Matrix Spikes. Performance of field matrix spiked sample collection is a best practice, but is not required. Field matrix spikes are prepared by spiking a blank DNPH cartridge with a known amount of analyte (either derivatized or underivatized) prior to dispatching to the field for collection. The field matrix spike is handled identically to field samples; sample storage, transport, and extraction are identical. Field matrix spiked samples are collected concurrently with a non-spiked primary sample as a duplicate sample per Section 4.3.8.2.3 via duplicate channel or split sample flow.

The primary field sample and matrix spiked sample analysis results are evaluated for spike recovery based on the amount spiked prior to shipment to the field as follows:

$$\%Recovery = \frac{(Field\ Matrix\ Spike\ Result - Primary\ Sample\ Result)}{Nominal\ Spiked\ Amount} \cdot 100$$

Spike recovery should be within ± 20% (80 to 120% recovery) of the nominal spiked amount. In the event of an exceedance, root cause analysis should be performed to determine sources of negative or positive bias, as needed, for example, sources of contamination or reasons for the loss of analyte. High recoveries may indicate contamination in the matrix spike sample collection channel or loss in the primary sample collection channel. Low recoveries may indicate a poorly functioning ozone denuder, which permits ozone to pass through the sample collection flow path and degrade the spiked analytes.

4.3.8.2.6 Breakthrough Samples. While not required, collection of breakthrough samples is a best practice. A breakthrough sample is a second DNPH cartridge connected immediately downstream of the primary sample cartridge. Periodic collection of breakthrough samples provides a level of assurance that the primary sample cartridge is efficiently trapping target carbonyls. For sites conducting breakthrough sampling the recommended frequency is once per month which should be described in the agency NATTS QAPP, SOP, or similar controlled document.

Note that this breakthrough cartridge will increase the pressure drop in the sampling system and may require an adjustment in the operation of the sampling unit to achieve the desired flow rate.

Breakthrough sample results must meet the field blank criteria listed in Table 4.3-3.

4.3.9 Carbonyls Extraction and Analysis. Target carbonyls collected on the DNPH cartridges are extracted and analyzed per EPA Compendium Method TO-11A[1] according to the following guidance.

4.3.9.1 Analytical Interferences and Contamination

4.3.9.1.1 Analytical Interferences. The carbonyl-hydrazone derivatives are separated with a HPLC system and are typically detected at 360 nm with a photodiode array or similar detector operating at UV wavelengths. Identification is based on retention time matching with known standards. MS and photodiode array (PDA) detectors are also an option if more definitive identification and quantification are desired or required. Minimally, analysis by HPLC-UV must be performed.

Interferences from co-eluting peaks may result from hydrazones formed by co-collected compounds or reactions with co-collected compounds which form artifacts. Such co-eluting peaks may form as dimers or trimers of acrolein or be the result of chemical reactions with nitrogen oxides. Target analyte peaks which indicate shoulders, tailing, or inflection points should be investigated to ensure these chromatographic problems are not related to a co-eluting interference.

4.3.9.1.2 Labware Cleaning. Labware must be thoroughly cleaned prior to use to eliminate potential interferences and contamination. Regardless of the specific procedures implemented, all method performance specifications for cleanliness must be met. Volumetric labware used for collection of cartridge eluent can show buildup of silica gel residue over time, requiring aggressive physical cleaning methods with laboratory detergent and hot water. Clean all associated labware by rinsing with ACN, washing with laboratory detergent, rinsing with deionized water, rinsing with ACN or methanol, and air drying or drying in an oven at no more than 80 to 90°C. [5] Heated drying of volumetric ware at temperatures > 90°C voids the manufacturer volumetric certification.

4.3.9.1.3 Minimizing Sources of Contamination. Several target analytes in this method are typically present in ambient air and may contaminate solvents and the DNPH reagent if appropriate preventive measures are not in place. ACN used for sample extraction, standards preparation, and mobile phase preparation must be carbonyl-free HPLC grade or better (as indicated by the supplier or on the COA) and must be stored tightly capped away from sources of carbonyls. DNPH cartridges must be handled properly per Section 4.3.5.2.

Laboratories which process environmental samples for organic compounds such as pesticides typically employ extraction with acetone or other solvents which may contaminate DNPH cartridge media and carbonyl extraction solvents. Laboratory areas in which cartridges are stored, extracted, and analyzed should be free of contaminating solvent fumes. Carbonyls handling areas should have heating, ventilation, and air conditioning systems separate from such laboratory operations.

4.3.9.2 Reagents and Standard Materials

4.3.9.2.1 Solvents. Solvents employed for extraction, preparation of standards solutions, and preparation of mobile phase must be high-purity carbonyl-free, HPLC grade, and shown by analysis to be free of contaminants and interferences. Such solvents include ACN, methanol, and deionized water. Deionized water must be ASTM Type I (18 MΩ·cm).

4.3.9.2.2 Calibration Stock Materials. Calibration source material must be of known high purity and must be accompanied by a COA. Calibration materials should be neat high purity solids or sourced as certified single component or component mixtures of target compounds in an appropriate solvent (i.e., ACN or methanol).

Neat solid material must be weighed with a calibrated analytical balance with the appropriate sensitivity for a minimum of three significant figures in the determined standard mass. The calibration of the balance must be verified on the day of use with certified weights bracketing the masses to be weighed. Calibration standards diluted from stock standards must be prepared by delivering stock volumes with mechanical pipettes or calibrated gastight syringes and the volumes dispensed into Class A volumetric labware to which ACN is added to establish a known final dilution volume.

4.3.9.2.3 Secondary Source Calibration Verification Stock Materials. A secondary source standard must be prepared to verify the calibration of the HPLC on an ongoing basis, minimally immediately following each ICAL. The secondary source stock standard must be purchased from a different supplier than the calibration stock material or, only if unavailable from a different supplier, may be of a different lot from the same supplier as the calibration material.

4.3.9.2.4 Holding Time and Storage Requirements. Unopened stock materials are appropriate for use until their expiration date provided they are stored per manufacturer requirements. Once opened, stock materials may not be used past the manufacturer recommended period or, if no time period is specified, not beyond six months from the opened date. To use the standard materials past this time period, standards must have been demonstrated to not be degraded or concentrated by comparison to freshly opened standards. Unopened stock materials must be stored per manufacturer recommendations. All stock and diluted working calibration standards must be stored at ≤ 4°C in a separate refrigeration unit from sample cartridges and sample extracts.

4.3.9.3 Cartridge Holding Time and Storage Requirements. All field-collected cartridges must be stored at ≤ 4°C and extracted within 14 days of the end of collection. These conditions similarly apply to laboratory-prepared QC samples, which must be stored at ≤ 4°C and extracted within 14 days of preparation. Extracts must be analyzed within 30 days of extraction. Results input to AQS must be appropriately qualified for failure to meet the holding time and/or storage criteria.

4.3.9.4 Cartridge Extraction

4.3.9.4.1 Laboratory Quality Control Samples. With each extraction batch of 20 or fewer field-collected cartridges, which may include the various field QC samples such as those listed in Section 4.3.8.2, the following negative and positive laboratory QC samples must be prepared (except LCS/LCSD which must be prepared/analyzed minimally quarterly – recommended with each batch). For batch sizes of more than 20 field-collected cartridges, *n* such QC samples of each type must be added to the batch, where *n* = batch size / 20, and where *n* is rounded to the next highest integer. Thus for batch sizes of 30, two of each of the following QC samples would be included in each batch. A best practice would be to process field-collected cartridges in batches of no more than 20 at a time.

- Extraction Solvent Method Blank (ESMB): An ESMB is prepared by transferring the extraction solvent into a flask just as an extracted sample. The purpose of this negative control is to demonstrate that the extraction solvent is free of interferences and contamination and that the labware washing procedure is effective. Analysis must show target compound responses are less than the laboratory MDL_{sp} for MDLs determined via Section 4.1.3.1 or the $s \cdot K$ portion of the MDL for MDLs determined via Section 4.1.3.2.
- Method Blank (MB): The MB is a negative control that may also be referred to as the cartridge blank. The MB is a blank unopened cartridge (that has not left the laboratory) which is extracted identically to field samples. All target analytes must meet criteria specified in Table 4.3-2.
- Laboratory Control Sample (LCS): The LCS, also referred to as the laboratory fortified blank (LFB), is a positive control prepared by spiking a known amount of underivatized or derivatized DNPH-carbonyl target analyte onto a cartridge such that the expected extract concentration is in the lower third of the ICAL range. The spiked cartridge is allowed to sit for minimally 30 minutes to allow the solvent to dry following addition of the DNPH-carbonyl in solution. The LCS is then extracted with the same extraction solvent and method employed for field samples to assess bias in matrix of the extraction and analysis procedures. Recovery of the LCS must be within 80 to 120% of nominal for formaldehyde and 70 to 130% of nominal for all other target carbonyls.
- Laboratory Control Sample Duplicate (LCSD): The LCSD is prepared and extracted identically to the LCS. The LCSD assesses precision through extraction and analysis. Recovery of the LCSD must be within 80 to 120% of nominal for formaldehyde and 70 to 130% for all other target carbonyls. The LCS and LCSD results must show RPD of $\leq$ 20%.

All field-collected and laboratory QC samples in a given extraction batch must be analyzed in the same analysis batch (an analysis batch is defined as all samples analyzed together within a 24-hour period).

Laboratories must take corrective action to determine the root cause of laboratory QC exceedances. Field-collected sample results associated with failing QC results (in the same

preparation batch or analysis batch) must be appropriately qualified when input into AQS. In order to simplify troubleshooting when experiencing QC failures, QC sample cartridge media and extraction solvent lots should be the same, where possible.

4.3.9.4.2 Cartridge Extraction Procedures. Cartridges are extracted with carbonyl-free HPLC grade ACN. Field-collected cartridges must be removed from cold storage and allowed to equilibrate to room temperature, approximately 30 minutes, prior to extraction. Cartridges are removed from the foil pouch, the end caps are removed, and the cartridges are installed in a holding rack with the inlet of the cartridge pointed down to facilitate elution. Field-collected samples and associated field and laboratory QC samples discussed in Section 4.3.9.4.1 must be extracted in the same batch.

The ACN extraction solvent must be added to the cartridge so that elution occurs in the direction opposite of sample air flow (unless the laboratory can demonstrate that reverse elution is not necessary). Luer syringe barrels or other commercially-available funnels are available for use as solvent reservoirs for extraction, if needed. Elution may be performed by gravity or vacuum methods. The cartridge eluent is collected in a clean volumetric flask or other appropriate volumetrically certified vessel. Once the eluent is collected, the extract is brought to a known final volume with ACN extraction solvent.

A minimum 2-mL extraction volume is necessary to ensure complete elution of the target analytes from the sorbent bed. An extraction volume up to 5 mL may be employed, however larger volumes do not increase the extraction efficiency and may overly dilute the extract.

Once brought to volume, it is highly recommended that an aliquot of the extract is transferred to an autosampler vial for analysis and the remaining extract stored in a sealed vial protected from light at ≤ 4°C. The stored extract affords reanalysis if there are problems during analysis (up to 40 days from extraction).

4.3.9.5 Analysis by HPLC

4.3.9.5.1 Instrumentation Specifications. For separation of the DNPH-carbonyls by HPLC, the analytical system must have the following components:

- Separations module capable of precise pumping of ACN, methanol, and/or deionized water at 1 to 2 mL/min
- Analytical column, C18 reversed phase, 4.6 × 50-mm, 1.8-µm, or equivalent
- Guard column
- Absorbance detector set to 360 nm or mass selective detector capable of scanning m/z range of 25 to 600
- Column heater capable of maintaining 25-35 ± 1 °C
- Degassing unit

4.3.9.5.2 Initial Calibration. On each day that analysis is performed, the instrument must be calibrated (meaning an ICAL must be performed) or the ICAL must be verified by analysis of a CCV according to the following guidance.

ICAL of the HPLC must be performed initially, when continuing calibration checks fail criteria, and when there are major changes to the instrument which affect the response of the instrument. Such changes include, but are not limited to: change of guard or analytical column (if analyte retention times change), backflushing of the analytical column (if analyte retention times change), replacement of pump mixing valves and/or seals (if analyte retention times change, replacement of the detector and/or lamp, and cleaning of the MS source (if HPLC/MS).

Working calibration standards are prepared in ACN at concentrations covering the desired working range of the detector, typically from approximately 0.01 to 3.0 µg/mL of the free carbonyl. In order to avoid confusion or error in concentration calculation, it is recommended that all concentrations be expressed as the free carbonyl and not the DNPH-carbonyl. The ICAL must consist of a minimum of five calibration standard levels which cover the entire calibration range.

Prior to calibrating the HPLC, the instrument must be warmed up and mobile phase should be pumped for a time sufficient to establish a stable baseline. All solutions to be analyzed must be removed from cold storage and equilibrated to room temperature prior to analysis.

Once a stable baseline is established, minimally one solvent blank (SB, an aliquot of extraction solvent dispensed directly into a vial suitable for the HPLC autosampler, or similar) must be analyzed to demonstrate the instrument is sufficiently clean, after which analysis of calibration standard solutions may commence. The SB must show target compound responses are less than the laboratory MDL_{sp} for MDLs determined via Section 4.1.3.1 or the $s \cdot K$ portion of the MDL for MDLs determined via Section 4.1.3.2.

To establish the ICAL, each standard solution must be injected minimally once and preferably in triplicate. The instrument response (area units) is plotted on the y-axis against the nominal concentration on the x-axis and the calibration curve generated by linear regression for each target compound. The calibration curve correlation coefficient (r) must be ≥ 0.999 for linear fit and the curve must not be forced through the origin. The calculated concentration of each calibration solution must be within 20% of its nominal concentration.

The absolute value of the concentration equivalent to the intercept of the calibration curve (|intercept/slope|) converted to concentration units (by division by the slope) must be less than the laboratory MDL_{sp} for MDLs determined via Section 4.1.3.1 or the $s \cdot K$ portion of the MDL for MDLs determined via Section 4.1.3.2. When this specification is not met, the source of contamination or suppression must be corrected and the calibration curve reestablished before sample analysis may commence.

RT windows are calculated from the ICAL by determining the mean RT for each target compound. For positive identification the RT of a derivatized carbonyl must be within three standard deviations (3*s*) or ± 2%, whichever is smaller, of its mean RT from the ICAL. Note that

heating the column to a constant temperature of approximately 25 to 30°C promotes consistent RT response by minimization of column temperature fluctuations.

4.3.9.5.3 Secondary Source Calibration Verification Standard. Following each successful ICAL, a second SSCV must be analyzed to verify the accuracy of the ICAL. The SSCV is prepared in ACN at approximately the mid-range of the calibration curve by dilution of the secondary source stock standard. Alternatively, two or more concentrations of SSCV may be prepared covering the calibration range. All SSCVs must recover within ± 15% of nominal.

4.3.9.5.4 Continuing Calibration Verification. Once the HPLC has met ICAL criteria and the ICAL verified by the SSCV, a CCV must be analyzed prior to the analysis of samples on days when an ICAL is not performed, and minimally every 12 hours of analysis. The CCV is also recommended to be analyzed after every 10 sample injections and at the end of the analytical sequence. On days when an ICAL is not performed, a SB must be analyzed prior to the CCV to demonstrate the instrument is sufficiently clean to commence analysis.

At a minimum, a CCV must be prepared at a single concentration recommended to be at approximately the mid-range or lower end of the calibration curve, must be diluted from the primary stock or secondary source stock material, and CCV recovery must be 85 to 115% for each target compound. As a best practice, two or more concentrations of CCV may be prepared and analyzed so as to better cover instrument performance across the range of the calibration curve.

Corrective action must be taken to address CCV failures, including, but not limited to, preparing and analyzing a new CCV, changing the guard or analytical column, backflushing of the analytical column, replacement of the detector and/or lamp (if HPLC/UV), and cleaning of the MS source (if HPLC/MS).

4.3.9.5.5 Replicate Analysis. For each analytical sequence of 20 or fewer field-collected samples, at least one field-collected sample extract should be selected for replicate analysis (as prescribed in the workplan). For sequences containing more than 20 field-collected samples, *n* such replicates must be analyzed, where *n* = batch size / 20, and where *n* is rounded to the next highest integer. Thus, for batch sizes of 30, two replicate analyses would be performed. Replicate analysis must demonstrate precision of ≤ 10% RPD for concentrations ≥ 0.5 µg/cartridge.

4.3.9.5.6 Compound Identification. The following criteria must be met in order to positively identify a target compound:

1. The signal-to-noise (S:N) ratio of the target compound peak must be > 3:1, preferably > 5:1. Refer to Section 4.2.5.10.3 for more information on S:N.
2. The RT of the compound must be within the acceptable RT window determined from the ICAL average (see Section 4.3.9.5.2).
3. **HPLC-MS only ** - The target and qualifier ion peaks must be co-maximized (peak apexes within one scan of each other). Refer to Section 4.2.5.10.3 for more information on co-maximization.

4. **HPLC-MS only ** - The abundance ratio of the qualifier ion response to target ion response for at least one qualifier ion must be within ± 30% of the average ratio from the ICAL. Refer to Section 4.2.5.10.3 for more information on ion abundances.

Item 1 above does not need to be evaluated closely with each identified peak. Rather the interpretation of the experienced analyst should weigh heavily on whether the peak meets the minimal signal-to-noise ratio. Item 2 above may be automated by the analysis software such that it is automatically flagged. RT windows must be updated with each new ICAL.

If any of these criteria (as applicable) are not met, the compound may not be positively identified. The only exception to this is when in the opinion of an experienced analyst the compound is positively identified. The rationale for such an exception must be documented.

4.3.9.5.7 Data Review and Concentration Calculations. Each chromatogram must be closely examined to ensure chromatographic peaks are appropriately resolved and integration does not include peak shoulders or inflections indicative of a coelution. The HPLC method may require modification to employ mobile phase gradient programming or other methods to resolve coeluting peaks.

Each chromatogram of an extracted cartridge (MB, LCS, LCSD, or any field-collected sample) must be examined to ensure a DNPH peak is present. Chromatograms in which the DNPH peak area is < approximately 50% of the typical peak area of the laboratory QC samples must be investigated for potential compound misidentification due to the likely appearance of additional chromatographic peaks as a result of formation of side products from the consumption of the DNPH. This verification can be estimated and should be prescribed within the SOP or similar controlled document. Once sample identification is confirmed, field-collected samples must be qualified as estimated concentrations when entered into AQS since depletion of the DNPH to below 50% of typical levels indicates the potential for negative bias in the measured concentrations.

The concentrations of target carbonyls in unknown samples are calculated by relating the area response of the target carbonyl to the relationship derived in the calibration curve generated in Section 4.3.9.5.2.

Concentration results which exceed the instrument calibration range must be diluted and analyzed such that peak within the calibration range. The diluted result must be reported and the associated MDL adjusted accordingly by the dilution factor (the MDL multiplied by the dilution factor).

While TO-11A allows for blank subtraction, this is not an acceptable practice and results must not be corrected for solvent blank or MB levels. Concentrations exceeding acceptance criteria for these blanks must prompt investigation as to the source of contamination and associated field collected sample results may require qualification.

For sampling units which do not provide an integrated collection volume, the beginning and ending flows are averaged to calculate the collected air volume. For computer controlled

sampling units, the integrated collected volume is typically available from the data logging system. Sampled air volumes must be in standard conditions of temperature and pressure (STP), 25°C and 760 mm Hg. Sampling unit flows should be calibrated in flows at standard conditions so conversion from local conditions to standard flows is not necessary.

The air concentration in µg/m^3 of each target carbonyl is determined by multiplying the concentration in the extract by the final extract volume and dividing by the collected sample air volume at standard conditions of 25°C and 760 mm Hg:

$$C_A = \frac{C_t \cdot V_e}{V_A}$$

where:

C_A = concentration of the target carbonyl in air (µg/m^3)
C_t = concentration of the target carbonyl in the extract (µg/mL)
V_e = final volume of extract (mL)
V_A = volume of collected air at STP (m^3)

Carbonyls concentrations can also be calculated in ppbv by multiplying by a conversion factor based on the molecular weight of the target carbonyl at STP is calculated as follows:

$$CF = \frac{MW}{0.082059 \cdot 298.15}$$

where:

CF = conversion factor (µg·m^{-3}·ppb^{-1})
MW = molecular weight of the target carbonyl (g/mol)

The air concentration of the target carbonyl in ppb is then calculated as follows:

$$C_{A,ppb} = \frac{C_A}{CF}$$

where:

$C_{A,ppb}$ = concentration of the target carbonyl in air (ppb)
C_A = concentration of the target carbonyl in air (µg/m^3)
CF = conversion factor (µg·m^{-3}·ppb^{-1})

4.3.10 Summary of Quality Control Parameters. A summary of QC parameters is shown in Table 4.3-4.

Table 4.3-4. Summary of Quality Control Parameters for NATTS Carbonyls Analysis

Parameter	Description and Details	Required Frequency	Acceptance Criteria
Solvent Blank (SB)	Aliquot of ACN analyzed to demonstrate instrument is sufficiently clean to begin analysis	Prior to ICAL and daily beginning CCV	All target carbonyls < MDL_{sp} (refer to Section 4.1.3.1) or $s \cdot K$ (refer to Section 4.1.3.2)
Initial Calibration (ICAL)	Analysis of a minimum of five calibration levels covering approximately 0.01 to 3.0 µg/mL	Initially, following failed CCV, or when changes to the instrument affect calibration response	Linear regression $r \geq 0.999$, the concentration of each target carbonyl at each calibration level must be within ± 20% of nominal
Second Source Calibration Verification (SSCV)	Analysis of a second source standard at the mid-range of the calibration curve to verify curve accuracy	Immediately following each ICAL	Recovery of each target carbonyl within ± 15% of nominal
Continuing Calibration Verification (CCV)	Analysis of a known standard at the mid-range of the calibration curve to verify ongoing instrument calibration	Prior to sample analysis on days when an ICAL is not performed, and minimally every 12 hours of analysis. Recommended following every 10 sample injections, and at the conclusion of each analytical sequence	Recovery of each target carbonyl within ± 15% of nominal
Extraction Solvent Method Blank (ESMB)	Aliquot of extraction solvent analyzed to demonstrate extraction solvent is free of interferences and contamination	One with every extraction batch of 20 or fewer samples, at a frequency of no less than 5%	All target carbonyls < MDL_{sp} (refer to Section 4.1.3.1) or $s \cdot K$ (refer to Section 4.1.3.2)
Method Blank (MB)	Unexposed DNPH cartridge extracted as a sample	One with every extraction batch of 20 or fewer samples, at a frequency of no less than 5%	Criteria in Table 4.3-2 must be met
Laboratory Control Sample (LCS)	DNPH cartridge spiked with known amount of target analyte at approximately the lower third of the calibration curve	Minimally quarterly. Recommended: One with every extraction batch of 20 or fewer samples, at a frequency of no less than 5%	Formaldehyde recovery 80-120% of nominal spike All other target carbonyls must recover 70-130% of nominal spike
Laboratory Control Sample Duplicate (LCSD)	Duplicate LCS to evaluate precision through extraction and analysis	Minimally quarterly. Recommended: One with every extraction batch of 20 or fewer samples, at a frequency of no less than 5%	Must meet LCS recovery criteria Precision ≤ 20% RPD of LCS
Replicate Analysis	Replicate analysis of a field-collected sample	Once with every analysis sequence of 20 or fewer samples, at a frequency of no less than 5% (as required by workplan)	Precision ≤ 10% RPD for concentrations ≥ 0.5 µg/cartridge
Retention Time (RT)	RT of each target compound in each standard and sample	All qualitatively identified compounds	Each target carbonyl within ± 3*s* or ± 2% of its mean ICAL RT

Table 4.3-4. Summary of Quality Control Parameters for NATTS Carbonyls Analysis (Continued)

Parameter	Description and Details	Required Frequency	Acceptance Criteria
Lot Blank Evaluation	Determination of the background of the DNPH cartridge media	Minimum of 3 cartridges or 1% (whichever is greater) for each new lot of DNPH cartridge media	All cartridges must meet criteria in Table 4.3-2
Zero Certification Challenge	Clean gas sample collected over 24 hours to demonstrate the sampling unit does not impart positive bias	Annually	Each target carbonyl in the zero certification ≤ 0.2 ppb above reference sample
Field Blank	Blank DNPH cartridge exposed to field conditions for minimally 5 minutes in the primary sampling location	Monthly	Must meet criteria in Table 4.3-3
Duplicate Sample	Field sample collected through the same inlet probe as the primary sample	10% of primary samples for sites performing duplicate sample collection (as required by workplan)	Precision ≤ 20% RPD of primary sample for concentrations ≥ 0.5 µg/cartridge
Collocated Sample	Field sample collected through a separate inlet probe from the primary sample	10% of primary samples for sites performing collocated sample collection (as required by workplan)	Precision ≤ 20% RPD of primary sample for concentrations ≥ 0.5 µg/cartridge

4.3.11 References

1. *Determination of Formaldehyde in Ambient Air using Adsorbent Cartridges Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology]*; EPA Compendium Method TO-11A; U.S. Environmental Protection Agency: January 1999. Available at (accessed October 19, 2016): https://www3.epa.gov/ttnamti1/files/ambient/airtox/to-11ar.pdf

2. MacGregor, I. C., Hanft, E. A., and Shelow, D. M. (2015). *Update on the Optimization of U.S. EPA Method TO-11A for the Measurement of Carbonyls in Ambient Air*. Paper presented at the National Ambient Air Monitoring Conference, St. Louis, MO, August 10, 2016.

3. Urone, P., & Ross, R. C. (1979). Pressure change effects on rotameter air flow rates. *Environmental Science & Technology*, *13*(6), 732-734. doi: 10.1021/es60154a003

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5. Care and Safe Handling of Laboratory Glassware. Corning Incorporated. RG-CI-101-REV2. 2011. Available at (accessed October 19, 2016): http://csmedia2.corning.com/LifeSciences/media/pdf/Care_and_Safe_Handling_Lab_Glassware_RG-CI-101Rev2.pdf

4.4 PM_{10} Metals Sample Collection and Analysis

Each agency must codify in an appropriate quality systems document, such as an SOP, or equivalent, its procedures for performing PM_{10} metals sampling, filter digestion, and digestate analysis. Various requirements and best practices for such are given in this section. Note that regardless of the specific procedures adopted, method performance specifications as given in Section 4.4.13 must be met.

4.4.1 Summary of Method. PM_{10} metals are collected onto a filter by either a low volume or high volume air sampling method. Following completion of either sampling procedure, the filter, or portion thereof, is digested to liberate (dissolve) the desired elements by heating in acid, and the digestate is analyzed via ICP/MS per EPA Compendium Method IO-3.5.[1] Briefly, digestates are introduced to the ICP/MS through pneumatic nebulization into a radio frequency argon plasma where the elements in solution are desolvated, atomized, and ionized. The ions are extracted from the plasma by vacuum and separated on the basis of their mass-to-charge ratio by a quadrupole or TOF MS capable of a resolution of 1 amu at 5% peak height. An electron multiplier is applied to the ions transmission response and the resulting signal information recorded and processed by the data system.

The particle-bound metals in the air are collected with a commercially-available standalone air sampler fitted with a size-selective inlet (SSI) such that only particulate matter (PM) with a mass median aerodynamic diameter less than 10 µm is captured. Particles are deposited on either 47-mm Teflon® filter (low volume) or 8 inch × 10 inch QFF media over the 24-hour collection period. The low volume sampling method flow is set to 16.7 liters per minute (LPM; at local conditions) for a total collection volume of 24.05 m^3. The high volume method flow is set to approximately 1.13 m^3/min (at local conditions) for a total collection volume of approximately 1627 m^3. For both low volume and high volume methods, the SSIs require a closely regulated flow rate to ensure PM cut points are accurate and temporally stable.

Following the completion of any desired gravimetric measurements for determining total PM_{10} gravimetric concentration, the filters are digested for metals analysis. Following collection, filters should be stored at ambient conditions and must be digested and analyzed within 180 days.

The target metals of interest to the NATTS Program are listed in Table 4.4-1.

Table 4.4-1. NATTS Program Metals Elements and Associated CAS Numbers

Element	CAS Number
Antimony [b]	7440-36-0
Arsenic [a b]	7440-38-2
Beryllium [a b]	7440-41-7
Cadmium [a b]	7440-43-9
Chromium	7440-47-3
Cobalt [b]	7440-48-4
Lead [a b]	7439-92-1
Manganese [a b]	7439-96-5
Nickel [a b]	7440-02-0
Selenium [b]	7780-49-2

[a] NATTS Tier I core analyte
[b] NATTS PT target analyte

4.4.2 Advantages and Disadvantages of High Volume and Low Volume Sample Collection. Summarized below are some of the advantages and disadvantages of the high and low volume air sampling for PM_{10} metals.

4.4.2.1 Low Volume Sampling

Advantages

- Many low volume samplers are already in use at PM monitoring sites to assess compliance with the National Ambient Air Quality Standards. As a result, many monitoring agencies are familiar with and have the infrastructure to support low volume PM sampling.
- Teflon® filters, as compared to QFFs, typically have lower background levels of metals such as chromium, nickel, manganese, and cobalt. As a result, MBs are cleaner and MDLs that account for MB levels are lower.
- Low volume instruments are available into which several filters may be simultaneously loaded so as to permit collection of several sampling events in sequence without the need for operator intervention.

Disadvantages

- The extraction and analysis method must have greater sensitivity and background contamination must be more strictly limited in order to achieve MDLs equivalent to high volume sampling, due to the lower total sample volume collected.
- The entire Teflon® filter is digested for analysis, thus error in preparation may require invalidation of results, and it not possible to prepare duplicate and/or spike duplicate field collected samples for QC purposes.

4.4.2.2 High Volume Sampling

Advantages

- At the listed flow rates, the high volume sampling method collects approximately 67 times more mass on the filter than low volume sampling, thereby providing greater

sensitivity (approximately seven-fold) for metals analysis even after taking into consideration that only a portion (typically approximately 1/9) of the QFF is digested for analysis.

- In the event of loss of the primary sample and when assessment of method precision and bias is desirable, duplicate and spike duplicate samples may be readily prepared by extraction and analysis of another filter field collected sample strip.

Disadvantages

- QFFs typically have higher background levels of target metals, such as chromium, nickel, manganese, and cobalt.
- Sequential sampling is not possible with high volume filter sampling instruments.

4.4.3 Minimizing Contamination, Filter Handling, and Filter Inspection

4.4.3.1 Minimizing Contamination. Careful handling of the filter media is required to ensure that metals measured on the filter are present as a result of sampling the ambient atmosphere, rather than due to contamination. Each agency must codify into an appropriate quality system document, such as an SOP, procedures that it will follow to minimize the introduction of metals contamination during filter handling, processing, extraction, and subsequent analysis of digestates. What follows in this section are practices either that are required or are recommended for adoption into an agency's quality system.

See also Section 4.4.6 for guidance on minimizing contamination during the preparation of labware.

4.4.3.2 Filter Handling. Filters must only be handled with gloved hands or plastic or Teflon®-coated forceps, and filter media must not be manipulated with metal tools. Tools for portioning filter strips must be ceramic or plastic. Forceps and work areas should be routinely decontaminated using a dilute nitric acid solution followed by rinses with deionized water. Use of volumetric syringes with metal needles must be avoided.

Teflon® filter media should be transported to and from the field in non-metallic cassettes which must be kept tightly capped except during installation of filters into sampling units. Placement of filters into, and subsequent removal of filters from cassettes should be performed in the laboratory in a clean area where measures are taken to control the levels of airborne particulate matter, such as a conditioning room for filter weighing. Such filter weighing rooms typically employ dust-reduction methods such as high efficiency particulate air (HEPA) filtration to minimize potential deposition contamination.

QFFs should be transported and maintained in manila or glassine envelopes which protect the filter from dust deposition and from physical damage. The filter should be placed into, and subsequently removed from, the cassette while the cassette is in a clean area, one without obvious dust contamination, away from visible sources of PM, and with minimal air movement. Following removal from the cassette after the conclusion of sampling, the filter must be folded lengthwise in half (with gloved hands) with the particulate matter inward, and placed into a

protective manila envelope or folder, or within a glassine envelope to protect the filter from loss of PM or from deposition of dust.

4.4.3.3 Filter Inspection. Filter media must be inspected for pinholes, discolorations, creases, thin spots, and other defects which would make them unsuitable for sample collection. Teflon® filters must additionally be inspected for separation of the support ring. Filters should be inspected on a light table or similar apparatus which allows backlighting of the filter to aid in the identification of defects. Any surface (such as the light table) coming into contact with the filter media must be decontaminated from dust and residue prior to use with deionized water and lint-free wipes. All filter handling requirements given in Section 4.4.3.2 must be followed.

4.4.4 Precision – Sample Collection and Laboratory Processing. Each agency must codify in an appropriate quality systems document, an SOP, or similar, procedures that it will follow to assess precision. Given below are the various types of precision and guidance on how to measure each.

4.4.4.1 Sample Collection Precision. Given that each PM_{10} metals instruments consists of a discrete inlet and sampling pump, collection of duplicate samples is not possible. Thus, evaluation of the precision of the entire PM_{10} metals sampling technique, from collection through extraction and analysis, may only be performed by way of collocated sampling.

For monitoring sites conducting collocated PM_{10} metals sampling, collocated samples must be collected as minimally 10% of the primary samples collected (as prescribed in the workplan). This is equivalent to a minimum of six collocated samples for sites conducting one-in-six days sampling for a total of 61 primary samples annually. More frequent collocated sample collection provides additional sample collection precision and is encouraged where feasible.

Collocated sample results must show precision of ≤ 20% RPD compared to the primary sample for concentrations ≥ 5x MDL. Root cause analysis must be performed for instances in which collocated samples fail this precision specification and the results of the primary and collocated sample must be qualified when entered into AQS.

4.4.4.2 Laboratory Precision

4.4.4.2.1 Low Volume Teflon® Filter Laboratory Precision. Teflon® filters must be extracted in their entirety. As a result, duplicate samples may not be prepared by subdividing a filter. However, the precision of filter digestion and analysis should be assessed by the preparation and analysis of duplicate LCSs. A sample digestate may be selected with each digestion batch to be analyzed in replicate to determine analytical precision. To summarize,

- A duplicate LCS informs the precision of digestion and analysis procedures, and
- Replicate analysis of a sample digestate provides precision for the analysis only.

4.4.4.2.2 High Volume QFF Laboratory Precision. Sample processing and analysis precision may be evaluated in several different ways with QFFs. For example, to evaluate the precision of the filter preparation, digestion, and analysis processes, duplicate strips

may be portioned from a field collected QFF filter and digested separately and duplicate LCSs may be prepared. Preparation, digestion, and analysis of a matrix spike (MS) and matrix spike duplicate (MSD) duplicate pair can additionally be performed to evaluate the matrix effects on precision of field collected samples. Finally, to determine analytical precision, a sample digestate may be analyzed in replicate. To summarize:

- Duplicate sample filter strips and duplicate LCSs provide precision of digestion and analysis procedures;
- Duplicate matrix spike filter strips provide information on the precision of digestion and analysis procedures, and include an assessment of potential matrix effects of that specific sample; and
- Replicate analysis of a sample digestate provides precision for the analysis only.

4.4.5 Field Blanks. For both high volume and low volume sampling methods, field blank samples must be collected minimally monthly for each primary sampling unit (total of 12 per year for a total of 18% of samples [12 out of 61]). For collocated sampling units, field blank samples should be collected minimally twice per year (two out of six) or for 18% of collocated samples collected, whichever is greater.

Field blanks must be generated by installing the field blank filter into the sampling unit to simulate a field sample, however the field blank does not experience sample flow. After minimally 5 minutes have elapsed (or the duration of sample switching required by the sampling unit, as applicable), the filter is retrieved and stored at the field site until the associated field sample can be retrieved and transported to the laboratory.

Field blank analysis must demonstrate all target elements < MDL.

An exposure blank is similar to a field blank, but is not required, and may be collected via several protocols. The exposure blank includes exposing the filter to the ambient conditions by installation in a sampling unit, and just like a field blank, air is not drawn through the exposure blank cartridge. The exposure blank filter sample may be installed in the primary sampling unit on non-sample collection days or could be installed in a collocated sampling unit during collection of the primary sample.

4.4.6 Labware Preparation for Digestion and Analysis. Regardless of how filters are digested, labware cleaning is essential to ensure background contamination is minimized. As with other contamination minimization procedures, each agency must codify in an appropriate quality systems document, such as an SOP, or equivalent, its procedures for effective cleaning and decontamination of labware. Regardless of the procedures adopted, method performance specifications as given in Section 4.4.13 must be met.

Labware for hot block digestions is typically single use; however, labware for microwave digestion and volumetric labware for preparation of standards and reagents must be effectively cleaned before each use. To do so, labware should be rinsed with tap water to remove as much of the previous contents as possible. Following this tap water rinse, labware should be soaked minimally overnight in a $\geq$ 10% HNO_3 (v/v) aqueous solution. Soaking should be followed by a

minimum of three rinses with deionized water and air drying. Alternatively, labware cleaning instruments are commercially available which may be programmed to provide washing, rinsing, and soaking cycles in various detergent and acid solutions.

Volumetric labware must not be heated above 80 to 90°C as this voids the volumetric certification. [2] Clean labware should be stored in a contaminant-free area, upside down or capped to minimize introduction of contamination. Elevated levels in calibration blanks and digested reagent blanks indicate the presence of contamination. Additional cleaning and acid rinsing steps should be considered when blanks exceed the specified acceptance criteria.

4.4.7 Reagents for Metals Digestion and Analysis. Due to the sensitivity of ICP/MS instruments, the purity of reagents and standards is paramount. Reagents and standards must be certified and traceable with COAs, and it is recommended that all reagents and standards be of the greatest purity possible and have minimal background levels of target elements. Regardless of the reagents and standards selected, calibration and reagent blanks must be meet method specifications as given in Section 4.4.13.

Reagent water for the preparation of digestion solutions and for dilution of standard materials should be ASTM Type I or equivalent (having an electrical resistivity greater than 18 MΩ·cm). Acids should be trace metals grade, ACS spectroscopic grade, UHP grade, or equivalent. Further polishing of reagent water and redistillation of acids may be necessary to achieve blank acceptance criteria. Borosilicate glass volumetric flasks and storage containers should be avoided. Teflon® or plastic (polyethylene, polypropylene, etc.) certified volumetric flasks and storage bottles are preferable as they do not leach contaminants into stored solutions. Solutions prepared in borosilicate glass volumetric flasks should be transferred as soon as possible to a Teflon® or plastic storage container.

4.4.8 Method Detection Limits. MDLs must be determined per the guidance provided in Section 4.1. Furthermore, MDLs must be determined with reagents, media, and sample handling techniques identical to those employed for the processing of field samples. Determined MDLs for Tier I core analytes must meet the requirements listed in the most recent workplan.

4.4.8.1 Teflon® Filter MDL. If the 40 CFR Part 136 Appendix B guidance in Section 4.1.3.1 is followed, Teflon® filter MDLs must be determined by digesting minimally seven spiked filters and seven method blank filters (all selected from the same lot of filters) in three temporally-separated and unique digestion and analytical batches. Both the MDL_{sp} and MDL_b must be tracked and documented. QC blanks, which are not prepared with the filter matrix, are compared to the MDL_{sp} regardless of whether it is reported as the laboratory MDL. Alternatively, MDLs may be determined following the procedure in Section 4.1.3.2. For laboratories determining MDLs according to Section 4.1.3.2, laboratories must track the portion of the MDL determined by $s \cdot K$ for comparison to QC blanks which are not prepared with the filter matrix.

4.4.8.2 QFF MDL. If the updated 40 CFR Part 136 Appendix B procedure in Section 4.1.3.1 is followed, QFF MDLs must be determined by digesting seven spiked filter strips and seven method blank filter strips in three temporally-separated and unique digestion and analytical batches. The filter strips should be from a different filter (from the same lot of filters) for each

batch. Both the MDL_{sp} and MDL_b must be tracked and documented. QC blanks, which are not prepared with the filter matrix, are compared to the MDL_{sp} regardless of whether it is reported as the laboratory MDL. Alternatively, MDLs may be determined following the procedure in Section 4.1.3.2. For laboratories determining MDLs according to Section 4.1.3.2, laboratories must track the portion of the MDL determined by $s \cdot K$ for comparison to QC blanks which are not prepared with the filter matrix.

4.4.9 Low Volume Sample Collection and Digestion

4.4.9.1 Air Sampling Instruments. Low volume sample collection instruments must comply with the Low-Volume PM_{10} FRM requirements as listed in 40 CFR Part 50 Appendix L, i.e., they must operate at the design flow rate of 16.67 L/min (at local conditions), utilize 47-mm Teflon® filter collection media, and be fitted with the "pie plate" PM_{10} inlet or the louvered inlet specified in 40 CFR 50 Appendix L, Figures L-2 through L-19, configured as in the PM_{10} reference method. The following instruments are among those that comply with these specifications:

- Andersen Model RAAS10-100
- Andersen Model RAAS10-200
- Andersen Model RAAS10-300
- BGI Incorporated Model PQ100
- BGI Incorporated Model PQ200
- Opsis Model SM200
- Thermo Scientific or Rupprecht and Pataschnick Partisol Model 2000
- Thermo Scientific Partisol 2000-FRM
- Thermo Scientific Partisol or 2000i
- Rupprecht and Patashnick Partisol-FRM 2000
- Thermo Scientific Partisol-Plus Model 2025
- Thermo Fisher Scientific Partisol 2025i
- Rupprecht and Patashnick Partisol-Plus 2025
- Tisch Environmental Model TE-Wilbur10

Sampler siting requirements are listed in Section 2.4.

4.4.9.2 Flow Calibration. Sampling unit flow calibration must be performed minimally annually against a traceable calibrated flow transfer standard by adjusting the sampling unit flow to match the certified standard.

Moreover, the instrument flow should be checked minimally quarterly, recommended to be monthly, and per 40 CFR Part 50 Appendix L, the flow adjusted if it is not within ± 4% of the transfer standard or within ± 5% of the design flow rate. Prior to performing flow checks, sampling units should be leak checked to ensure that flow path integrity is maintained. A leak check should be performed minimally every five sample collection events. A successful leak check indicates a total flow of less than 80 mL or loss of less than 25 mm Hg.

4.4.9.3 Filter Media. Low volume PM_{10} metals must be collected onto a 46.2-mm Teflon® filter substrate with a polypropylene support ring, 2-µm pore size, and a particle deposit area of 11.86 cm^2. Filters must be stamped or printed with a unique identifier on either the support ring or on the filter substrate.[3] EPA typically annually sends agencies the filter media.

4.4.9.3.1 Lot Background Determination. For each lot of filters, the concentration of metals in the lot background must be determined by digesting and analyzing five separate filters from a given lot.

While there is no prescribed threshold for the lot background concentration for each element, the lot blank concentrations must be reported to AQS. Note that the previous version of this TAD permitted lot blank subtraction provided results were flagged in AQS with the QA data qualifier "CB", however lot blank subtraction is not permitted. AQS guidance is provided in Section 3.3.1.3.15.

4.4.9.4 Filter Sampling, Retrieval, Storage, and Shipment. Teflon® filters will likely arrive at the field site already installed in a cassette. The filter must be installed per the requirements of the specific low volume instrument. A leak check may then be performed followed by verification of the correct sampling date, duration, and target flow rate.

Upon sample retrieval, instrument performance information including the average temperature, barometric pressure, average flow, total collected volume, collection duration, and any flags indicating a problem during collection should be recorded, downloaded, or otherwise recorded, as appropriate. Following removal from the instrument, the covers are placed back onto the filter cassette, and the cassette sealed into a resealable plastic bag. Filters need not be shipped or stored refrigerated. Filters must be handled per the procedures in Section 4.4.3.1. The sample custody form must be completed and accompany the collected sample at all times until relinquished to the laboratory. COC documentation must comply with Section 3.3.1.3.7.

4.4.9.4.1 Sampling Schedule and Duration. Metals sample collection must be performed on a 1-in-6 days schedule for 24 ± 1 hours beginning at midnight and concluding at midnight of the following day, standard time (unadjusted for daylight savings time), as per the national sampling calendar. For missed or invalidated samples, a make-up sample should be scheduled and collected per Section 2.1.2.1. Clock timers controlling sampling unit operation must be adjusted so that digital timers are within ±5 minutes of the reference time (cellular phone, GPS, or similar accurate clock) and mechanical timers within ±15 minutes.

4.4.9.5 Teflon® Filter Digestion

4.4.9.5.1 Laboratory Digestion QC Samples. Each sample digestion batch must consist of 20 or fewer field-collected filters (primary samples, collocated samples, and field blanks). The following laboratory QC is required with each digestion batch:

- Negative Control Samples (Blanks), one each:
  - Reagent Blank (RB) – digestion solution with no filter
  - MB – blank filter with digestion solution

- Positive Control Samples (Spikes), one each:
  - Reagent Blank Spike (RBS) – spiked digestion solution with no filter
  - LCS – spiked blank filter with digestion solution
  - LCSD – duplicate spiked blank filter with digestion solution

Laboratory QC samples must be processed, digested, and analyzed identically to field-collected samples, including, if applicable, filtration and/or centrifugation of digestates.

4.4.9.5.2 Digestion Procedure. Filter must be digested with one of three possible methods: hot block digestion, microwave digestion, or heated sonication. The three different techniques are described in the following sections.

4.4.9.5.2.1 Hot Block Digestion

The hot block digestion wells must be checked to ensure each reaches and is able to maintain the target digestion temperature initially when put into use and annually thereafter. To do so, the hot block is set to the target temperature (typically 95°C) and, after the temperature has been reached, a digestion vessel filled with deionized water, known as a temperature blank, is placed into each well. After approximately 5 minutes (or long enough for the temperature to stabilize), the temperature of the water in each temperature blank is measured. Temperatures across the block should be within ± 5°C of the target temperature setting.

To perform digestion of Teflon® filters, each is placed into a separate digestion vessel. Certified single-use metals-free vessels with certified volumetric graduations are commercially available for hot block digestions and other vessels may be utilized provided they meet the required blank specifications. The lot and manufacturer of the digestion vessels must be documented with each batch. Sufficient digestion solution must be added to each vessel so as to completely submerge the filter. Digestion solutions typically consist of approximately 2% (v/v) nitric acid (HNO_3) and 0.5% (v/v) hydrochloric acid (HCl). To assist in the recovery of antimony, it may be necessary to add 0.1% hydrofluoric acid (HF) to the digestion solution.

The hot block digester is powered on and warmed to the desired temperature (~95°C) prior to placing each digestion vessel into a digestion well. Each digestion vessel should be covered with a precleaned ribbed watch glass and the batch of filters should be digested for a recommended for 2.5 hours, though digestion must be for a minimum of 30 minutes. Note that this duration of digestion must be consistent from batch to batch. An automatic shutoff timer can ensure consistent digestion duration. A temperature blank must be included with each batch to ensure that the proper temperature is reached during the digestion period. Digestion vessels should be observed periodically throughout digestion to ensure none go to dryness and that the filters remain submerged. Deionized water should be added to digestion vessels to avoid going to dryness. Filters which float should be resubmerged with a clean plastic or Teflon® stirring rod.

Once digestion has completed, digestion vessels are removed from the block and cooled to room temperature (approximately 30 minutes). Once cooled, the walls of the digestion vessel should be rinsed down with approximately 10 mL of deionized water and the digestates should be allowed to settle for minimally 30 minutes. Following settling, digestates must be brought to their final volume with deionized water. The final volume may be measured with the graduations on the volumetrically-certified digestion vessel. Otherwise, digestates must be transferred to a Class A volumetric vessel and the digestion vessel must be rinsed several times with small (2 to 3 mL) volumes of deionized water to ensure a quantitative transfer. The transferred digestates must be then brought to volume with deionized water.

For transfer of aliquots for analysis, filtration or centrifugation may be necessary to eliminate particulate interference on the ICP/MS. All such processing steps must be performed on both the field-collected and laboratory batch QC samples.

4.4.9.5.2.2 Microwave Digestion

Microwave digestion has several disadvantages when compared to hot block digestion. For example, microwave digestion equipment and accessories are expensive. Digestion vessels and associated caps must be cleaned and decontaminated after each use. Microwave oven power must be calibrated on a specified, periodic basis to ensure that the digestion energy is appropriate, comparable, and stable from batch to batch. Calibration frequency should not exceed six months and a best practice is to verify microwave power monthly. To ensure the appropriate amount of heat is imparted to vessels in an incompletely filled digestion rack, blank vessels may need to be added or the microwave power may need to be reduced. Due to the higher pressure and temperature, digestion vessels may overpressurize and explode, resulting in loss of sample and possible injury to laboratory staff. While such is possible, modern microwave digestion units typically employ temperature and pressure monitoring to adjust the power to reduce the likelihood of explosion.

The advantages of microwave compared to hot block digestion are that digestion may be performed more quickly (in approximately 30 minutes), digestions are more reproducible due to the even heating, the closed digestion vessels ensure no loss of volatile analytes such as mercury and lead and decrease the likelihood of the introduction of external contamination, and digestions are more complete as a result of the increased temperature and pressure.

To digest air filter samples by microwave digestion the microwave program should permit ramping the temperature to 180°C over 10 minutes and holding at 180°C for 10 minutes followed by a 5-minute cool down. Other programs are also acceptable provided the requisite batch QC criteria are met.

For digestion, each Teflon® filter must be placed into a separate microwave digestion vessel. Sufficient digestion solution must be added to each vessel so as to completely submerge the filter. Digestion solutions typically consist of approximately 2% (v/v) HNO_3 and 0.5% (v/v) HCl. Addition of a small amount (~0.1%) of hydrofluoric acid (HF) to the digestion solution may be needed to maintain antimony in solution.

The vessel caps and pressure relief valves are installed on the microwave digestion vessels and each vessel weighed to the nearest 0.01 g with a calibrated analytical balance. Weighed digestion vessels are then installed in the carousel in the microwave. The microwave digestion program is run concluding with a cool down. At the end of the program, the microwave status should be checked to verify the program completed appropriately and the digestion vessel carousel is carefully removed from the microwave oven and allowed to cool in a fume hood. Once cooled, vessels must be weighed to the nearest 0.01 g to ensure no loss of sample. Vessels which exhibit mass loss of > 0.01 g must be invalidated or, minimally, their analysis results must be flagged. Once cooled and weighed, vessels may be opened. Caution must be used when opening vessels as the contents may still be under pressure.

After cooling, the walls of the digestion vessel should be rinsed down with approximately 10 mL of deionized water and the digestates should be allowed to settle for minimally 30 minutes. Following settling, digestates must be transferred to a Class A volumetric vessel and the digestion vessel rinsed several times with small (2 to 3 mL) volumes of deionized water to complete the quantitative transfer. The digestates are brought to volume with deionized water.

For transfer of aliquots for analysis, filtration or centrifugation may be necessary to eliminate particulate interference on the ICP/MS. All such processing steps must be performed on both the field-collected and laboratory batch QC samples.

4.4.9.5.2.3 Acid Sonication

Each filter is placed into a separate digestion vessel. Certified single-use metals-free vessels with certified volumetric graduations are commercially available and other vessels may be utilized provided they meet the required blank specifications. The lot and manufacturer of the digestion vessels must be documented with each batch. Sufficient 4% (v/v) HNO_3 digestion solution is added to each vessel so as to completely submerge the filter. Addition of a small amount (~0.1%) of hydrofluoric acid (HF) to the digestion solution may be needed to maintain antimony in solution.

The sonication bath is powered on and warmed to the desired temperature (~69°C) prior to placing the digestion vessels into the bath. Each digestion vessel should be capped and sonicated for a minimum of 3 hours. Digestion vessels should be observed periodically throughout digestion to ensure the filter remains submerged. Filters which float should be resubmerged with a clean plastic or Teflon® stirring rod.

Once the digestion program has completed, digestion vessels are removed from the bath and cooled. Once cooled, the walls of the digestion vessel should be rinsed down with approximately 10 mL of deionized water and the digestates should be allowed to settle for minimally 30 minutes. Following settling, digestates must be brought to their final volume with deionized water. The final volume may be measured with the graduations on the volumetrically-certified digestion vessel. Otherwise, digestates are transferred to a Class A volumetric vessel and the digestion vessel are rinsed several times with small (2-3 mL) volumes of deionized water to ensure a quantitative transfer. The transferred digestates are then brought to volume with

deionized water.

For transfer of aliquots for analysis, filtration or centrifugation may be necessary to eliminate particulate interference on the ICP/MS. All such processing steps must be performed on both the field-collected and laboratory batch QC samples.

4.4.10 High Volume Sample Collection and Digestion

4.4.10.1 Air Sampling Instruments. High volume sample collection instruments must comply with the High-Volume PM_{10} FRM requirements in 40 CFR Part 50 Appendix J, i.e., they must operate at a design flow rate of 1.13 m^3 (at local conditions), utilize 8 inch × 10 inch QFF collection media, and be fitted with the PM_{10} inlet per EPA Reference Method RFPS-0202-141, RFPS-1287-063, or equivalent. The following sampling units are among those that comply with these specifications:

- Ecotech Model 3000
- Graseby Andersen/GMW Model 1200
- Graseby Andersen/GMW Model 321-B
- Graseby Andersen/GMW Model 321-C
- Tisch Environmental Model TE-6070 or New Star Environmental Model NS-6070
- Wedding and Associates or Thermo Environmental Instruments Inc. Model 600

Sampler siting requirements are listed in Section 2.4.

4.4.10.2 Flow Calibration. Sampling unit flow calibration must be performed minimally annually against a traceable calibrated flow transfer standard by adjusting the sampling unit flow to match the certified standard.

Moreover, the instrument flow should be checked minimally quarterly, recommended to be monthly, and the flow adjusted if it is not within ± 7% of the transfer standard or within ± 10% of the design flow rate. Prior to performing flow checks, sampling units should be leak checked to ensure that flow path integrity is maintained. Leak checks are performed by installing a piece of polycarbonate or other suitable substrate to seal off the filter plate and briefly operating the sampling unit motor. If a high-pitched whistle is heard, there is a leak in the flow path which must be remedied before sample collection can commence. Leak checks should be performed approximately every fifth sample collection event.

4.4.10.3 Filter Media. Sampling media consist of 8 inch × 10 inch QFF substrate with a 2-µm pore size, capable of 99% particle sampling efficiency for particles 0.3 µm in diameter or larger. Filters must be stamped or printed with a unique identifier on the corner of the filter and are typically provided annually by EPA.[4]

4.4.10.3.1 Lot Background Determination. For each lot of filters, the concentration of metals in the lot background must be determined by digesting and analyzing five filter strips, each cut from a separate filter from a given lot of filters. For monitoring agencies contracting

analysis, filters for lot blanks should be supplied to the laboratory to determine the lot background.

QFFs typically have background levels higher than Teflon® filters; chromium, cobalt, lead, manganese, and nickel may be routinely found. Note that the previous version of this TAD permitted lot blank subtraction provided results were flagged in AQS with the QA data qualifier "CB", however lot blank subtraction is not permitted.

While there is no prescribed threshold for the lot background concentration for each element, the lot blank concentrations must be reported to AQS. Information on reporting to AQS may be found in section 3.3.1.3.15.

4.4.10.4 Filter Sampling, Retrieval, Storage, and Shipment. Filter media may be installed in a sampling cassette at the laboratory before shipment to the field, or the site operator may be required to install the filter into the cassette. Installation of the filter into the cassette must be performed in a clean (minimal dust) indoor environment, preferably protected from air movement, with the filter identifier oriented downward. A cover should be attached to the top of the cassette to protect the filter sampling surface. Storing the assembled filter and cassette in a sealed plastic bag during transport and storage is a best practice.

The cam-lock bolts of the size-selective inlet on the sampling unit are loosened to allow the inlet to open on the hinge and the inlet locked open using a prop. The swing bolts are then loosened to allow the assembled cassette and filter to be installed. Installation must be performed carefully to ensure that the rubber gasket on the base of the sampling unit forms a tight seal around the cassette. The swing bolts are then tightened in a diagonal pattern to ensure even pressure is applied to the cassette. Each time a sample is set up, the inside of the sampling head and mating surfaces should be given a quick visual inspection for loose debris or corrosion which could impact the filter and the integrity of the gasket on the size-selective inlet. Once the cassette is installed, the inlet is closed and secured to the body of the sampling unit using the cam-lock bolts.

If the sampling unit is equipped with electronic flow control to automatically adjust flow rate based on ambient temperature and pressure, the sample schedule program must be verified before the sampling unit is ready for collection. If the sampling unit is not equipped with electronic flow control, the sampling unit must be powered on and allowed to run for minimally five minutes (ten minutes are recommended) before a reading of the pressure drop across the flow venturi, which must be cross-referenced to a corresponding calibrated flow. The unit is then powered off and the sample schedule program verified.

Upon sample retrieval, instrument performance information including the average temperature, barometric pressure, average flow, total collected volume, collection duration, and any flags indicating a problem during collection should be recorded, downloaded, or otherwise recorded, as appropriate. For sampling units without electronic flow control, the sampling unit must be powered on and allowed to run for minimally five minutes (ten minutes are recommended) before recording the reading of the pressure drop across the flow venturi. The filter sample cassette is then removed from the sampling unit and the cover placed on the cassette (it is a best

practice to place the filter cassette into a resealable plastic bag) until the filter may be removed from the cassette in a clean area, free of obvious contamination, and with minimal air movement.

When removed from the cassette, the filter must be folded in half, lengthwise, with the particulate matter inward. Folding the filter lengthwise is the best way to ensure that the portioned filter strips include a portion of the fold. The folded filter must then be placed within a manila or glassine envelope for transportation to the laboratory. Alternatively, the cover may be replaced on the filter cassette and the cassette placed in a resealable plastic bag for transportation to the laboratory where the filter is removed. Filters need not be shipped or stored cold. Filters must be handled per the procedures in Section 4.4.3.1. The sample custody form must be completed and accompany the collected sample at all times until relinquished to the laboratory. COC documentation must comply with Section 3.3.1.3.7.

4.4.10.4.1 Sampling Schedule and Duration. Metals sample collection must be performed on a 1-in-6 days schedule for 24 ± 1 hours beginning at midnight and concluding at midnight of the following day, standard local time (unadjusted for daylight savings time), per the national sampling calendar. For missed or invalidated samples, a make-up sample should be scheduled and collected per Section 2.1.2.1. Clock timers controlling sampling unit operation must be adjusted so that digital timers are within ±5 minutes of the reference time (cellular phone, GPS, or similar accurate clock) and mechanical timers within ±15 minutes.

4.4.10.5 QFF Digestion

4.4.10.5.1 Laboratory Digestion QC Samples. Each sample digestion batch must consist of 20 or fewer field-collected filters (primary samples, collocated samples, and field blanks). The following laboratory QC is required with each digestion batch:

- Negative Control Samples (Blanks), one each:
  - Reagent Blank – digestion solution only (no filter strip)
  - Method Blank – blank filter strip with digestion solution

- Positive Control Samples (Spikes), one each:
  - RBS – spiked digestion solution only (no filter strip – ensures proper spike recovery without the filter matrix)
  - LCS – spiked blank filter strip with digestion solution (evaluates proper spike recovery with blank filter matrix)
  - LCSD – (optional) duplicate spiked blank filter strip with digestion solution (evaluates precision of proper spike recovery with blank filter matrix)

- Matrix QC Samples, one each:
  - Duplicate Sample Strip – An additional strip cut from a collected field sample (evaluates precision of the sample result and digestion process)
  - Matrix Spike – An additional strip cut from a collected field sample which is spiked at the same concentration as the LCS (provides information on matrix effects on spike recovery)

- Matrix Spike Duplicate – An additional strip cut from a collected field sample which is spiked at the same concentration as the LCS (provides precision information on matrix effects on spike recovery)

4.4.10.5.2 Digestion Procedure. Prior to digestion, filter samples must be examined for damage to the filter or other defects (presence of insects, large visible particulates, etc.) which may affect sample integrity or analysis results. Following inspection, the requisite number of filter strips is to be cut from each filter to complete the digestion batch as listed above in Section 4.4.10.5.1.

Sampled 8 inch × 10 inch QFF media have an exposed filter area of 7 inch × 9 inch, leaving a ½-inch border of unsampled area around the entire filter. Strips for digestion should be cut perpendicular to the fold line for filters folded lengthwise as shown in Figure 4.4-1 and must not include the unsampled ½ inch × 8 inch border section at each end (left and right in Figure 4.4-1). This results in a 1 inch × 7 inch exposed section of the filter for each strip, equivalent to 1/9 of the 63 in^2 exposed filter area. Other conventions for portioning filter strips are acceptable so long as they include 7 in^2 of exposed filter area and a portion of the fold.

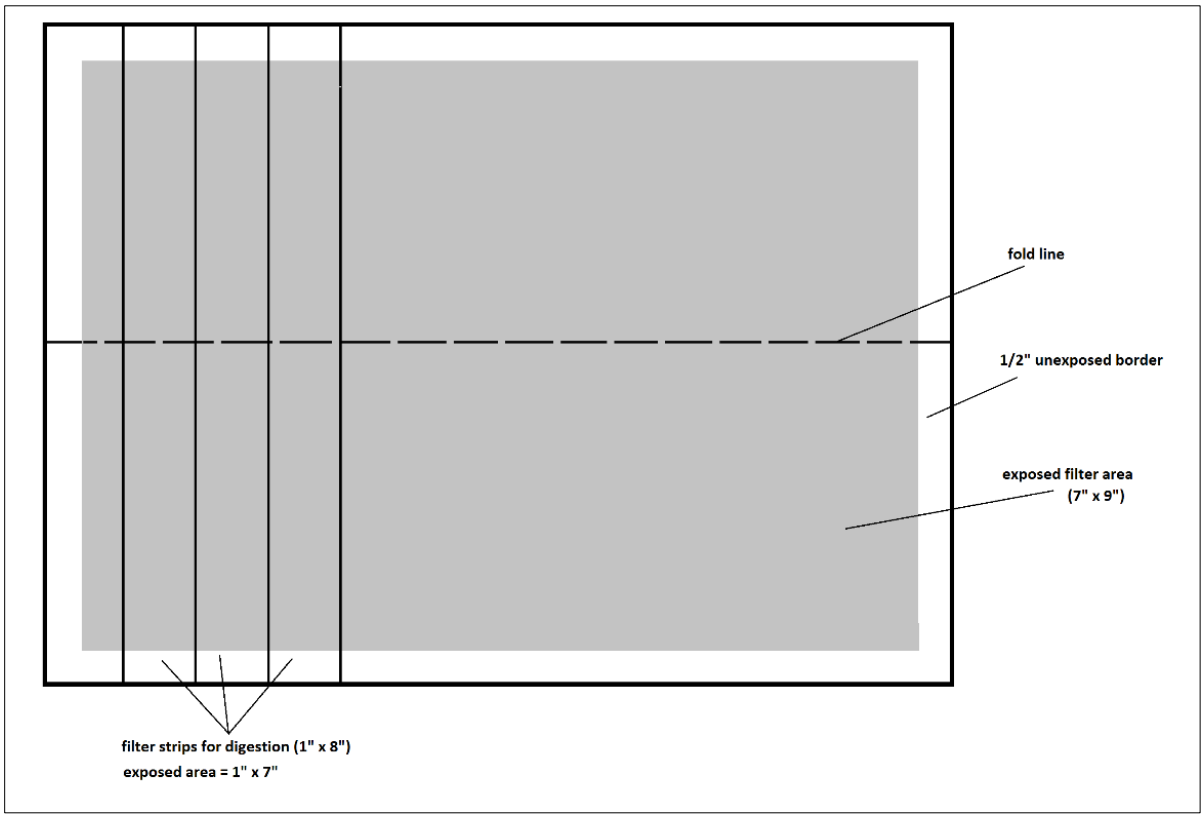

Figure 4.4-1. Portioning of QFF Strips for Digestion

Filter sample strips may be digested using one of three methods: hot block digestion, microwave digestion, or heated sonication.

4.4.10.5.2.1 Hot Block Digestion

Each filter strip must be accordion folded or coiled and placed into separate digestion vessels. Otherwise follow procedures as given in Section 4.4.9.5.2.1. Note that HF acid is not recommended for digestion of QFFs.

4.4.10.5.2.2 High Volume QFF Microwave Digestion

Each filter strip must be accordion folded or coiled and placed into separate digestion vessels. Otherwise follow procedures as given in Section 4.4.9.5.2.2. Note that HF acid is not recommended for digestion of QFFs.

4.4.10.5.2.3 High Volume QFF Acid Sonication

Each filter strip must be accordion folded or coiled and placed into separate digestion vessels. Otherwise follow procedures as given in Section 4.4.9.5.2.3. Note that HF acid is not recommended for digestion of QFFs.

4.4.11 PM_{10} Metals Analysis by ICP/MS – EPA IO-3.5

4.4.11.1 ICP/MS Instrumentation. In order to achieve the necessary sensitivity, PM_{10} metals for NATTS Program work must be analyzed via ICP/MS. Analysis via ICP-atomic emission spectroscopy (ICP-AES), graphite furnace atomic absorption (GFAA), or flame atomic absorption (FAA) is insufficiently sensitive and not permitted. ICP/MS instruments may be equipped with either a quadrupole MS or a TOF MS. For either system of MS, the general operation of the ICP is common and subject to the same interferences. The chosen instrument must have the capability to minimally scan for masses ranging from 7 to 238 amu.

4.4.11.2 ICP/MS Interferences. ICP/MS instruments are susceptible to interferences which can result in bias or saturation effects which overload the detector and require an extended period to bring detector response back into the acceptable sensitivity range. Such interferences are explained in more detail below.

- Isobaric interferences are caused by isotopes of different elements which have the same mass number as a target element. This results in a high bias for the target element, but such biases may be corrected with standard equations in ICP/MS software.
- Polyatomic, or molecular interferences are caused by combination of ions to form molecular ions which have the same mass as a target element. These interferences can result in high or low bias depending on the target element. Use of a collision reaction cell to remove polyatomic interferences upstream of the MS detector can greatly reduce or completely eliminate the effect of the interference.
- Transport interferences are a result of matrix effects which alters aerosol formation and results in changes to solution nebulization at the plasma. These interferences are typically not an issue with air filter analysis as the concentration of dissolved solids in digestates is fairly consistent from sample to sample.

- Matrix interferences are due to a chemical component in the solution which causes suppression or enhancement of the measured signal. This interference can be addressed by utilization of an internal standard or by diluting the sample digestate to minimize the impact of the interference.
- Memory, or carryover, interferences can occur when solutions of very high concentrations are analyzed. The high concentration may be difficult to effectively rinse from the ICP/MS sample introduction pathway resulting in contamination of subsequent solutions or in the electron multiplier becoming saturated resulting in a "burn in" where response factors of the ICP/MS are affected requiring substantial time for sensitivity to return. Extensive rinsing times and/or recalibration may be necessary to resolve such interferences.

4.4.11.3 Preparation of Calibration Standards for ICP/MS Analysis. Due to the instrument sensitivity effects of dissolved solids, the matrix of standard solutions must exactly match that of the final analyzed digestates. For example, if the final concentrations of acids in the analyzed digestates are 2% (v/v) nitric acid, 0.5% (v/v) hydrochloric acid, and 0.1% (v/v) hydrofluoric acid when samples are brought to volume, the acid concentrations in standard solutions must also be 2%, 0.5%, and 0.1%, respectively.

Aliquots of the stock standard solutions must be delivered with a Class A pipette or calibrated mechanical pipettor. All standard solutions must be brought to final volume in a Class A volumetric flask or equivalent Class A labware.

Stock single or multi-element solutions may be purchased commercially at certified concentrations in dilute nitric acid (typically 3% v/v) which are conveniently diluted to working concentration levels. Alternatively, stock solutions may be prepared gravimetrically by weighing appropriate amounts of high purity element solids and dissolving them into dilute nitric acid.

4.4.11.3.1 Primary Calibration Standards. Multi-element calibration standard solutions are prepared by diluting primary certified stock standard solutions in dilute nitric acid (typically 2% v/v). Calibration standard levels must cover a minimum of three non-zero concentrations spanning the desired concentration range (typically 0.1 to 250 µg/L depending on the element), however five levels are strongly recommended. These standard solutions are analyzed to generate the ICAL.

4.4.11.3.2 Secondary Source Calibration Verification Standard. A SSCV standard solution, also referred to as the QC sample, must be prepared by dilution of the secondary source stock standard solution with nitric acid (typically 2% v/v) to minimally a single concentration approximately at the mid-range of the curve. Preparation of the SSCV at three different concentrations covering approximately the lower third, mid-range, and upper third of the calibration range is a best practice and is recommended. This secondary source standard must be purchased from a different supplier. The SSCV stock may only be a different lot from the same supplier if unavailable from another supplier.

4.4.11.4 Internal Standards. ICP/MS analysis must include the evaluation of ISs to monitor ion response of analyzed solutions and to correct for instrumental drift and matrix interferences. A minimum of three IS elements must be co-analyzed with each solution. Suggested IS elements include Bi, Ge, In, ^{6}Li, Sc, Tb, ^{69}Ga, Rh, and Y.

As relative responses of the target elements and IS elements are used to determine the final concentration of the elements in solution, the concentration of the IS must be the same for each analyzed solution. To achieve such, a known volume of the IS at a known concentration may be added to a known volume of each solution to be analyzed, or the IS may be added to each analyzed solution via a mixing coil on the ICP/MS sample introduction system. Further, IS concentrations should approximate those in the analyzed samples. A concentration of no more than 200 µg/L is recommended.

As with the calibration stocks, acids, and reagent water, the IS stock solution must be from a high purity source so as to minimize background levels of target elements.

IS responses must be monitored throughout the analysis and must be within 60 to 125% of the response of the initial calibration blank (ICB). For samples or solutions which show responses outside of this range, the instrument should be investigated to be sure the response change is not due to instrument drift. Instrument drift causing failures in IS response require retuning of the instrument and recalibration prior to continuing sample analysis.

4.4.11.5 Tuning Solutions. A tuning solution must contain elements covering the mass range of interest so that the ICP/MS may be tuned and mass calibration and resolution checks may be performed. A typical tuning stock solution contains isotopes of Li, Mg, Y, Ce, Tl, and Co at approximately 10 mg/L and is diluted so that final concentrations are approximately 100 µg/L or less for each element.

4.4.11.6 ICP/MS Warm Up, MS Tuning, and Setup. The ICP/MS must be warmed up for a minimum of 30 minutes, or a duration prescribed by the manufacturer, prior to use. The tuning solution must be analyzed to perform mass calibration and resolution checks, which may be performed during the warm up period. The MS must be optimized to provide a minimum resolution of approximately 0.75 amu at 5% peak height and mass calibration within 0.1 amu of unit mass. At a minimum five aliquots of the tuning solution must be analyzed and absolute signal relative standard deviation for each analyte of $\leq$ 5% must be achieved. Manufacturer tuning recommendations may also be followed.

Standard, blank, and sample solutions should be aspirated for a minimum of 30 seconds to equilibrate the ICP/MS response prior to acquiring data. Accelerated sample introduction systems may lessen this equilibration time. The ICP/MS must be set up such that three replicate integrations are performed for each analyzed solution. Each analysis result must be the average of these replicate integrations.

A rinse blank of 2% nitric acid in deionized water should be used to flush the system between analyzed solutions. The rinse blank solution should be aspirated for a sufficient time to ensure complete return to baseline before the next sample, standard, or blank introduction. Depending

on the sample introduction system, this may take approximately 60 seconds. Sample introduction systems that increase the rinse blank speed are available to decrease rinse times.

4.4.11.7 ICP/MS Calibration and Analytical Sequence Batch. On each day that analysis is performed, the instrument must be calibrated and the analysis batch QC samples listed in the following subsections must be analyzed. Calibration acceptance criteria are given in the following sections and are summarized in Section 4.4.13.

An example analysis sequence is given in Table 4.4-2.

Table 4.4-2. Example ICP/MS Analysis Sequence

Sequence Number	Solution Analyzed		Sequence Number	Solution Analyzed
1	Tuning solution		26	field sample 6
2	ICB		27	field sample 7
3	ICAL 1(lowest concentration)		28	field sample 8
4	ICAL 2		29	field sample 9
5	ICAL 3(highest concentration)		30	field sample 7
6	ICV		31	field sample 8
7	ICB		32	field sample 9
8	ICS B		33	field sample 10
9	ICS A		34	field sample 11
10	CCV		35	field sample 12
11	CCB		36	field sample 13
12	RB		37	CCV
13	MB		38	CCB
14	LCS		39	field sample 14
15	LCSD		40	field sample 15
16	field sample 1		41	field sample 16
17	duplicate (field sample 1)		42	field sample 17
18	matrix spike (field sample 1)		43	field sample 18
19	matrix spike duplicate (field sample 1)		44	field sample 19
20	field sample 2		45	replicate analysis (field sample 16)
21	field sample 3		46	1:5 serial dilution (field sample 19)
22	CCV		47	ICS B
23	CCB		48	ICS A
24	field sample 4		49	CCV
25	field sample 5		50	CCB

4.4.11.7.1 Initial Calibration. Once the mass calibration and tuning have met the criteria listed in Section 4.4.11.6, the response of the instrument must be calibrated for the elements of interest. Analyze the initial calibration blank (ICB, an undigested reagent blank) followed by the calibration standard solutions. The calibration curve must include the ICB as the zero concentration standard. Linear regression must be performed on the calibration solution responses and must show appropriate linearity and the curve fit must have a correlation coefficient (r) of 0.995 or greater. Replicate analyses of the calibration standards must show %RSD $\leq$ 10%.

4.4.11.7.2 Initial Calibration Verification. Once the calibration curve is established, the SSCV (or QC sample) must be analyzed as the initial calibration verification (ICV) and must recover within ± 10% of the nominal value.

4.4.11.7.3 Initial Calibration Blank. The ICB is again analyzed following the ICV; all element responses must be less than the laboratory's established MDL_{sp} for MDLs determined via Section 4.1.3.1 or the portion of the MDL represented by $s \cdot K$ for MDLs determined via Section 4.1.3.2. If the ICB does not meet this criterion, the analysis sequence must be stopped and the source of the contamination found before analysis may continue.

4.4.11.7.4 Interference Check Standard. Once the instrument has been calibrated, the calibration verified by analysis of the ICV, and the system shown to be free of contaminants by analysis of the ICB, the instrument must be shown to be free of interferences by analysis of an interference check standard (ICS). The ICS must be analyzed immediately following the ICB, every 8 hours of continuous operation, and at the conclusion of the analysis sequence just prior to the final CCV.

Analysis of the ICS allows for the explicit demonstration that known isobaric and/or polyatomic interferences do not impact concentration results. Two types of ICS should be analyzed. A Type A ICS contains elements known to form interferences, and a Type B ICS consists of a standard solution of target elements subject to interferences from elements in ICS Type A. ICS Type A solutions should contain high levels of elements such as Al, Ca, Cl, Fe, Mg, Mo, P, K, Na, S, and Ti at 20 to 20,000 mg/L which are known interferences to target elements such as As, Cd, Cr, Co, Cu, Mn, Ni, and Se. These target elements should be present in ICS Type B solutions at concentrations of approximately 10 to 20 mg/L, or lower concentrations, as appropriate, anticipated to interfere with the analysis.

Analysis of ICS Type A must demonstrate that concentrations of all target analytes are less than 3x MDL_{sp} (for MDLs determined by Section 4.1.3.1) or three-fold the portion of the MDL represented by $s \cdot K$ for MDLs determined via Section 4.1.3.2. Note that ICS Type A solutions typically contain target analytes at quantifiable concentrations. ICS certificates of analysis should be examined to determine whether observed concentrations above this criterion are due to contaminant levels in the ICS Type A solution. Background subtraction of these levels may be necessary if observed concentrations exceed the acceptance criterion. The ICS Type B solution must show recovery of target elements of 80 to 120%. Concentrations of target elements in samples which exceed the concentrations in ICS Type B solutions should be diluted and reanalyzed.

ICP/MS equipped with reaction collision cells are less susceptible to isobaric and polyatomic interferences than those without and may demonstrate little to no measureable interferences when analyzing Type A ICS solutions. However, to ensure the collision reaction cell is operating properly, the ICS Type A and Type B solutions must be analyzed minimally once each day of analysis to ensure proper operation of the cell.

4.4.11.7.5 Continuing Calibration Verification. At a minimum, a CCV must be prepared at a single concentration at approximately the mid-range of the calibration curve, must

be diluted from the primary stock or secondary source stock solution, and must be analyzed following the ICS, prior to the analysis of samples, after the analysis of every 10 digestates, and at the end of the analytical sequence. CCV recovery must be 90 to 110% for each target element. As a best practice, two or more concentrations of CCV may be prepared and analyzed so as to better cover instrument performance across the range of the calibration curve.

4.4.11.7.6 Continuing Calibration Blank. The CCB is from the same solution as the ICB and must be analyzed after each CCV to ensure the instrument background remains acceptably low. A CCB is not required after the CCV concluding the analysis sequence. CCB analysis must show that the absolute value of the instrument concentration response for each target element is less than the laboratory's established MDL_{sp} for MDLs determined via Section 4.1.3.1 or the portion of the MDL represented by $s \cdot K$ for MDLs determined via Section 4.1.3.2. If the CCB does not meet this criterion, the analysis sequence must be stopped and the source of the contamination found before analysis may continue. Samples analyzed since the last acceptable CCB require reanalysis.

4.4.11.7.7 Laboratory Digestion Batch Quality Control Samples. Laboratory digestion batch QC samples for low volume Teflon® and high volume QFF media described in Sections 4.4.9.5 and 4.4.10.5, respectively, are analyzed with each analysis batch. Laboratory QC samples (consisting of RBs, MBs, RBSs, and LCSs) are analyzed after the first CCV and CCB pair and should be analyzed prior to the analysis of field samples in the same digestion batch. Duplicate digested samples, matrix spikes, and matrix spike duplicates similarly should be analyzed immediately following their parent field sample. In order to minimize reanalysis if more than one digestion batch is included in an analysis batch, each digestion batch should be analyzed altogether and separated by a CCV and CCB prior to analysis of the next digestion batch.

4.4.11.7.8 Serial Dilution. A sample must be chosen for each analysis batch for serial dilution. A sample digestate should be diluted five-fold and fortified with IS (so that the concentration of the IS is the same as in the parent sample). Element concentrations for elements ≥ 5x MDL in the serially diluted sample must recover within 90 to 110% of the undiluted sample.

4.4.11.7.9 Replicate Analysis. A replicate of digestate from a field-collected sample must be analyzed at the minimum rate of one for every 20 field-collected samples in the analysis batch. Precision of the replicate analysis must be ≤ 10% RPD for elements ≥ 5x MDL.

4.4.11.8 ICP/MS Data Review and Concentration Calculations. The concentration for each field-collected sample must be reported in ng/m^3 in local conditions. Results may additionally be reported by correction to standard atmospheric conditions of 25°C and 760 mm Hg. Conversion of collected volume in local conditions to standard conditions is performed as follows:

$$Q_s = \frac{P_a \cdot Q_a \cdot T_s}{P_s}$$

where:

Q_s = flow at standard conditions (760 mmHg and 25°C)
P_s = standard barometric pressure = 760 mmHg
T_s = standard temperature in K = 298.15K
Q_a = flow at ambient conditions
P_a = ambient barometric pressure in mmHg
T_a = ambient temperature in K

Results must not be corrected for calibration blank or MB levels. Concentrations exceeding acceptance criteria for these blanks must prompt investigation as to the source of contamination.

Concentration results which exceed the instrument calibration range must be diluted and analyzed within the calibration range. The diluted result must be reported and the associated MDL adjusted accordingly by the dilution factor. For example, if the sample is diluted by a factor of two to analyze nickel within the calibration curve, the MDL should be increased by a factor of two when reporting to AQS.

Negative concentration results which exceed the absolute value of the laboratory's established MDL_{sp} for MDLs determined via Section 4.1.3.1, or the portion of the MDL represented by $s \cdot K$ for MDLs determined via Section 4.1.3.2. MDL_{sp} for field-collected samples indicate the likely existence of contamination problems in the reagents, standards, or labware used to prepare the calibration curve. Negative concentrations should not be qualified as "9" when entered in AQS as this qualifier indicates that negative concentrations were replaced with zero. Overly negative concentrations are further discussed in Section 6.6.1.

4.4.11.8.1 Concentration Calculations for Low Volume Sampling. To calculate the airborne concentration of each element measured on the Teflon® filter, the ICP/MS measured concentration in µg/mL is multiplied by the sample digestate final volume in mL and by the dilution factor (if dilution of the digestate was performed), and is divided by the sampled air volume in m^3, as follows:

$$C_{air} = \frac{C_{ICP/MS} \cdot V_{dig} \cdot DF}{1000 \cdot V_{air}}$$

where:

C_{air} = Concentration of the element in air at local conditions (ng/m^3)
$C_{ICP/MS}$ = Concentration measured in the sample digestate (µg/mL)
V_{dig} = Volume of digestate (mL)
DF = Dilution factor
V_{air} = Volume of air sampled (m^3)

4.4.11.8.2 Reporting of Concentrations for High Volume Sampling. To calculate the airborne concentration of each element measured on the QFF, the ICP/MS measured concentration in µg/mL is multiplied by the final digestate volume in mL, by the fraction of the

filter digested for analysis, and by the dilution factor (if dilution of the digestate was performed), then is divided by the sampled air volume in m^3, as follows:

$$C_{air} = \frac{C_{ICP/MS} \cdot V_{dig} \cdot DF \cdot F_f}{1000 \cdot V_{air}}$$

where:

C_{air} =	Concentration of the element in air at local conditions (ng/m^3)
$C_{ICP/MS}$ =	Concentration measured in the sample digestate (µg/mL)
V_{dig} =	Volume of digestate (mL)
DF =	Dilution factor
F_f =	Fraction of exposed filter digested [a]
V_{air} =	Volume of air sampled (m^3)

[a] For a 1 inch × 8 inch strip portioned as described in Section 4.4.11.5.2, this is equivalent to 1/9 by dividing the exposed area of the portioned strip by the area of the exposed filter.
(1 inch × 7 inch = 7 $in.^2$)/(7 inch × 9 inch = 63 $in.^2$) = 1/9

4.4.12 Summary of Method Quality Control Requirements. QC requirements are summarized in Table 4.4-3.

Table 4.4-3. Method Criteria Parameters for NATTS Metals Analysis

Parameter	Description and Details	Required Frequency	Acceptance Criteria
ICP/MS Tuning	ICP/MS mass calibration and resolution checks	Analysis of a minimum of five aliquots of the tuning solution each day of analysis prior to ICAL	Absolute signal of five replicates RSD ≤ 5% Mass calibration within 0.1 amu of unit mass Resolution check within 0.75 amu at 5% peak height Alternatively, must meet manufacturer tuning criteria
Internal Standards Addition	Elements other than target elements used to monitor instrument performance and correct for matrix effects	Added to each analyzed solution	Recovery within 60-125% of the response of the initial calibration blank
Rinse Blank	2% (v/v) HNO_3 aspirated to eliminate memory effects between solutions	Following each analyzed solution	Duration of aspiration sufficient to eliminate element carryover as evidenced by successful CCVs and CCBs
Initial Calibration (ICAL)	Minimum of three levels covering the desired concentration range plus the calibration blank	Each day analysis is performed	Correlation coefficient (r) ≥ 0.995
Initial Calibration Verification (ICV)	Second source calibration verification (SSCV) or QC standard analyzed to verify the ICAL	Each day of analysis immediately following the ICAL	Recovery within 90-110% of nominal for all target elements
Initial Calibration Blank (ICB)	Calibration blank analyzed to ensure instrument is sufficiently clean to continue analysis	Each day of analysis immediately following the ICV	All target elements < MDL_{sp} (refer to Section 4.1.3.1) or $s \cdot K$ (refer to Section 4.1.3.2)
Interference Check Standard (ICS) A	Solution containing known interferences analyzed to demonstrate that the effect of such interferences is sufficiently low	Following the ICB, after every 8 hours of analysis, and just prior to the concluding CCV Once daily for ICP-MS equipped with collision reaction cell	All target elements < MDL_{sp} (refer to Section 4.1.3.1) or $s \cdot K$ (refer to Section 4.1.3.2) – may be subtracted for ICS A certificate of analysis
Interference Check Standard (ICS) B	Solution containing target elements at high concentrations to demonstrate acceptable recovery	Following the ICB, after every 8 hours of analysis, and immediately preceding ICS A Once daily for ICP-MS equipped with collision reaction cell	Recovery within 80-120% of nominal for all target elements
Continuing Calibration Verification (CCV)	Calibration or second source standard analyzed to verify instrument remains in calibration	Immediately following the initial ICS, after every 10 samples and at the conclusion of the analysis sequence	Recovery within 90-110% of nominal for all target elements

Table 4.4-3. Method Criteria Parameters for NATTS Metals Analysis (Continued)

Parameter	Description and Details	Required Frequency	Acceptance Criteria
Continuing Calibration Blank (CCB)	Analysis of the calibration blank solution to ensure instrument is sufficiently clean to continue analysis	After each CCV except at the conclusion of the analysis sequence	All target elements < MDL_{sp} (refer to Section 4.1.3.1) or $s \cdot K$ (refer to Section 4.1.3.2)
Reagent Blank (RB)	Aliquot of digestion solution taken through the digestion process	One per digestion batch of 20 or fewer field-collected samples	All target elements < MDL_{sp} (refer to Section 4.1.3.1) or $s \cdot K$ (refer to Section 4.1.3.2)
Method Blank (MB)	Blank filter or filter strip taken through the digestion process	One per digestion batch of 20 or fewer field-collected samples	All target elements < MDL
Reagent Blank Spike (RBS)	Aliquot of digestion solution spiked with known amount of target elements and taken through the digestion process	One per digestion batch of 20 or fewer field-collected samples	Recovery within 80-120% of nominal for all target elements
Laboratory Control Sample (LCS)	Filter or filter strip spiked with a known amount of each target element and taken through the digestion process	One per digestion batch of 20 or fewer field-collected samples	Recovery within 80-120% of nominal for all target elements, Sb recovery 75-125%.
Laboratory Control Sample Duplicate (LCSD)	Duplicate filter or filter strip spiked with a known amount of each target element and taken through the digestion process	(Optional) One per digestion batch of 20 or fewer field-collected samples	Recovery within 80-120% of nominal for all target elements, Sb recovery 75-125%, precision ≤ 20% RPD of LCS
Duplicate Sample Strip	Additional strip from a field-collected filter taken through the digestion process	*QFF only* One per digestion batch of 20 or fewer field-collected samples	Precision ≤ 20% RPD for elements ≥ 5x MDL
Matrix Spike	Strip from a field-collected filter spiked with a known amount of each target element and taken through the digestion process	*QFF only* Once per analysis batch of 20 or fewer samples	Recovery within 80-120% of the nominal spiked amount for all target elements, Sb recovery 75-125%.
Matrix Spike Duplicate	Additional strip from the same field-collected filter as the MS, and spiked with the same amount of each target element as the MS, and taken through the digestion process	*QFF only* One per digestion batch of 20 or fewer field-collected samples	Recovery within 80-120% of the nominal spiked amount for all target elements, Sb recovery 75-125%, precision ≤ 20% RPD of MS
Collocated Sample	Sample collected from a separate sampling unit concurrently with the primary sample	10% of primary samples for sites conducting collocated sampling (as required by workplan)	Precision ≤ 20% RPD of primary sample for elements ≥ 5x MDL
Serial Dilution	Five-fold dilution of a sample digestate to assess matrix effects	One per digestion batch of 20 or fewer field-collected samples	Recovery within 90-110% of undiluted sample for elements ≥ 25x MDL
Replicate Analysis	Second aliquot of a sample digestate chosen for replicate analysis	One per digestion batch of 20 or fewer field-collected samples	Precision ≤ 20% RPD for elements ≥ 5x MDL

4.4.13 References

1. Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma/Mass Spectrometry (ICP/MS); EPA Compendium Method IO-3.5; *Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air*; EPA/625/R-96/010a; U.S. Environmental Protection Agency: Center for Environmental Research Information. Office of Research and Development. Cincinnati, OH. June 1999. Available at (accessed October 19, 2016): https://www3.epa.gov/ttnamti1/files/ambient/inorganic/mthd-3-5.pdf
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4.5 Collection and Analysis of PAHs via EPA Compendium Method TO-13A

Each agency must codify in an appropriate quality systems document, such as an SOP, or equivalent, its procedures for performing PAHs sampling, media extraction, and extract analysis. Various requirements and best practices for such are given in this section. Note that regardless of the specific procedures adopted, method performance specifications as given in Section 4.5.6 must be met.

4.5.1 Summary of Method. PAHs, which are semivolatile organic compounds (SVOCs), are collected per the guidance given in EPA Method TO-13A [1] and ASTM D6209.[2] These two methods are similar and share collection media specifications: utilizing a quartz fiber particulate filter and glass thimble containing PUF and styrene-divinylbenzene polymer resin sorbent (XAD-2 or equivalent) to collect PAHs from ambient air.

Approximately 200 to 350 m^3 of ambient air is drawn through a quartz fiber particulate filter and cartridge containing a "sandwich" of PUF-resin-PUF over 24 hours. The QFF and contents of the cartridge are extracted by way of accelerated solvent extraction (ASE) [3] or in a Soxhlet apparatus, and the extract is analyzed by GC/MS. Concentrations of PAHs in ambient air are generally low (0.02 to 160 ng/m^3), thus a large volume of air must be collected to ensure sufficient mass is present for quantification with a typical quadrupole MS in SIM mode.

The more volatile PAHs, such as naphthalene, are subject to potential loss from the cartridges due to, for example, volatilization and decomposition from exposure to light. [4, 5] Thus, PAH cartridges should be collected from the sampling unit, protected from light, and brought to $\leq 4°C$ as soon as possible after the end of the sampling period. Shipment and storage at refrigerated temperatures will further minimize evaporative losses of the more volatile PAHs. PAHs with higher volatility may also be lost from the sorbent cartridge during sampling due to migration out of the cartridge outlet (breakthrough) or from volatilization from the QFF, especially during warm weather. [6, 7]

The PAHs including, but not limited to, those in Table 4.5-1 may be determined by this method.

4.5.2 Sample Collection Equipment. A high volume PS-1 style sampler, or equivalent, which is able to maintain a minimum flow rate of 140 L/min over a 24-hour sampling period is required. Such sampling units are commercially available with various conveniences. The most basic units are equipped with an event timer and an elapsed time counter to control and indicate duration of sample collection. Flow rate is controlled by the fan motor speed, ball valve, or combination. A manometer (such as a magnehelic) is attached to the ports on a venturi located between the sampling inlet and the fan motor to indicate the pressure differential which correlates to the flow rate. Computer control is available on more expensive systems; such units have an automatic start/stop timer, indicate elapsed sampling time, monitor and record flow rates over the course of the collection event, indicate start and stop times, and monitor the pressure differential and adjust the blower speed to ensure a user defined flow setpoint is maintained.

Each high volume sampler should have an extension tube for the motor exhaust to ensure that the sampled atmosphere is not resampled. If so equipped, the exhaust tube must terminate in the

predominant downwind direction minimally 3 meters away from the unit. Care should be taken to ensure that the exhaust does not interfere with other sampling units at the site. The sampling unit inlet must minimally be 2 meters from all other sampling inlets. Sampler siting requirements are listed in Section 2.4.

Table 4.5-1. PAHs and Associated Chemical Abstract Numbers (CAS)

Target Compound	CAS Number
Acenaphthene [b]	83-32-9
Acenaphthylene	208-96-8
Anthracene [b]	120-12-7
Benzo(a)anthracene	56-55-3
Benzo(a)pyrene [a b]	50-32-8
Benzo(e)pyrene	192-97-2
Dibenzo(g,h,i)perylene	191-24-2
Benzo(b)fluoranthene	205-99-2
Benzo(k)fluoranthene	207-08-9
Chrysene	218-01-9
Coronene	191-07-1
Dibenzo(a,h)anthracene	53-70-3
Fluoranthene [b]	206-44-0
Fluorene [b]	86-73-7
9-Fluorene	486-25-9
Indeno(1,2,3-cd)pyrene	193-39-5
Naphthalene [a b]	91-20-3
Perylene	198-55-0
Phenanthrene [b]	85-01-8
Pyrene [b]	129-00-0
Retene	483-65-8

[a] NATTS Tier I core analyte
[b] NATTS PT target analyte

4.5.2.1 Sampler Flow Calibration and Verification. Sampler flow must be calibrated initially and when flow verification checks indicate flows deviate by more than 10% from the flow transfer standard flow or design flow. Flow verification checks must be performed quarterly, and are recommended to be performed monthly. Flow verifications must be performed at approximately the setting utilized to collect field samples.

Flow calibration of a non-mass flow controlled sampler (those without computer control) must be performed with a traceable, calibrated flow transfer standard capable of inducing various backpressures to generate different sampling unit flow rates that bracket the target flow rate. Such may be accomplished with an electronic flow meter, a variable orifice, or a series of fixed plate orifices, or similar. The known inlet flows must then be correlated to the measured manometer readings at the flow venturi. Computer controlled units must be electronically adjusted so the flow settings correlate to the calibrated flow rate as indicated by the flow transfer standard.

4.5.2.2 Sampling Unit Maintenance. Each site must have a defined maintenance schedule for the PAHs sampling units, recommended to be monthly, but may not exceed quarterly. Included in this maintenance must be the schedule for the periodic cleaning of the sampling

heads. Sampling heads should be washed with chromatographic grade hexane, acetone, or other suitable solvent to ensure subsequent samples are not contaminated. Use of such solvents should be performed with proper ventilation (e.g. fume hood) and with proper personal protective equipment (PPE – such as solvent impermeable gloves, lab coat, and safety glasses). Other maintenance items should include: inspection of sampling unit electrical connections, check of timers for proper operation, replacement of motors and motor brushes, removal of debris from underneath the gable and inside the upper portion of the sampling unit, and inspection of sealing gaskets.

4.5.3 Sampling Media and Their Preparation. Regardless of the source of materials or the specific cleaning procedures each agency adopts, the QFF and PUF/XAD-2/PUF present in cartridges must meet the batch blank acceptance criteria of < 10 ng each for all target compounds. A batch blank is a complete cartridge (including a QFF) selected from among those purchased in a single lot or from among each batch of cartridges prepared with a specific batch of cleaned media. Note that media components may be analyzed separately, but must meet the cleanliness criterion.

Particulate filters for sample collection are quartz fiber, 102 to 104 mm diameter with 2-µm pore size. All filters must be inspected on a light table or similar for pinholes, discolorations, tears, or other defects such as thin spots; air samples must not be collected with those found to be unsuitable. After inspection, filters should be baked (in a muffle furnace) at 400°C for a minimum of 4 hours to remove potential impurities and interferences. Once cooled, the filters should be stored in a sealed container to ensure they do not become contaminated prior to sample collection.

PUF plugs are available commercially, or they may be prepared by cutting plugs of the proper diameter (2 3/8 inch) from PUF sheets of 1.5-inch thickness. PUF plugs may be purchased raw and cleaned by the laboratory prior to use, or may be purchased precleaned. Some precleaned PUF plugs do not meet cleanliness criteria for target analytes or may contain interferences which require subsequent cleaning procedures prior to use for sample collection. Precleaned PUF plugs are typically shipped with a certificate of analysis listing the contaminant levels for common PAHs. Following sample extraction, used PUF plugs may be cleaned for reuse, if so desired.

Styrene-divinylbenzene polymer resin, such as XAD-2, is commercially available and may be purchased with or without precleaning. As with precleaned PUF, some precleaned resins do not meet cleanliness criteria for target analytes or may contain interferences which require subsequent cleaning procedures before use for sample collection. Precleaned resin sorbent is generally shipped with a certificate of analysis listing the contaminant levels for common PAHs. Following sample extraction, used resin may be cleaned for reuse. The resin physically degrades and disintegrates over time, requiring periodic replacement.

PUF and/or resin sorbents should be cleaned before reuse with a specialized solvent extraction program that is slightly different than the method by which the QFF, PUF, and resin from a sample cartridge are extracted. A more aggressive solvent or combination of solvents such as methylene chloride (not suitable for PUF cleaning), toluene, hexane, and/or acetone should be

employed to remove target analytes and interferences from the PUF and resin media for cleaning.

All clean media should be stored in sealed containers protected from light (aluminum foil, amber glass, etc.).

4.5.3.1 Glassware Cleaning. Glass thimbles, extraction glassware, and volumetric glassware for preparing standard solutions must be thoroughly cleaned and contaminant-free prior to use such that blank criteria are met as given in Section 4.5.6. Aggressive washing with hot water and laboratory grade soap, tap water rinsing, deionized water rinsing, acid or base rinsing, and solvent (methylene chloride) rinsing may be necessary to ensure that contaminants and interferences are removed from labware prior to use. Non-volumetric glassware may be baked at 400°C for 4 hours. Volumetric glassware must not be heated above 80 to 90°C unless otherwise indicated by the manufacturer as such heating voids the volumetric certification.[8] Following the final solvent rinse, clean labware should be capped or covered (as appropriate) with solvent rinsed foil to prevent contamination with dust, etc.

4.5.3.2 Cartridge Preparation. If cartridges are assembled in house, they must be assembled in batches, and the lots of media contained in the cartridges must be traceable so as to maintain the ability to track potential contamination. One assembled cartridge from each batch of 20 or fewer assembled cartridges must be extracted as a batch blank. The batch blank ensures the cleaned media and preparation results in acceptably low background levels of target PAHs.

The following procedure should be followed to prepare cartridges. Tools contacting sampling media are solvent rinsed and technicians must wear gloves during cartridge preparation. One 1.5-inch thick PUF plug is placed into the inlet of the cartridge and pushed down to contact the support screen. Note that glass thimble cartridges equipped with a glass frit support are not suitable for NATTS sample collection. The glass frit creates an excessive flow restriction resulting in pre-mature wear and failure of motors and brushes. A 15-gram aliquot of clean resin is then added to the cartridge on top of the PUF plug and distributed evenly. The second 1.5-inch thick PUF plug is then placed on top of the resin layer to retain the resin layer in place.

For storage, cartridges should be wrapped in solvent rinsed foil, sealed in a resealable plastic bag or other container, and kept at ≤ 4°C.

4.5.3.3 Field Surrogate Addition. Prior to dispatching sample cartridges to the field, field surrogate compounds must be added to the sorbent media. The recovery of field surrogate compounds is evaluated to assess the retention of PAHs during air sampling as well as the performance of the sample media handling, extraction, and analysis procedures.

Field surrogates should be added by spiking 1 µg (e.g., 100 µL of a 10 µg/mL solution in methylene chloride, toluene, hexane, or other suitable solvent) of, for example, fluoranthene-d_{10} and benzo(a)pyrene-d_{12} directly into the PUF and resin sorbent. Field surrogates are added no sooner than two weeks prior to the scheduled sample collection date.

4.5.4 PAH Sampling. Sample media must be installed into the sampling unit as close to the sampling date as possible to minimize positive bias due to passive sampling of the sorbent media. At the time of installation, sampling units without computerized flow control must be allowed to warm up for minimally five ten minutes (ten minutes are recommended) prior to recording the initial flow rate, i.e., the manometer reading. Computer-controlled sampling instruments do not require this warm-up period to record the initial flow. The ambient barometric pressure and temperature must be measured with calibrated instruments and recorded.

The QFF and cartridge are loaded into a sampling head. At the head's outlet is a cam-lock connection which connects the head to the PS-1 sampling unit, and at the head inlet is a threaded ring filter holder to accept the QFF. The head may be unscrewed in the middle such that the glass cartridge may be inserted inside into a cartridge body. Inert gaskets (such as silicone rubber) are placed in the top and bottom of the cartridge body inside the sampling head. A filter is placed onto the support screen of the filter holder, and an inert gasket (such as polytetrafluoroethylene [PTFE]) seals the filter to the top filter retaining ring. The filter is protected during handling by a cover secured to the filter holder with three swing bolts.

4.5.4.1a Sampling Schedule and Duration. PAHs sample collection must be performed on a 1-in-6 days schedule for 24 ± 1 hours beginning at midnight and concluding on midnight of the following day, local time unadjusted for daylight savings time, per the national sampling calendar. For missed or invalidated samples, a make-up sample should be scheduled and collected per Section 2.1.2.1. Clock timers controlling sampling unit operation must be adjusted so that digital timers are within ±5 minutes of the reference time (cellular phone, GPS, or similar accurate clock) and mechanical timers within ±15 minutes.

4.5.4.1b Retrieval, Storage, and Transport of QFFs and Cartridges. The QFF and glass cartridge must be retrieved as soon as possible after the conclusion of sampling in order to minimize the evaporative loss of the more volatile PAHs, preferably within 24 hours, but not to exceed 72 hours of the end of collection. Such is particularly important during warm weather. As with sample setup, units without computerized flow control must be allowed to warm up for minimally five minutes (ten minutes are recommended) prior to recording the manometer reading, which is recorded as the ending flow setting. Computer-controlled sampling units do not require this warm-up period. The ambient barometric pressure and temperature must be measured with calibrated instruments and recorded.

To retrieve a sample, the following procedure should be followed. It is recommended that the operator dons non-latex powder-free gloves to place the filter cover onto the filter inlet and secure the cover with the swing bolts. The operator then releases the cam-locks, disconnects the sampling head from the sampling unit, and covers the outlet end of the sampling head with foil or suitable plug. The assembled sampling head is transported to a clean indoor environment, free of obvious PAHs sources, for disassembly. If the disassembly is to occur more than 10 minutes following sample retrieval, the sampling head is stored and transported refrigerated.

For sampling head disassembly, gloves must be donned, the filter cover removed, and the filter carefully retrieved and folded into fourths with the particulate matter inward. The folded filter is then inserted into the glass thimble cartridge with the sorbent media. It is not acceptable to place

the folded filter into a secondary container such as a petri dish, as jostling of the filter inside the petri dish may result in loss of PM to the inside of the dish. Storage inside the glass cartridge minimizes disturbance of PM to ensure that PM is either on the filter or within the PUF inside the glass thimble. The glass thimble cartridge is removed from the sampling head, wrapped in solvent-rinsed foil, and placed within a protective jar or case for shipment.

The protective jar or case containing the cartridge must be stored at ≤ 4°C until shipment to the laboratory. The sample should be kept cold during shipment such that the temperature remains ≤ 4°C, and the temperature of the shipment must be determined upon receipt at the laboratory. For transport of samples which are retrieved at a site and delivered to the laboratory on the day of retrieval, it may be difficult to sufficiently cool samples to ≤ 4ºC by the time they are received at the laboratory. It is imperative that samples be placed into cold storage for transport as soon as possible after retrieval, so samples arrive at the laboratory chilled. Samples which are shipped overnight should be packed with sufficient cold packs or ice to ensure they arrive at the laboratory at ≤ 4ºC. The sample custody form must be completed and accompany the collected sample at all times until relinquished to the laboratory. COC documentation must comply with Section 3.3.1.3.7. If cartridges are broken, resin has escaped, or the sampling media otherwise compromised, the sample must be voided.

4.5.4.2 Field Blanks. Field blanks must be collected minimally monthly. A field blank is a complete blank cartridge and QFF fortified with field surrogates and assembled in a sampling head identically to a field-collected sample except that there is no sample flow. To collect a field blank, the assembled sampling head is minimally installed into the sampling unit and the filter cover removed for minimally 5 minutes. The field blank is then retrieved as a regularly collected field sample and placed into cold storage until the co-collected field sample is transported/shipped to the laboratory for analysis.

Field blanks must show that all target PAHs are ≤ 5x MDL. Results for field collected samples associated with the failing field blank and collected since the last acceptable field blank must be appropriately qualified when entered into AQS.

An exposure blank is similar to a field blank, but is not required, and may be collected via several protocols. The exposure blank includes exposing the filter and sorbent media to the ambient conditions by installation in a sampling unit, and just like a field blank, air is not drawn through the exposure blank sampling head. The exposure blank sample may be installed in the primary sampling unit on non-sample collection days or may be installed in a collocated sampling unit during collection of the primary sample.

4.5.4.3 Collocated Sampling. Collocated samples must be collected at a frequency of 10% of the primary samples for sites conducting collocated sampling (as required by the workplan). A collocated sample is a second assembled sampling head (cartridge and QFF) collected via a separate PAHs sampling unit. The collocated sampling unit inlet must be between 2 to 4 meters from the primary sampling inlet.

Collocated samples must demonstrate precision ≤ 20% RPD for instrument measured concentrations ≥ 0.5 µg/mL. Root cause analysis must be performed for instances in which

collocated samples fail this precision specification and the results of the primary and collocated samples must be qualified when entered into AQS.

4.5.5 PAH Extraction and Analysis

4.5.5.1 Reagents and Standard Materials

4.5.5.1.1 Solvents. Solvents employed for extraction and preparation of standards solutions must be high-purity chromatographic grade, and shown by analysis to be free of contaminants and interferences. Suitable solvents include dichloromethane, n-hexane, methanol, diethyl ether, and acetone.

4.5.5.1.2 Calibration Stock Materials. Calibration source material must be of known high purity and must be accompanied by a COA. Calibration materials should be neat high purity solids or sourced as certified single component or component mixtures of target compounds in solvent.

Neat solid material must be weighed with a calibrated analytical balance with the appropriate sensitivity for a minimum of three significant figures in the determined standard mass. The calibration of the balance must be verified on the day of use with certified weights bracketing the masses to be weighed. Calibration standards diluted from stock standards should be prepared by delivering stock volumes with mechanical pipettes (preferably positive displacement) or gastight syringes calibrated and the volumes dispensed into Class A volumetric glassware to which solvent is added to establish a known final dilution volume.

4.5.5.1.2.1 Secondary Source Calibration Verification Stock Material

A secondary source standard must be prepared to verify the calibration of the GC/MS on an ongoing basis. This secondary source stock standard must be purchased from a different supplier than the calibration stock. The SSCV stock may only be a different lot from the same supplier if unavailable from another supplier.

4.5.5.1.3 Internal Standards. ISs are required to correct for both short-term variability in GC/MS performance and for potential matrix effects. ISs must be added to all analyzed solutions at the same concentration. IS compounds should be chemically and chromatographically similar to the target compounds.

Deuterated analogs of target compounds are recommended as ISs. Suggested deuterated standards include: naphthalene-d_8, acenaphthene-d_{10}, perylene-d_{12}, phenanthrene-d_{10}, and chrysene-d_{12}. These ISs should be purchased as high purity single or multi-component mixtures in solvent. Note that deuterated standards also contain small amounts of the target compound which may appear as contamination if the concentration of IS added is too high.

4.5.5.1.4 Surrogate Compounds. Surrogate compounds are required to monitor and assess the retention of PAHs on the adsorbent media and the performance of the sample media handling, extraction, and analysis procedures. Two types of surrogate compounds are prescribed

for the subject method, field surrogates and extraction surrogates. As with ISs, deuterated analogs of target compounds are recommended for surrogate compounds.

4.5.5.1.4.1 Field Surrogate Compounds

Field surrogates are required and were previously described in Section 4.5.3.3. Fluoranthene-d_{10} and benzo(a)pyrene-d_{12} are the recommended field surrogate compounds. Stock standard solutions of these two surrogate compounds in solvent are commercially available and are diluted to working concentrations in suitable solvent (i.e., hexane).

4.5.5.1.4.2 Extraction Surrogate Compounds

Extraction surrogate compounds must be added to the sample media just prior to extraction and their recoveries are evaluated to assess the performance of the extraction and analysis procedures. Fluorene-d_{10} and pyrene-d_{10} are the recommended extraction surrogate compounds and 1 µg should be added to the media (e.g., 10 µL of 10 µg/mL solution). Stock standard solutions of these two surrogate compounds in solvent are commercially available and are diluted to working concentrations in suitable solvent (i.e., hexane).

4.5.5.2 Hold Times and Storage Requirements. Collected samples must be transported and stored at ≤ 4°C until extraction, and must be extracted within 14 days of collection. Extracts must be stored in amber or foil-wrapped vials at ≤ 4°C, however storage in a freezer at ≤ -10°C is preferable. Extracts must be analyzed within 40 days of extraction. Working standards and open ampules of stock standards must be stored protected from light at ≤ -10°C in Teflon sealed amber vials in a storage unit separate from sampled cartridges and sample extracts.

4.5.5.3 Extraction, Concentration, and Cleanup. Extraction of samples may be performed by Soxhlet or ASE; these techniques are described in more detail below.

4.5.5.3.1 Soxhlet Extraction. Each Soxhlet extraction batch must include 20 or fewer field-collected samples and a MB. An LCS, and LCSD are required quarterly, but recommended with each extraction batch. Prior to extraction, each field-collected sample and QC sample must be fortified with extraction surrogate standards (typically fluorene-d_{10} and pyrene-d_{10}). Extraction should be performed by combining the QFF, PUF plugs, and resin sorbent into the soxhlet extraction vessel and extracting with sufficient 90:10 hexane:diethyl ether to cover the sample media. Extraction should be performed for a minimum of 18 hours and the temperature of heating mantle should be set such that reflux occurs at a rate of at least three cycles per hour.

Extracts must be capped, protected from light, and stored refrigerated at ≤ 4°C if they are not to be concentrated immediately following extraction.

4.5.5.3.2 Accelerated Solvent Extraction. To perform ASE, a 100 mL ASE cell should be packed as follows: QFF, top PUF plug, resin, bottom PUF plug, and clean Ottawa sand to fill the cell. Each extraction batch must include 20 or fewer field-collected samples and an MB. An LCS and LCSD are required quarterly, and recommended with each batch. Prior to

extraction, each field sample and quality control sample must be fortified with extraction surrogate standards (typically fluorene-d_{10} and pyrene-d_{10}). To ensure the cell seals properly, stray resin grains should be removed from the threads with a horsehair brush or compressed air.

The following procedure should then be followed: install the cells into the extractor, install the clean extract collection bottles, verify that the solvent reservoirs are full, and start the extraction program. A recommended solvent combination for ASE is 2:1 or 3:1 hexane:acetone (v:v). [3] An example ASE program follows:

temperature:	60°C
cycles:	minimum of 3
purge:	60 seconds
static time:	5 minutes
flush:	50%

Extracts must be capped, protected from light, and stored refrigerated at ≤ 4°C if they are not to be concentrated immediately following extraction.

4.5.5.3.3 Extract Concentration and Cleanup

4.5.5.3.3.1 Extract Concentration

Refrigerated extracts are equilibrated to room temperature prior to concentration. It is recommended that extracts be dried by passage through approximately 10 g of sodium sulfate, where the eluate is collected into a concentration flask or tube. The extraction flask and sodium sulfate are then rinsed three times with extraction solvent and the rinsate collected into the concentration vessel.

Prior to use, sodium sulfate should be solvent rinsed and placed in an oven at 400°C for a minimum of 4 hours to remove impurities. Muffled sodium sulfate should be cooled and stored in a desiccator to minimize contact with humidity in ambient air.

Extracts should be concentrated by either Kuderna-Danish (K-D) or nitrogen blowdown techniques. The extracts must not be allowed to evaporate to dryness.

4.5.5.3.3.1.1 Concentration via Kuderna-Danish

To concentrate via K-D, the following procedure should be followed. Attach a Snyder column to the K-D apparatus and concentrate to approximately 5 mL on a water bath set to 30 to 40°C. Rinse the Snyder column and concentrator flask with several mLs of n-hexane and allow the solvent to drain into the concentrator tube. Concentrate to < 1 mL final volume via nitrogen blow-down or via micro-Snyder column. Bring the extract to 1.0 mL final volume via syringe, rinsing the concentration tube with n-hexane as the extract is drawn into the syringe. Following concentration to 1 mL, the extract is ready for analysis unless further cleanup is required. Extract cleanup is explained in Section 4.5.5.3.3.2.

4.5.5.3.3.1.2 Concentration via Nitrogen Blowdown

Several nitrogen blowdown evaporator concentrator instruments are commercially available. As the release of large volumes of solvent is detrimental to air quality, systems which capture the evaporated solvent are preferable.

The solvent should be concentrated to < 1 mL final volume in a water bath set to 30-40°C and the final volume of the extract should be established as 1.0 mL with a calibrated syringe. The concentration tube should be rinsed with GC-grade n-hexane as the extract is drawn into the syringe.

Following concentration to 1 mL, the extract is ready for analysis unless further cleanup is required. Extract cleanup is explained in Section 4.5.5.3.3.2.

4.5.5.3.3.2 Extract Cleanup

A cleanup step may be required in order to clarify cloudy extracts or remove interfering compounds from extracts showing significant chromatographic interferences.

To clarify cloudy extracts, they are passed through a packed column of 10 g of silica gel as detailed in EPA Compendium Method TO-13A and ASTM D6209. Ambient air matrices typically do not result in cloudy extracts and therefore likely do not require additional cleanup.

4.5.5.4 PAH Method Detection Limits. MDLs for PAHs must be determined minimally annually by following the procedures in Section 4.1. To ensure that the variability of the media and the extraction process is characterized in the MDL procedure, cartridges and QFFs must be extracted (it does not suffice to simply analyze a low-concentration solution of PAHs) and blank and spiked cartridges with QFFs must be prepared. For example, laboratories determining the MDL following Section 4.1.2.1 must prepare and extract a minimum of seven method blank cartridges and QFFs and a minimum of seven spiked cartridges and QFFs over the course of three different dates (preferably non-consecutive). The resulting extracts must be analyzed in three separate analytical batches (three different calendar dates – preferably non-consecutive). All steps performed in the preparation and analysis of field sample cartridges must be included in the MDL procedure.

Note that at very low levels approximating the MDL, the qualitative identification criteria related to qualifier ion abundance ratio and/or signal-to-noise ratio listed in Section 4.5.5.5.7 may not be strictly met when determining the MDL. As the MDL spikes are prepared in a clean matrix with standard materials, the presence of the analyte is expected.

As discussed in Section 4.1.3.1, one MDL spike sample can be added to analysis periodically. Together with the MB from each batch, once results for seven or more MDL spike samples and method blanks are available, the MDL can be calculated.

4.5.5.5 PAH Analysis via GC/MS

4.5.5.5.1 GC/MS Instrumentation. The GC should be capable of temperature programming such that the temperature may be ramped from 25°C to 290°C at a rate of 8°C/minute or faster. A 30 to 50 m by 0.25 mm fused silica capillary column coated with 0.25 µm crosslinked or bonded 5% phenyl methylsilicone film, or equivalent suitable column capable of separating the target analytes, surrogates, and ISs with appropriate resolution, should be installed in the GC. The carrier gas should be helium or hydrogen. Injector and transfer line should be capable of maintaining 275-300°C. GC injection volume should be 1.0 µL.

Electron ionization should be performed at 70 eV and the MS should be operated in SIM mode to maximize sensitivity to ions of the target compounds of interest. Alternatively, for instruments which are capable, operation in combination SIM/scan mode is preferred. Spectrometers operating in full scan mode may lack sufficient sensitivity. If full scan is performed, the MS should be capable of scanning from 35-500 amu in ≤ 1 second.

4.5.5.5.2 Tuning of the MS. The GC/MS must be tuned prior to calibration and every 12 hours of analysis thereafter via analysis of 5 to 50 ng of DFTPP.

If operated in full scan mode or SIM/scan mode, the MS tune must be optimized to achieve the ion abundances below in Table 4.5-2.

For instruments operated in SIM mode, the above ion abundance criteria do not apply. Tuning for SIM instruments is optimized to maximize the signal for DFTPP masses greater than 150 amu. The SIM MS tune must maximize the signal for masses 198, 275, 265, and 442 while maintaining unit resolution between masses 197, 198, and 199 as well as 441, 442, and 443.

Table 4.5-2. DFTPP Key Ions and 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, assigned 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

4.5.5.5.3 Calibration of the GC/MS. All solutions to be analyzed, including calibration standards, should be removed from refrigerated storage for sufficient time (typically one hour) to equilibrate to ambient temperature prior to analysis.

Calibration standard solutions must be prepared at minimally five separate concentration levels in hexane covering approximately 0.1 to 2.0 µg/mL and must contain surrogate compounds at concentrations bracketing those expected in the sample extracts.

ICAL must be established initially, when continuing calibration criteria are not met, or when an instrument change (ion source cleaning, column trim or change, etc.) may affect instrument calibration (including alteration of retention times). Calibration is recommended every six weeks.

An SB which is not fortified with IS must be analyzed just prior to calibration to ensure the instrument is sufficiently clean to continue analysis. Analysis of the SB must show all target compounds, IS, and surrogate compounds are not detected.

A known volume of each standard should be transferred to a GC analysis vial and fortified with IS just prior to analysis. Recommended quantitation and secondary ions are listed in Table 5 of method TO-13A. Each compound must be assigned to the IS compound with the nearest retention time.

Following data acquisition for the calibration standards, the relative response factor (RRF) of each surrogate and target compound in each calibration level is determined as follows:

$$\mathrm{RRF} = \frac{A_s \cdot C_{IS}}{A_{IS} \cdot C_s}$$

where:

A_s = peak area for quantitation ion of the surrogate or target compound
A_{IS} = peak area for quantitation ion of the assigned internal standard compound
C_s = concentration of the surrogate or target compound
C_{IS} = concentration of the assigned internal standard compound

The RSD of the RRFs for each surrogate and target compound must be ≤ 30%. Alternatively, a calibration curve may be prepared by linear or quadratic regression. The correlation coefficient for linear or quadratic curves must be ≥ 0.995 for target compounds. Irrespective of the curve fit method selected, the calculated concentration of each calibration level must be within 30% of the nominal concentration when quantitated against the resulting calibration curve. Exclusion of calibration standard levels is not permitted unless justifiable (for example, a known error in standard preparation). Sample analysis must not be performed, and if performed, results must not be reported when calibration acceptance criteria are not met. Rather corrective action, possibly including recalibration, must be taken.

The absolute value of the concentration equivalent to the intercept of the calibration curve (|intercept/slope or equivalent|) converted to concentration units (by division by the slope or equivalent) must be less than the laboratory MDL. When this specification is not met, the source of contamination or suppression must be corrected and the calibration curve reestablished before sample analysis may commence.

RRTs are calculated for each concentration level of each surrogate and target compound by dividing the surrogate or target RT by the associated IS compound RT. The RRTs of each surrogate or target compound across the ICAL are then averaged to determine the ICAL $\overline{RRT}$. All RRTs must be within ± 0.06 RRT units of $\overline{RRT}$.

4.5.5.5.4 Secondary Source Calibration Verification. Following each successful initial calibration, a SSCV must be analyzed to verify the initial calibration. The SSCV is prepared at approximately the mid-range of the calibration curve. Alternatively, two or more concentrations of SSCV may be prepared covering the calibration range. All SSCVs must recover within ± 30% of nominal or demonstrate an RRF within ± 30% of the average RRF of the calibration curve.

4.5.5.5.5 Continuing Calibration Verification. Once the GC/MS instrument has met tuning and calibration criteria, a CCV must be analyzed every 12 hours of analysis following the 12-hour DFTPP tuning check standard. The CCV must recover within ± 30% of nominal or demonstrate RRF within 30% of the mean ICAL RRF for all target PAHs. Corrective action must be taken to address CCV failures, including, but not limited to, preparing and analyzing a new CCV, cleaning or replacing the injector liner, trimming or replacing the column, retuning the MS, or preparing a new initial calibration.

4.5.5.5.6 Analysis of QC Samples and Field Samples. The MS must be tuned and the calibration determined or verified prior to the analysis of field samples. ISs should be added to each extract just prior to analysis. Note that a best practice is not to add IS to the entire 1 mL of extract. An aliquot of the extract should be taken for fortification with ISs to preclude loss of the entire extract in the event of IS spiking errors.

The following QC samples are required with each analysis sequence:

- Solvent method blank (SMB)
- MB
- Replicate extract analysis

Prior to analysis of laboratory QC samples or field-collected samples, a SMB consisting of an aliquot of the batch extraction solvent fortified with IS must be analyzed and demonstrate target compounds are < MDL.

Target PAHs must not be present in MBs at concentrations > 2x MDL. Replicate analysis must demonstrate precision of ≤ 10% RPD for all measured concentrations > 0.5 µg/mL.

An LCS/LCSD pair is required quarterly and recommended with each extraction batch to monitor recovery and precision in matrix. Target PAHs in the LCS and LCSD must recover within 60 to 120% of nominal and the LCSD must demonstrate precision of ≤ 20% RPD for all target PAHs.

4.5.5.5.7 Compound Identification. Four criteria must be met in order to positively identify a surrogate compound or target PAH:

1. The signal-to-noise ratio of the target and qualifier ions must be > 3:1, preferably > 5:1.
2. The target and qualifier ion peaks must be co-maximized (peak apexes within one scan of each other).
3. The RT of the compound must be within the acceptable RT window determined from the ICAL average.
4. The abundance ratio of the qualifier ion response to target ion response for at least one qualifier ion must be within ± 15% of the average ratio from the ICAL.

If any of these criteria are not met, the compound may not be positively identified. The only exception to this is when in the opinion of an experienced analyst, the compound is positively identified. The rationale for such an exception must be documented. For examples of the qualitative identification criteria and calculation of S:N, refer to Section 4.2.10.5.3.

4.5.5.5.8 Internal Standards Response. IS response must be monitored for each injection (except for the SB immediately preceding the initial calibration or 12-hour tune check). Area responses of the IS must be 50 to 200% of the area responses in the initial calibration mid-level standard and they must elute within ± 20 seconds (± 0.33 minute) of the mean RT of the initial calibration. Extracts which do not meet these response acceptance criteria should be diluted, and the dilution analyzed to examine for matrix interferences. If the IS still does not meet criteria in the dilution, the MS tune should be evaluated for a degradation or enhancement of sensitivity and corrective action taken to address the failure. Sample results calculated from IS criteria failures must be appropriately qualified when entered into AQS.

4.5.5.5.9 Surrogate Evaluation. Following calibration, each analyzed extract should be evaluated to ensure the recovery of each surrogate compound is within 60 to 120% of the nominal spiked value. Results which fall outside of these limits indicate potential analyte loss or enhancement either through sample collection and handling and/or extraction process and must be qualified appropriately when reported to AQS.

4.5.5.5.10 Data Review and Concentration Calculations. For sampling units without computerized flow control, the beginning and ending flows are averaged to calculate the collected air volume. For computer controlled sampling units, the integrated collected volume is typically available from the data logging system. Sampled air volumes must be in STP, 25°C and 760 mm Hg. Sampling unit flows should be calibrated in flows at standard conditions so conversion from local conditions to standard flows is not necessary. For units which do not have computerized flow control, temperature and barometric pressure at sample setup and take down must be recorded.

Each chromatogram must be closely examined to ensure chromatographic peaks are appropriately resolved and integration does not include peak shoulders or inflections indicative of a coelution.

The concentrations of target PAHs in unknowns are calculated by relating the area response ratio of the target PAH and internal standard in the unknown to the relationship derived in the

calibration curve selected in Section 4.5.5.5.3. The final air concentration of each target PAH is determined by multiplying the concentration in the extract by the final extract volume and dividing by the collected sample air volume at standard conditions of 25°C and 760 mm Hg:

$$C_A = \frac{1000 \cdot C_t \cdot V_e}{V_A}$$

where:

C_A = concentration of the target compound in air (ng/m^3)
C_t = concentration of the unknown sample in the extract (µg/mL)
V_e = final volume of extract (mL)
V_A = volume of collected air volume at STP (m^3)

4.5.6 Summary of Quality Control Parameters. A summary of QC parameters is shown in Table 4.5-3.

Table 4.5-3. Summary of Quality Control Parameters for NATTS PAHs Analysis

Parameter	Description and Details	Required Frequency	Acceptance Criteria
Solvent Blank (SB)	Aliquot of solvent (without IS) analyzed to ensure the GC/MS is free of interferences and of compounds of interest (target PAHs, internal standards, and surrogates)	Prior to each DFTPP tune check	No target compound, IS, or surrogates qualitatively detected
DFTPP Tune Check	5 to 50 ng injection of DFTPP for tuning of MS detector	Prior to initial calibration and every 12 hours of analysis thereafter	Abundance criteria listed in table 4.5-2 must be met
Initial Calibration (ICAL)	Analysis of a minimum of five calibration levels covering approximately 0.1 to 2 µg/mL	Initially, following failed DFTPP tune check, failed CCV, or when changes to the instrument affect calibration response. Recommended every six weeks.	Average RRF ≤ 30% RSD and each calibration level must be within ± 30% of nominal For quadratic or linear regression, $r \geq 0.995$, each calibration level must be within ± 30% of nominal
Secondary Source Calibration Verification (SSCV)	Analysis of a second source standard at the mid-range of the calibration curve to verify curve accuracy	Immediately after each ICAL	Recovery within ± 30% of nominal or RRF within 30% of mean ICAL RRF

Table 4.5-3. Summary of Quality Control Parameters for NATTS PAHs Analysis (Continued)

Parameter	Description and Details	Required Frequency	Acceptance Criteria
Continuing Calibration Verification (CCV)	Analysis of a known standard at the mid-range of the calibration curve to verify ongoing instrument calibration	Following each DFTPP tune check not followed by ICAL and recommended at the conclusion of each sample sequence	Recovery within ± 30% of nominal or RRF within 30% of mean ICAL RRF
Cartridge Batch Blank	A cartridge (and QFF) selected for analysis to ensure acceptable background levels in the batch of cartridges	One cartridge for each batch of 20 or fewer prepared cartridges	All target compounds each ≤ 10 ng/cartridge
Field Surrogate Compounds	Deuterated PAHs which assess recovery during sample collection, handling, and analysis	Added to every cartridge prior to field deployment	Recovery 60-120% of nominal spiked amount
Internal Standards (IS)	Deuterated PAHs added to extracts to assess the impact of and correct for variability in instrument response	Added to all calibration standards, QC samples, and field sample extracts except the SB	Area response within 50-200% of the response of the mid-level calibration standard in the ICAL.
Extraction Surrogate Compounds	Deuterated PAHs which assess recovery during sample extraction and analysis	Added to media before extraction	Recovery 60-120% of nominal spiked amount
Solvent Method Blank (SMB)	Aliquot of extraction solvent fortified with IS to ensure extraction solvent is free of interferences and target compounds	One with every extraction batch of 20 or fewer field-collected samples	Target compounds < MDL
Method Blank (MB)	Blank cartridge and QFF taken through all extraction and analysis procedures	One with every extraction batch of 20 or fewer field-collected samples	Target analyte amounts ≤ 2x MDL
Laboratory Control Sample (LCS)	Cartridge spiked with known amount of target analyte	Minimally quarterly. Recommended as one with every extraction batch of 20 or fewer field-collected samples	Recovery 60-120% of nominal spiked amount
Laboratory Control Sample Duplicate (LCSD)	Duplicate cartridge spiked with known amount of target analyte	Minimally quarterly. Recommended as one with every extraction batch of 20 or fewer field-collected samples	Recovery 60-120% of nominal spiked amount and precision ≤ 20% RPD compared to LCS
Replicate Analysis	Replicate analysis of a field sample extract	Once with every analysis sequence	Precision ≤ 10% RPD for concentrations ≥ 0.5 µg/mL
Field Blank (FB)	Blank cartridge and QFF assembly exposed to ambient atmosphere for minimally five minutes	One per month	Target analyte amounts ≤ 5x MDL
Collocated Samples	Sample collected concurrently with the primary sample	10% of primary samples for sites conducting collocated sampling (as required by workplan)	Precision ≤ 20% RPD for concentrations ≥ 0.5 µg/mL
Retention Time (RT)	RT of each target PAH, surrogate compound, and internal standard	All qualitatively identified compounds	Target analytes within ± 0.06 RRT units of mean ICAL RRT Internal standards within ± 0.33 minutes of mean ICAL RT

4.5.7 References

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7. Galasyn, J.F.; Hornig, J.F.; Soderberg, R.H. The Loss of PAH from Quartz Fiber High Volume Filters. *J. Air Pollut. Contr. Assoc.* 1984, *34*, 57-59.
8. Care and Safe Handling of Laboratory Glassware. Corning Incorporated. RG-CI-101-REV2. 2011. Available at (accessed October 19, 2016): http://csmedia2.corning.com/LifeSciences/media/pdf/Care_and_Safe_Handling_Lab_Glassware_RG-CI-101Rev2.pdf

5.0: METEOROLOGICAL MEASUREMENTS

A goal of the NATTS network is to leverage existing monitoring sites (such as those conducting criteria pollutant monitoring, PAMS sites, and NCore sites, etc.) to conduct NATTS Program sample collection. Many of the existing 27 NATTS sites conduct site-specific meteorological measurements.

While such site-specific meteorological measurements such as wind speed, wind direction, solar radiation, precipitation, etc. are highly desirable and complement collected NATTS data, only temperature and barometric pressure measurements are required for NATTS sample collection events. If temperature and barometric pressure measurements are not recorded from calibrated temperature and barometric pressure functions on sampling units themselves, they must be recorded from site-specific calibrated meteorological instruments. If site-specific meteorological monitoring is not performed, each site must acquire the applicable temperature and barometric pressure from the closest off-site meteorological monitoring station (i.e., National Weather Service, local airport, etc.). For sites collecting additional meteorological parameters beyond temperature and barometric pressure, please consult EPA's Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV Meteorological Measurements for more information, available at (accessed October 19, 2016):
https://www3.epa.gov/ttnamti1/files/ambient/met/draft-volume-4.pdf

6.0: DATA HANDLING

6.1 Data Collection

All records must be documented in detail sufficient to reconstruct the activities and transformations to generate reported concentration data. If such records are not available, validity of the data cannot be determined. Such records minimally include observations, laboratory measurements, and photographs as well as instrument calibration records and COAs. Records related to manipulation of data such as through data reduction spreadsheets, peak integrations, hand calculations, or calculations handled by a LIMS must be maintained and must be transparent so the transformations may be verified.

6.2 Data Backup

Electronic data acquired from laboratory instruments, field instruments, databases, and data manipulation software in support of NATTS Program work must be maintained for a minimum of six years following acquisition. As previously discussed, this six-year period is needed to cover two consecutive three-year periods needed to assess trends for the NATTS DQO. In order to maintain electronic records for this duration, it is necessary to prevent data loss and corruption by ensuring data redundancy. Each NATTS agency must prescribe data redundancy policies and procedures, which may be included in the NATTS QAPP, SOP, or similar controlled document.

For data acquisition software systems such as CDSs, ICP-MS control and operation software, and environmental control tracking software systems which are connected via computer network, a best practice is to enable automated nightly backups of data to a separate physical hard drive or server, preferably one at a different physical location. Backing up of data to a separate partition on the same hard drive provides little additional security if the hard drive fails. For software systems which are not networked to a server, a best practice is to manually back up the data after completion of each day's activities to removable media (thumb drive, external hard drive, etc.) for transfer to a networked computer or server.

These daily backups must be protected from inadvertent alteration and compiled on a regular frequency, recommended weekly but not to exceed monthly, to an archival system such as a tape drive, DVD, additional external server, cloud storage, etc. This archival must be access-limited by password and/or other security means to a select few individuals as deemed responsible by cognizant management.

Archived electronic data must remain accessible such that retired computer or software systems must be maintained to access data, or archived data converted such that it remains accessible and legible until the archival period has lapsed.

Once archived, archived data should be reviewed or tested to ensure complete records are maintained and data have not been corrupted. Such a review is recommended every six months, but should not exceed annually.

6.3 Recording of Data

Data generated as in Section 6.1 must be recorded so that it is clear who performed the activity, when the activity was performed, and, if applicable, who documented performance of the activity.

6.3.1 Paper Records. Data entries created on paper records such as field collection forms, COC forms, or laboratory notebooks, must be recorded in legibly in indelible ink and must identify the individual creating the entry. Measurements must clearly indicate appropriate units. Individuals creating paper data records must be identified by way of signature or initials unique to the individual and in such a manner that unambiguous identification is possible. One method by which such may be accomplished is to create a cross-reference for each staff person that shows each staff person's printed name, signature, and initials.

6.3.2 Electronic Data Capture. Electronic data recording systems such as electronic logbooks, LIMS, and instrumental data acquisition software generally require a user to log in with a username and password to utilize the system. Each action (entry, manipulation, instrument operation) recorded by such software systems must be attributable to an individual and the corresponding date and time recorded. If so equipped, audit trails must be enabled on software systems in order to record changes made to electronic records.

6.3.3 Error Correction. Changes to recorded data or data manipulation may be required due to calculation errors, incorrectly recorded measurements, or errors noted during data verification and validation. When records are amended, whether paper or electronic, the original record must remain legible or otherwise intact, and the following information must be recorded: the identity of the individual responsible for making the change, the date the change was made and the rationale for the change. For example, hand-written data records may be corrected by a single line through the entry with the correction, the initials of the responsible individual, the date of correction, and the rationale for change documented in close proximity to the correction or identifiable by annotated footnote. For common corrections such as those for incorrect date, illegible entry, calculation errors, etc., a list of abbreviations may be developed to document change rationale. Any such abbreviations must be defined in a quality systems document such as an SOP, or in the front of a logbook, etc.

6.3.3.1 Manual Integration of Chromatographic Peaks. Automated functions for the integration of chromatographic peaks are included in the chromatography data systems (CDS) that control all GC/MS and HPLC instruments. These integration functions should be configured such that little intervention or correction is needed by the analyst, so as to best ensure that peak integration is as reproducible and introduces as little human error as possible. While these functions ensure consistent integration practices, subtle differences in peak shape, coeluting peaks, and baseline noise may result in inconsistent or incorrect peak integration.

Analysts must be properly trained to review and adjust peak integration performed by CDS automated functions, and specific procedures must be codified into each agency's quality system. All manual changes to automated peak integration must be treated as error corrections. Typical corrections to peak integration may include: adjustment of the baseline, addition or removal of a

vertical drop line, or peak deletion if the requisite compound identification criteria are not met. The identification criteria for the chromatography methods are listed as follows:

VOCs:	Section 4.2.10.5.3
Carbonyls:	Section 4.3.9.5.6
PAHs:	Section 4.5.5.5.7

Manual peak deletion, that is, effectively reporting that the compound was not detected, is not permitted in instances in which the peak specified identification criteria are met.

For each adjustment to chromatographic peak integration (manual integration), the record of the original automated integration must be maintained and it is *strongly recommended* that the adjustment be justified with the documented rationale (signal-to-noise too low, incorrect retention time, incorrectly drawn baseline, etc.), analyst initials, and date.

6.4 Numerical Calculations

Numerous calculations and manipulations are necessary to determine the target analyte concentration of a given field-collected sample or QC sample or to determine evaluate whether data generated during calibration verifications meet acceptance criteria.

6.4.1 Rounding. Rounding of values must be avoided until the final step of a calculation. Rounding during intermediate steps risks the loss of fidelity of the calculation which may lead to significant calculation error.

EPA Region IV SESD has developed guidance for rounding which is adopted into the revision of the Volume II of EPA's QA Handbook. This guidance is included in Appendix C of this TAD.

6.4.2 Calculations Using Significant Digits. Final reported results should be rounded to the correct number of significant digits per the rules below. To the extent feasible, carry the maximum number of digits available through all intermediate calculations and do not round until the final calculated result. Non-significant digits that are carried through calculations may be represented using subscripted numerals. (For example, 2.32_1 has three significant figures, with the final 1 being non-significant and carried through to avoid unnecessarily introducing additional error into the final result.)

6.4.2.1 Addition and Subtraction. The number of significant digits in the final result is determined by the value with the fewest number of digits after the decimal place. For example:

A	5.6
B	63.71
C	+ 9.238
	78.5

The final result is limited to one decimal place due to the uncertainty introduced in the tenths place by measurement A.

6.4.2.2 Multiplication and Division. The number of significant digits in the final result is determined by the value with the fewest number of significant digits. For example, acrolein was measured by the GC/MS at a concentration of 2.721 ppb from a canister that was diluted with zero air resulting in a dilution factor of 1.41. The dilution factor is applied to the measured result to calculate the in air concentration:

$$2.721 \text{ ppb} \cdot 1.41 = 3.83_7 \text{ ppb}$$

$$= \quad 3.84 \text{ ppb}$$

The final result is limited to three significant digits due to the dilution factor containing three significant digits.

6.4.2.3 Standard Deviation. Standard deviation in a final result must not display digits in a place that the sample average does not have a significant digit. Take, for example, the following average and standard deviation of the form $\bar{x} \pm s$:

$$107.2 \pm 2.3\underline{1} \quad \text{is reported as} \quad 107.2 \pm 2.3$$

The standard deviation is rounded to the appropriate significant digit of the sample average.

6.4.2.4 Logarithms. For converting a value to its logarithm, retain as many places in the mantissa of the logarithm (to the right of the decimal point in the logarithm) as there are significant figures in the number itself. For example (mantissa underlined):

$$\log_{10} 24.5 = 1.\underline{389}$$

For converting antilogarithms to values, retain as many places in the value as there are digits in the mantissa of the logarithm. For example (mantissa underlined):

$$\text{antilog } (1.\underline{131}) = 13.5$$

6.5 In-house Control Limits

The analysis methods detailed in Section 4 specify acceptance criteria for routine QC samples. These acceptance criteria are the maximum allowable ranges permitted, however, laboratories may find that they rarely or never exceed the acceptance criteria. As each laboratory and the associated analyst, instruments, and processes are unique, development of in-house control limits is recommended to evaluate trends and identify problem situations before exceedances to method acceptance criteria occur.

In-house control limits may be generated to evaluate the bias of quality control samples such as the LCS, CCV, SSCV, and to evaluate precision of LCSD, matrix spike duplicate, etc. Warning

limits and control limits are established following acquisition of sufficient data points, generally more than seven, per the guidance in the subsequent sections. Under no circumstances may data be accepted which exceeds method specified acceptance criteria even if in-house warning or control limits have not been exceeded.

6.5.1 Warning Limits. Warning limits are established as a window of two standard deviations surrounding the mean ($\bar{x} \pm 2s$). Exceedance of the warning limit should prompt monitoring of the parameter for values which remain outside the warning limits. For repeated values exceeding the warning limits, corrective action should be taken to address the trend.

6.5.2 Control Limits. Control limits are established as a window of three standard deviations surrounding the mean ($\bar{x} \pm 3s$). Corrective action is required when control limits are exceeded.

6.6 Negative Values

In general, negative values of small magnitude may be expected from certain analytical platforms in the NATTS program, specifically those which do not apply calibration regressions which are forced through the origin. However, depending on the situation, negative numbers can be problematic and indicative of bias due to faulty sensors, contamination in reagents and labware, improper calibration, or calculation errors.

Negative values must be evaluated to ensure that their magnitude does not significantly impact the resulting measurements.

Minimum values will be updated in AQS to permit the reporting of negative values for NATTS parameters. Negative values for all qualitatively identified analytes must be reported to AQS as-is without censoring or replacing with zero.

6.6.1 Negative Concentrations. For analysis measurements, a negative concentration result generated by a positive instrument response (i.e., positive area count) must be investigated to ensure that the negative concentration is of small magnitude such that the absolute value of the concentration is less than the MDL_{sp} (for MDLs determined via Section 4.1.3.1) or $s \cdot K$ for MDLs determined via Section 4.1.3.2. Where negative concentrations fail this criterion, corrective action must be taken to determine and remediate the source of the bias.

6.6.2 Negative Physical Measurements. For physical measurements such as mass, absolute pressure, and flow, negative values generated by an instrument must be evaluated to ensure they do not adversely impact future measurements.

For example, a VOCs sampling unit pressure transducer reads -0.4 psia upon connection to a canister at hard vacuum. The acceptable canister pressure threshold is 0.5 psia. Since negative absolute pressures are impossible, the -0.4 psia reading is significant, especially when compared to an acceptance criterion of 0.5 psia. Due to the -0.4 psia bias, the pressure in another canister at 0.8 psia would be read 0.4 psia and would incorrectly meet the acceptance criterion for sample collection due to the incorrect calibration of the pressure transducer.

7.0: DATA VALIDATION TABLES

The following tables are a distillation of the general quality control guidance and requirements in Section 3 and of the individual methods described in Section 4. More information on each data validation parameter can be located within the text identified in the reference column. Each parameter is assigned a category of importance. The categories in order of decreasing importance are:

1. Critical – Criteria must be met for reported results to be valid – Samples for which these criteria are not met are invalidated.
2. MQO – Required NATTS Measurement Quality Objective which must be attained – Failure to meet these criteria does not necessarily invalidate data, but may compromise data and result in exclusion from trends analysis.
3. Operational – Failure to meet criteria does not invalidate reported results; the results are compromised and on a case-by-case basis may require qualification – refer to Section 3.3.1.3.15 for the list of AQS qualifiers
4. Practical – Failure to meet criteria does not invalidate reported results; results may be compromised but do not require qualification.

The validation tables in the following sections will be available on AMTIC in Microsoft Excel® format so the parameters may be sorted according to importance.

7.1 VOCs via EPA Compendium Method TO-15

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Field Readiness Checks and Collection Activities				
Canister Cleaning Batch Blank	Minimally one canister selected for analysis from a given batch of clean canisters to ensure acceptable background levels in the batch of cleaned canisters - must represent no more than 10 canisters	Each target VOC's concentration < 3x MDL or 0.2 ppb, whichever is lower	Section 4.2.6.2.4 TO-15 Section 8.4.1.6	Critical
Canister Viability	All canisters	Canister must be used within 30 days from final evacuation	Section 4.2.6.2 TO-15 Section 1.3	Operational
Sampling Unit Clock/Timer Check	Verified with each sample collection event	Clock/timer accurate to ±5 minute of reference for digital timers, ±15 minutes for mechanical timers, set to local standard time Sample collection period verified to be midnight to midnight	Section 4.2.5.3 and Table 3.3-1	Operational
Canister Starting Pressure Determination	Each canister prior to collection of a field sample or preparation of a calibration standard or laboratory QC sample	Vacuum > 28" Hg as determined with calibrated pressure gauge or transducer	Section 4.2.5.2.1	Critical
Sample Setup Leak Check	Each canister prior to collection - draw vacuum on canister connection	Leak rate must be < 0.2 psi over 5 minutes	Section 4.2.5.2.1	Critical
Sampling Frequency	One sample every six days according to the EPA National Monitoring Schedule	Sample must be valid or a make-up sample should be scheduled (refer to Section 2.1.2.1)	Section 4.2.5.3	Critical and MQO
Sampling Period	All field-collected samples	1380-1500 minutes (24 ± 1 hr) starting and ending at midnight	Section 4.2.5.3	Critical and MQO
Pre-Sample Collection Purge	Each sampling event	Minimum of ten air changes just prior to sample collection	Section 4.2.5.4	Practical
Field-collected Sample Final Pressure	All field-collected samples	Must be determined with a calibrated pressure gauge or transducer per agency quality system specification	Section 4.2.5.2.4	Operational
Sample Receipt				
Chain-of-custody	All field-collected samples including field QC samples	Each canister must be uniquely identified and accompanied by a valid and legible COC with complete sample documentation	Sections 3.3.1.3.7 and 4.2.5.2.4	Critical

7.1 VOCs via EPA Compendium Method TO-15 (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Sample Holding Time	All field-collected samples, laboratory QC samples, and standards	Analysis within 30 days of end of collection (field-collected samples) or preparation (QC samples or standards)	Section 4.2.1 TO-15 Sections 1.3, 2.3, and 9.2.8.1	Operational
Canister Receipt Pressure Check	All field-collected samples upon receipt at the laboratory – measured with calibrated pressure gauge or transducer	Pressure change of ≤ 0.5 psi from the final pressure at retrieval	Section 4.2.8	Critical for subambient sample collection, operational for pressurized sample collection
GC/MS Analysis				
Instrument Blank (IB)	Analysis of swept carrier gas through the preconcentrator to demonstrate the instrument is sufficiently clean prior to analysis of ICAL or daily beginning CCV	Each target VOC's concentration < 3x MDL or 0.2 ppb, whichever is lower	Section 4.2.10.5.2.2	Operational
BFB Tune Check	50 ng injection of BFB for tune verification of MS detector analyzed prior to initial calibration and every 24 hours of analysis thereafter (for quadrupole MS only)	Must meet abundance criteria listed in Table 4.2-2	Section 4.2.10.5.1 TO-15 Section 10.4.2	Critical
GC/MS Multi-Point Initial Calibration (ICAL)	Analysis of a minimum of five calibration levels covering approximately 0.1 to 5 ppb Initially and minimally every three months thereafter, following failed BFB tune check, failed CCV, or when changes to the instrument affect calibration response	Average RRF ≤ 30% RSD and each calibration level must be within ± 30% of nominal For linear regression (with either a linear or quadratic fit), r ≥ 0.995 and each calibration level must be within ± 30% of nominal	Section 4.2.10.5.2.2 TO-15 Section 10.5.5.1	Critical
Secondary Source Calibration Verification (SSCV)	Analysis of a secondary source standard at the mid-range of the calibration curve to verify ICAL accuracy immediately after each ICAL	Recovery within ± 30% of nominal	Section 4.2.10.5.2.3	Critical
Continuing Calibration Verification (CCV)	Analysis of a known standard at the mid-range of the calibration curve to verify ongoing instrument calibration; following each daily BFB tune check and at the conclusion of each analytical sequence	Each target VOC must recover within 70-130% of the nominal spiked amount or the RRF must be within 30% of the mean ICAL RRF	Section 4.2.10.5.2.4 TO-15 Section 10.6.5	Critical

7.1 VOCs via EPA Compendium Method TO-15 (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Internal Standards (IS)	Deuterated or non-naturally occurring compounds co-analyzed with all calibration standards, laboratory QC samples, and field-collected samples so as to monitor instrument response and assess matrix effects	Area response for each IS compound within ± 40% of the average response of the ICAL	Section 4.2.10.5.4 TO-15 Section 10.7.5	Critical
Preconcentrator Leak Check	Pressurizing or evacuating each canister connection to the preconcentrator to verify as leak-free prior to analysis	< 0.2 psi change/minute or manufacturer specifications	Section 4.2.10.5.2.1	Operational
Method Blank (MB)	Canister filled with clean humidified diluent gas (gas employed for dilution of standards and /or samples) One with every analysis batch of 20 or fewer field-collected samples	Each target VOC's concentration < 3x MDL or 0.2 ppb, whichever is lower	Section 4.2.10.4.3 TO-15 Section 10.7.5	Operational
Laboratory Control Sample (LCS)	Canister spiked with known amount of target analyte at approximately the lower third of the calibration curve *Recommended:* One with every analysis batch of 20 or fewer field-collected samples	Each target VOC's recovery must be 70 to 130% of its nominal spiked amount	Section 4.2.10.5.2.5	Operational
Retention Time (RT)	RT of each target compound and internal standard for all qualitatively identified compounds and internal standards	Each target VOC's RRT must be within ± 0.06 RRT units of its mean ICAL RRT Each IS RT must be within ± 0.33 minutes of its mean ICAL RT	Sections 4.2.10.5.2.2 and 4.2.10.5.4 TO-15 Sections 10.5.5.2, 10.5.5.3, and 10.5.5.4	Critical
Compound Identification	Qualitative identification of each target VOC in each standard, blank, QC sample, and field-collected sample (including field QC samples)	Signal-to-noise ≥ 3:1 RT within prescribed window Ion abundances of at least one qualifier ion within 30% of ICAL mean Peak apexes co-maximized (within one scan for quadrupole MS) for quantitation and qualifier ions	Section 4.2.10.5.3	Critical
Replicate Analysis	A single additional analysis of a field-collected canister Once with every analysis sequence (as prescribed in workplan)	Precision ≤ 25% RPD for target VOCs with concentrations ≥ 5x MDL	Section 4.2.10.5.2.5 TO-15 Section 11.1.1	Operational

7.1 VOCs via EPA Compendium Method TO-15 (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Duplicate Sample	Field sample collected through the same inlet probe as the primary sample 10% of primary samples for sites performing duplicate sample collection (as prescribed in workplan)	Precision ≤ 25% RPD of primary sample for concentrations ≥ 5x MDL	Sections 4.2.4; 4.2.4.1	Operational
Collocated Sample	Field sample collected through a separate inlet probe as the primary sample 10% of primary samples for sites performing duplicate sample collection (as prescribed in workplan	Precision ≤ 25% RPD of primary sample for concentrations ≥ 5x MDL	Sections 4.2.4 and 4.2.4.1	Operational
Laboratory Readiness and Proficiency				
Method Detection Limit	Determined initially and minimally annually thereafter and when method changes alter instrument sensitivity	MDL determined via 4.1 must be: Acrolein ≤ 0.09 µg/m^3 Benzene ≤ 0.13 µg/m^3 1,3-Butadiene ≤ 0.10 µg/m^3 Carbon Tetrachloride ≤ 0.017 µg/m^3 Chloroform ≤ 0.50 µg/m^3 Tetrachloroethylene ≤ 0.17 µg/m^3 Trichloroethylene ≤ 0.20 µg/m^3 Vinyl Chloride ≤ 0.11 µg/m^3 These MDL MQOs current as of October 2015. Refer to current workplan template for up-to-date MQOs.	Sections 4.1 and 4.2.7	MQO
Stock Standard Gases	Purchased stock standard gases for each target VOC All standards	Certified and accompanied by certificate of analysis Recertified or replaced annually unless a longer expiration is specified by the supplier	Section 4.2.10.3.1	Critical

7.1 VOCs via EPA Compendium Method TO-15 (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Proficiency Testing	Blind sample submitted to each laboratory to evaluate laboratory bias Two per calendar year[1]	Each target compound within ± 25% of the assigned target value Failure of one PT must prompt corrective action. Failure of two consecutive PTs (for a specific core analyte) must prompt qualification of the analyte in field collected samples until return to conformance.	Section 2.1.4.1	Operational and MQO
Canister and Sampling Unit Testing and Maintenance				
Canister Leak Test	Testing of the leak tightness of each canister in the agency fleet Annually, may be performed simultaneously with canister zero air check	Leak rate must be ≤ 0.1 psi/day	Section 4.2.6.1.1.1	Operational
Canister Zero Check	Verification that a canister does not contribute to positive bias over an approximate 30-day period *Strongly Recommended:* Each canister in the agency fleet once annually (or as defined by agency policy) or after major maintenance such as replacement of valve	All Tier I core target compounds must be < 0.2 ppb or < 3x MDL, whichever is lower	Section 4.2.6.1.1.1 TO-15 Section 8.4.3	Operational
Canister Known Standard Gas Check	Verification that a canister does not contribute to bias over an approximate 30-day period *Strongly Recommended:* Each canister in the agency fleet once annually (or as defined by agency policy) or after major maintenance such as replacement of valve	All Tier I core target compounds must be within ± 30% of nominal	Section 4.2.6.1.1.2	Operational
Sampling Unit Flow Calibration	Calibration of sampling unit flow controller Initially and when calibration checks demonstrate flows are out of tolerance, or when components affecting flow are adjusted or replaced	Flow set to match the certified flow primary or transfer standard	Table 3.3-1 TO-15 Section 8.3.5	Practical

7.1 VOCs via EPA Compendium Method TO-15 (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Sampling Unit Non-biasing Certification	Verification that the sampling unit does not contribute to bias Prior to field deployment and annually thereafter, or when flow path components are repaired or replaced Sampling units must be subject to a Zero Check and Known Standard Challenge	Zero Check – All Tier I core target analytes < 0.2 ppb or < 3x MDL, whichever is lower Known Standard Challenge – All Tier I core target analytes within ±15% of the reference sample	Section 4.2.5.5	Operational
Sampling Unit Flow Calibration Check or Audit	Verification of sampling unit flow rate Minimally quarterly, monthly recommended	Flow within ±10% of certified primary or transfer standard flow and design flow	Table 3.3-1	Practical
Site Specifications and Maintenance				
Sampling Unit Siting	Verify conformance to requirements Annually	270° unobstructed probe inlet Inlet 2-15 meters above-ground level ≥ 10 meters from drip line of nearest tree Collocated sampling inlets spaced within 4 meters of primary sampling unit inlet	Section 2.4	Operational
Sample Probe and Inlet	Sample probe and inlet materials composition Annually	Chromatographic grade stainless steel or borosilicate glass	Section 4.2.3.2	Operational
Sample Inlet Filter	Particulate filter maintenance Minimally annually	Clean or replace the 2-µm sintered stainless steel filter	Section 4.2.3.3 TO-15 Section 7.1.1.5	Operational
Sampling Inlet and Inlet Line Cleaning	Sample inlet and inlet line cleaning or replacement Minimally annually - More often in areas with high airborne particulate levels	Cleaned with distilled water or replaced	Section 4.2.3.1	Operational
Data Reporting				
Data Reporting to AQS	Reporting of all results a given calendar quarter Quarterly, within 180 days of end of calendar quarter	All field-collected sample concentrations reported including data less than MDL. Field QC sample and laboratory replicates must also be reported (as required by workplan).	Section 3.3.1.3.15	Operational

7.1 VOCs via EPA Compendium Method TO-15 (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
AQS Reporting Units	Units must be as specified with each submission to AQS	ppbv	Section 3.3.1.3.15	Critical
Data Completeness	Valid samples compared to scheduled samples Annually	≥ 85% of scheduled samples	Section 3.2	MQO

[1] Dependent upon EPA contract with PT provider

7.2 Carbonyls via EPA Compendium Method TO-11A

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Field Readiness Checks and Collection Activities				
Collection Media	All field-collected samples and matrix quality control samples	Cartridge containing silica gel solid sorbent coated with DNPH	Section 4.3.5 TO-11A Section 8.2	Critical
Media Handling	All field-collected samples and all quality control samples	Sample retrieval as soon as possible, not to exceed 72 hours post-sampling. Retrieved sample shipped and stored at ≤ 4°C, protected from light until extraction. Damaged cartridges (water damage or cracked) must be voided.	Sections 4.3.5.2, 4.3.5.3, and 4.3.8.1.2 TO-11A Sections 6.5 and 10.12	Critical
Cartridge Lot Blank Check	Analysis of a minimum of 3 cartridges or 1% of the total lot, whichever is greater, for each new lot	Formaldehyde < 0.15 µg/cartridge, Acetaldehyde < 0.10 µg/cartridge, Acetone < 0.30 µg/cartridge, all others < 0.10 µg/cartridge	Section 4.3.5.1 and Table 4.3-4 TO-11A Section 9.2.5.17	Critical
Sampling Unit Clock/Timer Check	Verified with each sample collection event	Clock/timer accurate to ±5 minute of reference for digital timers and ±15 minutes for mechanical timers, set to local standard time Sample collection period verified to be midnight to midnight	Table 3.3-1	Operational
Sampling Unit Leak Check	Pressurization or evacuation of internal sampler flow paths to demonstrate as leak-free Prior to each sample collection	Must show no indicated flow	Section 4.3.8.1.1	Operational
Sampling Frequency	One sample every six days according to the EPA National Monitoring Schedule	Sample must be valid or a make-up sample should be scheduled (refer to Section 2.1.2.1)	Section 4.3.8.1.3	Critical and MQO
Sampling Period	All field-collected samples	1380-1500 minutes (24 ± 1 hr) starting and ending at midnight	Section 4.3.8.1.3	Critical and MQO

7.2 Carbonyls via EPA Compendium Method TO-11A (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Pre-Sample Collection Purge	Each sampling event	Minimum of ten air changes just prior to sample collection	Section 4.3.7.2	Practical
Sample Receipt				
Chain-of-custody	All field-collected samples	Each cartridge must be uniquely identified and accompanied by a valid and legible COC with complete sample documentation	Section 3.3.1.3.7	Critical
Sample Holding Time	All field-collected samples, laboratory QC samples, and standards	Extraction: 14 days from sample collection (cartridge storage ≤ 4 °C) Analysis: 30 days from extraction (extract storage ≤ 4 °C)	Section 4.3.9.3 TO-11A Sections 11.1.2 and 11.2.5	Operational
Sample Receipt Temperature Check	All field-collected samples upon receipt at the laboratory	Must be ≤ 4°C	Section 4.3.8.1.2 TO-11A Section 10.12	Operational
HPLC Analysis				
Solvent Blank (SB)	Prior to ICAL and daily beginning CCV	All target compounds < MDL_{sp} (refer to Section 4.1.3.1) or $s \cdot K$ (refer to Section 4.1.3.2)	Section 4.3.9.5.2	Operational
HPLC Initial Multi-Point Calibration (ICAL)	Initially, following failed CCV, or when changes to the instrument affect calibration response Injection of a minimum of 5 points covering approximately 0.01 to 3.0 µg/mL	Correlation coefficient (r) ≥ 0.999; relative error for each level against calibration curve ≤ 20%. Absolute value of intercept divided by slope must not exceed MDL_{sp} (MDLs determined by Section 4.1.3.1) or $s \cdot K$ (MDLs determined by Section 4.1.3.2)	Section 4.3.9.5.2 TO-11A Section 11.4.3	Critical
Secondary Source Calibration Verification (SSCV)	Secondary source standard prepared at the mid-range of the calibration curve, analyzed immediately after each ICAL	85 to 115% recovery	Section 4.3.9.5.3 TO-11A Section 11.4.4	Critical
Continuing Calibration Verification (CCV)	Prior to sample analysis on days when an ICAL is not performed and minimally every 12 hours of analysis; recommended following analysis of every 10 field-collected samples and at the conclusion of each analytical sequence	85 to 115% recovery	Section 4.3.9.5.4 TO-11A Section 11.4.5	Critical

7.2 Carbonyls via EPA Compendium Method TO-11A (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Extraction Solvent Method Blank (ESMB)	An aliquot of extraction solvent delivered to a volumetric flask. One with each extraction batch of 20 or fewer field-collected samples.	Each target carbonyl's concentration < MDL_{sp} (refer to Section 4.1.3.1) or $s \cdot K$ (refer to Section 4.1.3.2)	Section 4.3.9.4.1	Operational
Method Blank (MB)	Unexposed DNPH cartridge extracted as a sample One with every extraction batch of 20 or fewer field-collected samples	Formaldehyde < 0.15 µg/cartridge, Acetaldehyde < 0.10 µg/cartridge, Acetone < 0.30 µg/cartridge, all others < 0.10 µg/cartridge	Section 4.3.9.4.1	Operational
Laboratory Control Sample (LCS)	DNPH cartridge spiked with known amount of target analyte at approximately the lower third of the calibration curve, minimally quarterly, one recommended with every extraction batch of 20 or fewer field-collected samples	Formaldehyde recovery 80-120% of nominal spike All others recovery 70-130% of nominal spike	Section 4.3.9.4.1	Operational
Laboratory Control Sample Duplicate (LCSD)	Duplicate LCS to evaluate precision through extraction and analysis, minimally quarterly, one recommended with every extraction batch of 20 or fewer samples	Formaldehyde recovery 80-120% of nominal spike All others recovery 70-130% of nominal spike Precision ≤ 20% RPD of LCS	Section 4.3.9.4.1	Operational
Retention Time (RT)	Every injection	Each target carbonyl's RT within ± 3*s* or ± 2% of its mean ICAL RT	Section 4.3.9.5.2	Critical
Replicate Analysis	A single additional analysis of a field-collected sample extract Once with every analysis sequence of 20 or fewer samples	Precision ≤ 10% RPD for concentrations ≥ 0.5 µg/cartridge	Section 4.3.9.5.5 TO-11A Section 13.2.3	Operational
Field Blank	Minimally monthly, sample cartridge installed in primary sampling position and exposed to field conditions for minimally 5 minutes	Formaldehyde < 0.30 µg/cartridge, Acetaldehyde < 0.40 µg/cartridge, Acetone < 0.75 µg/cartridge, Sum of all other target compounds < 7.0 µg/cartridge	Section 4.3.8.2.1 TO-11A Section 13.3.1	Operational
Collocated Sample Collection	Field sample collected through a separate inlet probe from the primary sample 10% of primary samples for sites performing collocated sample collection (as prescribed in workplan)	Precision ≤ 20% RPD of primary sample for concentrations ≥ 0.5 µg/cartridge	Section 4.3.8.2.3 TO-11A Section 13.4.1	Operational

7.2 Carbonyls via EPA Compendium Method TO-11A (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Duplicate Sample Collection	Field sample collected through the same inlet probe as the primary sample 10% of primary samples for sites performing collocated sample collection (as prescribed in workplan)	Precision ≤ 20% RPD of primary sample for concentrations ≥ 0.5 µg/cartridge	Section 4.3.8.2.4 TO-11A Section 13.4.1	Operational
DNPH Chromatography Evaluation	All cartridges	DNPH peak must be present	Section 4.3.9.5.7	Critical
	For all field-collected cartridges	DNPH must be ≥ 50% of the DNPH area in the laboratory QC samples		Critical
Laboratory Readiness and Proficiency				
Proficiency Testing	Blind sample submitted to each laboratory to evaluate laboratory bias Two per calendar year[1]	Each target compound within ± 25% of the assigned target value Failure of one PT must prompt corrective action. Failure of two consecutive PTs (for a specific core analyte) must prompt qualification of the analyte in field collected samples until return to conformance.	Section 2.1.4.1	Operational and MQO
Method Detection Limit	Determined initially and minimally annually thereafter, and when method changes alter instrument sensitivity	MDL must be: Formaldehyde ≤ 0.08 µg/m^3 Acetaldehyde ≤ 0.45 µg/m^3 These MDL MQOs current as of October 2015. Refer to current workplan template for up-to-date MQOs.	Sections 4.1 and 4.3.6	MQO
Stock Standard Solutions	Purchased stock materials for each target carbonyl All standards	Certified and accompanied by certificate of analysis	Section 4.3.9.2.2	Critical
Working Standard Solutions	Storage of all working standards	Stored at ≤ 4°C, protected from light	Section 4.3.9.2.4 TO-11A Section 9.4.3	Critical

7.2 Carbonyls via EPA Compendium Method TO-11A (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Sampling Unit Testing and Maintenance				
Field Sampler Flow Rate Calibration	Calibration of sampling unit flow controller Initially and following failure of flow verification checks	Flow set to match a certified flow transfer standard	Table 3.3-1 and 4.3.7.1.2	Critical
Ozone Scrubber Recharge	Recharge ozone scrubber with KI Minimally annually	Scrubber capacity sufficient to be effective (ozone removal > 95%) for 12 months of 24-hour sampling every sixth day	Section 4.3.4.1 TO-11A Section 10.1	Critical
Sampling Unit Non-biasing Certification	Verification with humidified zero air or nitrogen that the sampling unit does not contribute to positive bias Prior to field deployment and annually thereafter, or when flow path components are repaired or replaced	Difference between challenge and reference cartridge < 0.2 ppbv for each target carbonyl	Section 4.3.7.1.1	Operational
Sampling Unit Flow Calibration Check or Audit	Verification of sampling unit flow rate Minimally quarterly, monthly recommended	Flow within ± 10% of certified primary or transfer standard flow and design flow	Table 3.3-1	Critical
Site Specifications and Maintenance				
Sampling Unit Siting	Verify conformance to requirements Annually	270° unobstructed probe inlet Inlet 2-15 meters above-ground level ≥ 10 meters from drip line of nearest tree Collocated sampling inlets spaced no more than 4 meters from primary sampling unit inlet	Section 2.4	Operational
Sample Probe and Inlet	Sample probe and inlet materials composition Annually	Chromatographic grade stainless steel, PTFE Teflon, or borosilicate glass	Section 4.3.7.2	Critical
Sample Inlet Filter	Particulate filter maintenance Minimally annually, if equipped	Clean or replace the inline particulate filter (if equipped)	Section 4.3.7.3	Operational
Sampling Inlet and Inlet Line Cleaning	Sample inlet and inlet line cleaning or replacement Minimally annually - More often in areas with high airborne particulate levels	Cleaned with distilled water or replaced	Section 4.3.7.3	Operational

7.2 Carbonyls via EPA Compendium Method TO-11A (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Data Reporting				
Data Reporting to AQS	Reporting of all results a given calendar quarter Quarterly, within 180 days of end of calendar quarter	All field-collected sample concentrations reported including data less than MDL. All data must be in standard conditions. Field QC sample and laboratory replicates must also be reported.	Section 3.3.1.3.15	Operational
AQS Reporting Units	Units must be as specified with each quarterly submission to AQS	mass/volume (ng/m^3 or $\mu g/m^3$)	Section 3.3.1.3.15	Critical
Data Completeness	Valid samples compared to scheduled samples Annually	≥ 85% of scheduled samples	Section 3.2	MQO

7.3 Metals via EPA Compendium Method IO 3.1 and IO 3.5

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Field Readiness Checks and Collection Activities				
Collection Media	All field-collected samples and matrix quality control samples	Low volume collection: 47-mm Teflon filters with polypropylene support ring and 2-µm pore size	Section 4.4.9.3 40CFR Part 50 Appendix Q Section 6.2.3	Critical
		High volume collection: 8"x10" quartz fiber filter (QFF) filters with 2-µm pore size	Section 4.4.10.3 IO3.1 Section 4.1.6	Critical
Media Inspection	Filters inspected for pinholes, tears, or other imperfections unsuitable for sample collection All filters	Filters with defects must be discarded	Section 4.4.3.3 IO3.1 Section 4.2 IO2.3 Section 7.2	Critical
Media Handling	All field-collected samples and quality control samples	Low volume: Plastic or Teflon coated forceps or powder-free gloves	Section 4.4.3.2 IO3.1 Section 5.2.1.1 IO2.3 Section 7.2	Practical
		High volume: Plastic or Teflon coated forceps or powder-free gloves		Practical
Lot Background Determination	For each new lot of media: • As part of the MDL process when determining MDLs via Section 4.1.3.1 or • Five separate filters digested and analyzed	Low volume: No acceptance criterion Lot blank subtraction is not permitted	Section 4.4.9.3.1	Practical
		High volume: No acceptance criterion Lot blank subtraction is not permitted	Section 4.4.10.3.1 IO3.1 Table 9	Practical
Sampling Unit Clock/Timer Check	Verified with each sample collection event	Clock/timer accurate to ±5 minute of reference for digital timers and within ±15 minutes for mechanical timers, set to local standard time Sample collection period verified to be midnight to midnight	Table 3.3-1	Operational

7.3 Metals via EPA Compendium Method IO 3.1 and IO 3.5 (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Sampling Unit Leak Check	Verification that sampling train is leak tight Every five sample collection events	Low volume: Leak rate of ≤ 25 mmHg over 30 seconds or 80 mL/min	Section 4.4.9.4 EPA QA Handbook Vol II Appendix D	Practical
		High volume: absence of a whistle	Section 4.4.10.4 IO2.1 Section 7.3.1.6	Practical
Sampling Frequency	One sample every six days according to the EPA National Monitoring Schedule	Sample must be valid or a make-up sample should be scheduled (refer to Section 2.1.2.1)	Sections 4.4.9.4.1 and 4.4.10.4.1	Critical and MQO
Sampling Period	All field-collected samples	1380-1500 minutes (24 ± 1 hr) starting and ending at midnight	Sections 4.4.9.4.1 and 4.4.10.4.1	Critical and MQO
Pre-Sample Collection Warm-up	Only for high volume sampling units without computer controlled flow	Minimum of five minutes (ten minutes recommended) after filter installation but before sample collection	Section 4.4.10.4 IO2.1 Section 7.4.2.9	Operational
Post-Sample Collection Warm-up	Only for high volume sampling units without computer controlled flow	Minimum of five minutes (ten minutes recommended) before filter retrieval	Section 4.4.10.4 IO2.1 Section 7.4.2.9	Operational
Sample Receipt				
Chain-of-custody	All field-collected samples	Each filter must be uniquely identified and accompanied by a valid and legible COC with complete sample documentation	Section 3.3.1.3.7	Critical
Sample Holding Time	All field-collected samples and laboratory QC samples	Digestion: within 180 days from sample collection or preparation Analysis: within 180 days from sample collection	Section 4.4.1 IO3.1 Section 6.1.2	Operational
Acid Digestion and ICP/MS Analysis				
Microwave Calibration	Standardization of microwave power output Output calibration not to exceed six months; monthly recommended	Level of output should differ by no more than 10% across batches	Section 4.4.9.5.2.2	Operational

7.3 Metals via EPA Compendium Method IO 3.1 and IO 3.5 (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Hot Block Temperature Verification	Reagent water blank with thermometer to ensure digestion temperature consistent for all wells Initially and annually thereafter for each well in the hot block digester	Within ± 5°C of desired temperature	Section 4.4.9.5.2.1	Operational
Hot Block Temperature Check	Reagent water blank with thermometer to monitor digestion temperature Each digestion batch	Within ± 5°C of desired temperature	Section 4.4.9.5.2.1	Operational
ICP/MS Warm Up	Warm up of ICP torch and MS detector Each day of analysis	Minimum of 30 minutes (or according to manufacturer specifications) prior to performing initial calibration	Section 4.4.11.6 IO3.5 Section 10.1.1	Practical
ICP/MS Tuning	Analysis of tuning solution containing low (e.g. Li), and medium (e.g. Mg), and high (e.g. Pb) mass elements Each day of analysis during or immediately following warm up	• Minimum resolution of 0.75 amu at 5% peak height • Mass calibration within 0.1 amu of unit mass • Five replicates of tuning solution with %RSD ≤ 5% • Manufacturer specifications may be followed	Section 4.4.11.6 IO3.5 Section 10.1.1	Critical
Initial Calibration Blank (ICB)	Analysis of undigested reagent blank Each day of analysis prior to initial calibration (ICAL) and immediately following the initial calibration verification (ICV)	ICB following ICV: each target element's concentration < MDL_{sp} (refer to Section 4.1.3.1) or $s \cdot K$ (refer to Section 4.1.3.2)	Sections 4.4.11.7.1 and 4.4.11.7.3 IO3.5 Section 11.3.3	Critical
ICP/MS Initial Multi-Point Calibration (ICAL)	Minimum of three standard concentration levels plus ICB covering approximately 0.1 to 250 µg/L Each day of analysis, following failed CCV, or retuning of the MS	Linear regression correlation coefficient (r) ≥ 0.995 Replicate integrations RSD ≤ 10%	Section 4.4.11.7.1	Critical

7.3 Metals via EPA Compendium Method IO 3.1 and IO 3.5 (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Initial Calibration Verification (ICV)	Analysis of second source calibration verification Each day of analysis immediately following ICAL	Within ± 10% of nominal	Section 4.4.11.7.2 IO3.5 Section 11.3.2	Critical
Interference Check Standard (ICS)	Each day of analysis following the second ICB and every 8 hours of analysis thereafter. Once daily for ICP-MS with collision reaction cells Analysis of two solutions which contain interferants (ICS A) and target elements with known interferences (ICS B)	ICS A: all target elements < 3x MDL_{sp} (refer to Section 4.1.3.1) or 3x $s \cdot K$ (refer to Section 4.1.3.2) – may be subtracted for background indicated on certificate of analysis ICS B: 80 to 120% recovery	Section 4.4.11.7.4 IO3.5 Section 11.3.5	Operational
Continuing Calibration Verification (CCV)	Each day of analysis immediately following the ICS, following every 10 sample injections, and at the conclusion of each analytical sequence	90 to 110% recovery	Section 4.4.11.7.5 IO3.5 Section 11.3.6	Critical
Continuing Calibration Blank (CCB)	Each day of analysis immediately after each CCV	all target elements < MDL_{sp} (refer to Section 4.1.3.1) or $s \cdot K$ (refer to Section 4.1.3.2)	Section 4.4.11.7.6 IO3.5 Section 11.3.7	Critical
Reagent Blank (RB)	Digested reagent blank Once with each extraction batch of 20 or fewer samples	Low volume: All target elements < MDL_{sp} (refer to Section 4.1.3.1) or $s \cdot K$ (refer to Section 4.1.3.2)	Sections 4.4.9.5.1, 4.4.11.7.7, and Table 4.4-3	Operational
		High volume: All target elements < MDL_{sp} (refer to Section 4.1.3.1) or $s \cdot K$ (refer to Section 4.1.3.2)	Sections 4.4.10.5.1, 4.4.11.7.7, and Table 4.4-3	Operational
Method Blank (MB)	Low volume: Digested blank filter Once with each extraction batch of 20 or fewer samples High volume: Digested blank filter Once with each extraction batch of 20 or fewer samples	Low volume: All target elements < MDL	Sections 4.4.9.5.1, 4.4.11.7.7, and Table 4.4-3	Operational
		High volume: All target elements < MDL	Sections 4.4.10.5.1, 4.4.11.7.7, and Table 4.4-3 IO3.5 Section 11.3.8	Operational
Reagent Blank Spike (RBS)	Spiked digested reagent blank (no filter)	Low volume: Recovery within 80-120% of nominal for all target elements	Sections 4.4.9.5.1, 4.4.11.7.7, and Table 4.4-3	Operational

7.3 Metals via EPA Compendium Method IO 3.1 and IO 3.5 (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
	Once with each digestion batch of 20 or fewer field-collected samples	High volume: Recovery within 80-120% of nominal for all target elements	Sections 4.4.10.5.1, 4.4.11.7.7, and Table 4.4-3	Operational
Laboratory Control Sample (LCS)	Low volume: Digested spiked filter Once with each extraction batch of 20 or fewer field-collected samples High volume: Digested spiked filter strip Once with each extraction batch of 20 or fewer field-collected samples	Low volume: Recovery within 80-120% of nominal for all target elements	Sections 4.4.9.5.1, 4.4.11.7.7, and Table 4.4-3	Operational
		High volume: Recovery within 80-120% of nominal for all target elements	Sections 4.4.10.5.1, 4.4.11.7.7, and Table 4.4-3 IO3.5 Section 11.3.9	Operational
Laboratory Control Sample Duplicate (LCSD)	Low volume: Duplicate digested spiked filter Once with each extraction batch of 20 or fewer field-collected samples High volume: Duplicate digested spiked filter strip Once with each extraction batch of 20 or fewer field-collected samples	Low volume: Recovery within 80-120% of nominal for all target elements and precision ≤ 20% RPD of LCS	Sections 4.4.9.5.1, 4.4.11.7.7, and Table 4.4-3	Operational
		High volume: Recovery within 80-120% of nominal for all target elements and precision ≤ 20% RPD of LCS – Not required if batch contains MSD	Sections 4.4.10.5.1, 4.4.11.7.7, and Table 4.4-3	Operational
Duplicate Digested Filter Strip	High volume only Digested duplicate field-collected filter strip Once with each extraction batch of 20 or fewer field-collected samples	Precision ≤ 20% RPD for elements ≥ 5x MDL	Sections 4.4.10.5.1, 4.4.11.7.7, and Table 4.4-3 IO3.5 Section 11.3.11	Operational
Matrix Spike (MS)	High volume only Digested spiked field-collected filter strip Once with each extraction batch of 20 or fewer field-collected samples	Recovery within 80-120% of the nominal spiked amount for all target elements – 75-125% for Sb	Sections 4.4.10.5.1, 4.4.11.7.7, and Table 4.4-3 IO3.5 Section 11.3.10	Operational

7.3 Metals via EPA Compendium Method IO 3.1 and IO 3.5 (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Matrix Spike Duplicate (MSD)	High volume only Duplicate digested spiked field-collected filter strip Once with each extraction batch of 20 or fewer field-collected samples	Recovery within 80-120% of the nominal spiked amount for all target elements - 75-125% for Sb and precision ≤ 20% RPD of MS	Sections 4.4.10.5.1, 4.4.11.7.7, and Table 4.4-3 IO3.5 Section 11.3.11	Operational
Serial Dilution	Five-fold dilution of a field-collected sample digestate Once with every analysis sequence of 20 or fewer field-collected samples	Recovery of 90-110% of undiluted sample for elements ≥ 25x MDL	Section 4.4.11.7.8 IO3.5 Section 11.3.12	Operational
Replicate Analysis	A single additional analysis of a field-collected sample digestate Once with every analysis sequence of 20 or fewer field-collected samples	Precision ≤ 10% RPD for concentrations ≥ 5x MDL	Section 4.4.11.7.9	Operational
Internal Standards (IS)	Non-target elements added to each analyzed solution at the same concentration	60 to 125% recovery	Section 4.4.11.4 IO3.5 Section 11.5	Critical
Field Blank	Sample filter installed in primary sampling unit for minimally 5 minutes Minimally monthly for primary sampling units, as 18% (approximately 1 out of 5) of collocated samples	All target elements < MDL	Section 4.4.5	Operational
Collocated Sample Collection	Field sample collected with a separate sampling unit between 2 and 4 meters from primary sampling unit 10% of primary samples for sites performing collocated sample collection (as prescribed in workplan)	Precision ≤ 20% RPD of primary sample for concentrations ≥ 5x MDL	Section 4.4.4.1	Operational

7.3 Metals via EPA Compendium Method IO 3.1 and IO 3.5 (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Laboratory Readiness and Proficiency				
Proficiency Testing	Blind sample submitted to each laboratory to evaluate laboratory bias Two per calendar year[1]	Each target compound element within ± 25% of the assigned target value Failure of one PT must prompt corrective action. Failure of two consecutive PTs (for a specific core analyte) must prompt qualification of the analyte in field collected samples until return to conformance.	Section 2.1.4.1	Operational and MQO
Method Detection Limit	Determined initially and minimally annually thereafter, with each new lot of filter media, and when method changes alter instrument sensitivity	MDL must be: Arsenic ≤ 0.00023 µg/m^3 Beryllium ≤ 0.00042 µg/m^3 Cadmium ≤ 0.00056 µg/m^3 Lead ≤ 0.15 µg/m^3 Manganese ≤ 0.005 µg/m^3 Nickel ≤ 0.0021 µg/m^3 These MDL MQOs current as of October 2015. Refer to current workplan template for up-to-date MQOs.	Sections 4.1 and 4.4.8	MQO
Stock Standard Solutions	Purchased stock materials for each target element All standards	Certified and accompanied by certificate of analysis	Section 4.4.7	Critical
Working Standard Solutions	Storage of all working standards	Stored in Teflon or suitable plastic bottles	Section 4.4.7 IO3.5 Section 7.2.4	Practical
Sampling Unit Testing and Maintenance				
Field Sampler Flow Rate Calibration	Calibration of sampling unit flow controller Initially and when flow verification checks fail criteria	Flow set to match a certified transfer flow standard	Table 3.3-1 and 4.4.9.2 and 4.4.10.2	Critical

7.3 Metals via EPA Compendium Method IO 3.1 and IO 3.5 (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Sampling Unit Flow Calibration Check	Verification of sampling unit flow rate Minimally quarterly, monthly recommended	Low volume: Within ± 4% of certified transfer standard flow and within ± 5% of design flow	Table 3.3-1 and 40 CFR 58 Appendix A Section 3.3.3 – EPA QA Guidance Document 2.12	Operational
		High volume: Within ± 7% of certified transfer standard flow and within ± 10% of design flow	Table 3.3-1 and 40 CFR 58 Appendix A Section 3.3.3 EPA QA Handbook Section 2.11.7	Operational

7.3 Metals via EPA Compendium Method IO 3.1 and IO 3.5 (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Site Specifications and Maintenance				
Sampling Unit Siting	Verify conformance to requirements Annually	270° unobstructed probe inlet Inlet 2-15 meters above-ground level ≥ 10 meters from drip line of nearest tree Low volume collocated sampling inlets spaced 1-4 meters from primary sampling unit inlet High volume collocated sampling inlets spaced 2-4 meters from primary sampling unit inlet	Section 2.4 40 CFR Part 58 Appendix E	Operational
Data Reporting				
Data Reporting to AQS	Reporting of all results a given calendar quarter Quarterly, within 1820 days of end of calendar quarter	All field-collected sample concentrations reported including data less than MDL. All data must be in local conditions and may additionally be reported in standard conditions Field QC sample and laboratory replicates must also be reported (as prescribed in workplan)	Section 3.3.1.3.15	Operational
AQS Reporting Units	Units must be as specified With each quarterly submission to AQS	mass/volume (ng/m^3 or $\mu g/m^3$)	Section 3.3.1.3.15	Critical
Data Completeness	Valid samples compared to scheduled samples Annually	≥ 85% of scheduled samples	Section 3.2	MQO

7.4 PAHs via EPA Compendium Method TO-13A

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Field Readiness Checks and Collection Activities				
Collection Media	All field-collected samples and matrix quality control samples	Glass cartridge containing two PUF plugs totaling 3" in height, 15 g styrene-divinyl polymer resin, 104-mm quartz fiber filter with 2-µm pore size	Section 4.5.3 TO-13A Section 9.1	Critical
Media Handling	All field-collected samples and laboratory quality control samples	Sample retrieval as soon as possible recommended, preferably within 24 hours, not to exceed 72 hours post-sampling Retrieved sample shipped and stored at ≤ 4°C, protected from light until extraction Damaged cartridges (leaking resin) must be voided.	Section 4.5.4.1 TO-13A Section 11.3.4.10	Operational
Cartridge Lot Blank Check	Analysis of a cartridge from each lot to demonstrate appropriate media cleanliness Minimum of 1 cartridge for each new lot	All target PAHs ≤ 10 ng/cartridge	Section 4.5.3 TO-13A Section 14.2.1	Critical
Sampling Unit Clock/Timer Check	Verified with each sample collection event	Clock/timer accurate to ± 5 minutes of reference for digital timers, within ± 15 minutes for mechanical timers, set to local standard time Sample collection period verified to be midnight to midnight	Table 3.3-1	Operational
Sampling Frequency	One sample every six days according to the EPA National Monitoring Schedule	Sample must be valid or a make-up sample scheduled (refer to Section 2.1.2.1)	Section 4.5.4.1	Critical and MQO
Sampling Period	All field-collected samples	1380-1500 minutes (24 ± 1 hr) starting and ending at midnight	Section 4.5.4.1	Critical and MQO
Sample Flow Rate	All field-collected samples	0.140 to 0.245 m^3/minute for total collection volume of 200 to 350 m^3 (at standard conditions of P = 1 atm and T = 25°C)	Section 4.5.1	Critical
Pre-Sample Collection Warm-up	Only for sampling units without computer controlled flow	Minimum of five minutes (ten minutes are recommended) after sampling head installation but before sample collection	Section 4.5.4 TO-13A Section 11.3.3.3	Practical

7.4 PAHs via EPA Compendium Method TO-13A (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Post-Sample Collection Warm-up	Only for sampling units without computer controlled flow	Minimum of five minutes (ten minutes are recommended) before sampling head retrieval	Section 4.5.4.1	Practical
Sample Receipt				
Chain-of-custody	All field-collected samples including field QC samples	Each cartridge/QFF must be uniquely identified and accompanied by a valid and legible COC with complete sample documentation	Section 3.3.1.3.7	Critical
Sample Holding Time	All field-collected samples and laboratory QC samples	Extraction: 14 days from sample collection (cartridge storage ≤ 4 °C) Analysis: 40 days from extraction (extract storage ≤ 4 °C)	Section 4.5.5.2 TO-13A Section 11.3.4.10	Operational
Sample Receipt Temperature Check	Verification of proper shipping temperature for all field-collected samples upon receipt at the laboratory	Must be ≤ 4°C unless delivery time from field site is ≤ 4 hours	Section 4.5.4.1	Operational
Extraction and GC/MS Analysis				
DFTPP Tuning	5-50 ng injected to tune MS prior to ICAL and every 12 hours of analysis thereafter	For GC/MS operated in full scan or SIM/full scan must meet criteria listed in Table 4.5-2 GC/MS operated in SIM mode must tune to meet criteria in Section 4.5.5.5.2	Section 4.5.5.5.2 TO-13A Section 13.3.3	Critical
Solvent Blank (SB)	Aliquot of solvent analyzed to demonstrate the instrument is sufficiently clean to begin analysis Prior to ICAL and daily beginning CCV	All target, surrogate, and IS compounds not qualitatively detected	Section 4.5.5.5.3 TO-13A Section 14.1.2	Critical
GC/MS Initial Multi-Point Calibration (ICAL)	Minimum of 5 points covering approximately 0.1 to 2.0 µg/mL Initially, following failed CCV, following failed DFTPP tune check, or when changes to the instrument affect calibration response	Average RRF ≤ 30% and each calibration level must be within ± 30% of nominal For linear regression (with either a linear or quadratic fit) correlation coefficient (r) ≥ 0.995 and each calibration level within ± 30% of nominal	Section 4.5.5.5.3 TO-13A Section 13.3.4.5	Critical
Secondary Source Calibration Verification (SSCV)	Secondary source standard prepared at the mid-range of the calibration curve, analyzed immediately after each ICAL	70 to 130% recovery of nominal or RRF within ±30% of ICAL average RRG	Section 4.5.5.5.4	Critical

7.4 PAHs via EPA Compendium Method TO-13A (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Continuing Calibration Verification (CCV)	Mid-range standard analyzed prior to sample analysis on days when an ICAL is not performed, every 12 hours of analysis following the DFTPP check, and at the conclusion of each analytical sequence	70 to 130% recovery of nominal or RRF within ±30% of ICAL average RRG	Section 4.5.5.5.5 TO-13A Section 13.3.5.5	Critical
Method Blank (MB)	Unexposed PUF/resin cartridge and QFF extracted as a sample One with every extraction batch of 20 or fewer field-collected samples	All target PAHs < 2x MDL	Section 4.5.5.5.6 TO-13A Section 13.3.6	Operational
Laboratory Control Sample (LCS)	PUF/resin cartridge and QFF spiked with known amount of target analyte at approximately the lower third of the calibration curve Minimally quarterly; recommended one with every extraction batch of 20 or fewer field-collected samples	All target PAHs 60-120% recovery of nominal spike	Section 4.5.5.5.6 TO-13A Section 13.3.7	Operational
Laboratory Control Sample Duplicate (LCSD)	Duplicate LCS to evaluate precision through extraction and analysis Minimally quarterly, recommended one with every extraction batch of 20 or fewer field-collected samples	All target PAHs 60-120% recovery of nominal spike Precision ≤ 20% RPD of LCS	Section 4.5.5.5.6	Operational
Internal Standards	Deuterated homologues of target PAHs added to every injection except beginning SB	50-200% of the area response of the mid-level ICAL standard from ICAL	Section 4.5.5.5.8 TO-13A Section 13.4.7	Critical
Field Surrogate Compounds	Deuterated homologues of target PAHs added to each cartridge before field deployment, also added to cartridges for laboratory and field QC	Recovery 60-120%	Sections 4.5.3.3 and 4.5.5.5.9 TO-13A Section 13.4.6.3	Operational
Extraction Surrogate Compounds	Deuterated homologues of target PAHs added to each extracted field sample, field QC sample, and laboratory QC sample	Recovery 60-120%	Sections 4.5.5.1.4.2 and 4.5.5.5.9 TO-13A Section 13.4.6.3	Operational

7.4 PAHs via EPA Compendium Method TO-13A (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Retention Time (RT)	Every injection	Target and surrogate compound RT within ± 0.06 relative retention time units (RRT) of mean ICAL RRT Internal standard RT within ± 0.33 minute of the most recent CCV	Section 4.5.5.5.3 TO-13A Sections 13.4.6.3 and 13.3.4.5	Critical
Replicate Analysis	A single additional analysis of a field-collected sample extract Once with every analysis sequence of 20 or fewer field-collected samples (as required by workplan)	Precision ≤ 10% RPD for concentrations ≥ 0.5 µg/mL	Section 4.5.5.5.6	Operational
Field Blank	Blank sample cartridge installed in sampling unit for minimally five minutes Minimally monthly	All target PAHs ≤ 5x MDL	Section 4.5.4.2 TO-13A Section 11.3.4.9	Operational
Collocated Sample Collection	Field sample collected with a separate sampling unit between 2 and 4 meters from primary sampling unit 10% of primary samples for sites performing collocated sample collection (as required by workplan)	Precision ≤ 20% RPD of primary sample for concentrations ≥ 0.5 µg/mL	Section 4.5.4.3	Operational
Compound Identification	Qualitative identification of each target PAH in each standard, blank, QC sample, and field-collected sample (including field QC samples)	Signal-to-noise ≥ 3:1 RT within prescribed window At least one qualifier ion abundance within 15% of ICAL mean Peak apexes co-maximized (within one scan for quadrupole MS) for quantitation and qualifier ions	Section 4.5.5.5.7 TO-13A Section 13.4.3	Critical

7.4 PAHs via EPA Compendium Method TO-13A (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Laboratory Readiness and Proficiency				
Proficiency Testing	Blind sample submitted to each laboratory to evaluate laboratory bias Two per calendar year[1]	Each target compound within ± 25% of the assigned target value Failure of one PT must prompt corrective action. Failure of two consecutive PTs (for a specific core analyte) must prompt qualification of the analyte in field collected samples until return to conformance.	Section 2.1.4.1	Operational and MQO
Method Detection Limit	Determined initially and minimally annually thereafter and when method changes alter instrument sensitivity	MDL must be: Benzo(a)pyrene ≤ 0.00091 µg/m^3 Naphthalene ≤ 0.029 µg/m^3 These MDL MQOs current as of October 2015. Refer to current workplan template for up-to-date MQOs.	Sections 4.1 and 4.5.5.4	MQO
Stock Standard Materials	Purchased stock materials for each target PAH All standards	Certified and accompanied by certificate of analysis	Section 4.5.5.1.2	Critical
Working Standard Solutions	Storage of all working standards	Stored at ≤ -10°C, protected from light	Section 4.5.5.2	Critical
Sampling Unit Testing and Maintenance				
Field Sampler Flow Rate Calibration	Calibration of sampling unit flow controller Initially, when flow verification checks fail criteria, or when instrument maintenance changes flow characteristics of the sampling unit	Flow set to match a certified flow transfer standard	Table 3.3-1 and 4.5.2.1	Critical
Sampling Unit Flow Calibration Check or Audit	Verification of sampling unit flow rate Minimally quarterly, monthly recommended	Flow within ± 10% of certified primary or transfer standard flow and design flow	Table 3.3-1	Critical
Site Specifications and Maintenance				
Sampling Unit Siting	Verify conformance to requirements Annually	270° unobstructed probe inlet Inlet 2-15 meters above-ground level ≥ 10 meters from drip line of nearest tree Collocated sampling inlets spaced 2-4 meters from primary sampling unit inlet	Section 2.4	Operational

7.4 PAHs via EPA Compendium Method TO-13A (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Data Reporting				
Data Reporting to AQS	Reporting of all results a given calendar quarter Quarterly, within 180 days of end of calendar quarter	All field-collected sample concentrations reported including data less than MDL. All data must be in standard conditions. Field QC sample and laboratory replicates must also be reported.	Section 3.3.1.3.15	Operational
AQS Reporting Units	Units must be as specified With each quarterly submission to AQS	mass/volume (ng/m^3 or $\mu g/m^3$)	Section 3.3.1.3.15	Critical
Data Completeness	Valid samples compared to scheduled samples Annually	≥ 85% of scheduled samples	Section 3.2	MQO

APPENDIX A

DRAFT REPORT

ON

DEVELOPMENT OF DATA QUALITY OBJECTIVES (DQOS) FOR THE NATIONAL AMBIENT AIR TOXICS TRENDS MONITORING NETWORK

SEPTEMBER 27, 2002

September 27, 2002

DRAFT REPORT

on

DEVELOPMENT OF DATA QUALITY OBJECTIVES (DQOS) FOR THE NATIONAL AMBIENT AIR TOXICS TRENDS MONITORING NETWORK

Contract No. 68-D-98-030
Work Assignment 5-12

for

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BATTELLE DISCLAIMER

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EXECUTIVE SUMMARY

The Data Quality Objective (DQO) process described in EPA's QA/G-4 document provides a general framework for ensuring that the data collected by EPA meets 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 a program's goals. This process was applied to one of the primary goals of the National Air Toxics Monitoring Network, namely to establish trends and evaluate the effectiveness of HAP reduction strategies. This report documents the results of the DQO process for the local monitoring data requirements for: benzene, 1,3-butadiene, arsenic, chromium, acrolein, and formaldehyde.

The technical approach used followed the conceptual model developed for the $PM_{2.5}$ Federal Reference Method (FRM) DQOs. This conceptual model of simulating daily deviations from a seasonal curve was followed mainly due to its success in use with $PM_{2.5}$ and the flexibility of the conceptual model. It is a quite general model for simulating the characterization of ambient concentrations in terms of annual or multi-year averages from 1 in n day sampling. The model incorporates several sources of variability: seasonal variability, natural day-to-day variability, sampling incompleteness, and measurement error. The measurement error was restricted to a precision component without a bias component, because the mathematical form of the assessment of trends is robust to multiplicative bias. Pollutant specific parameters were used in the modeling. The parameters describing the natural variation of the pollutants were based on data analyses of the Pilot City data and EPA's Air Toxics Data Archive. Finally, separate urban and rural DQOs were established for the pollutants that were sufficiently measured in rural locations of the Pilot Study.

While there are pollutant specific requirements with respect to measurement detection limits, the DQOs established all fall into the same framework. Each pollutant needs to be measured on a schedule of at least once every six days with at least an 85 percent quarterly completeness. The measurement precision needs to be controlled with a coefficient of variation no more than 15 percent. Under these conditions, true decreasing trends of 30 percent or more can be detected at least 90 percent of the time between successive three-year periods. Moreover, the error rate for when there is no true change between successive three-year periods is controlled to be at most 10 percent. Sampling frequency and natural or environmental day-to-day variation are the primary factors affecting these error rates.

1.0 INTRODUCTION

The Data Quality Objective (DQO) process described in EPA's QA/G-4 document provides a general framework for ensuring that the data collected by EPA meets the needs of the intended 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 a program's goals. This process was applied to one of the primary goals of the National Air Toxics Monitoring Network, namely to establish trends and evaluate the effectiveness of HAP reduction strategies. This report documents the results of the DQO process for the local monitoring data requirements for: benzene, 1,3-butadiene, arsenic, chromium, acrolein, and formaldehyde.

The technical approach used followed the conceptual model developed for the $PM_{2.5}$ FRM DQOs. This conceptual model was followed mainly due to its success in use with $PM_{2.5}$ and the flexibility of the conceptual model. It is a quite general model for simulating the characterization of ambient concentrations in terms of annual or multi-year averages from 1 in n day sampling. The model incorporates several sources of variability: seasonal variability, natural day-to-day variability, sampling incompleteness, and measurement error. The measurement error was restricted to a precision component without a bias component because the final mathematical form of the assessment of trends is robust to multiplicative bias. Pollutant specific parameters were used in the modeling. The parameters describing the natural variation of the pollutants were based on data analyses of the Pilot City data and the Air Toxics Archive. Finally, separate urban and rural DQOs were established for the pollutants that were sufficiently measured in rural locations of the Pilot Study.

A workgroup organized by EPA/OAQPS/EMAD provided representatives of data users, decision makers, state and local parties, and monitoring and laboratory personnel. Battelle provided technical statistical support throughout the process with examples and data analyses. The workgroup guided the DQO development and made the decisions that were not driven by data analyses in the DQO development during a series of conference calls. These decisions included items such as establishing a specific mathematical form for measuring trends and establishing limits on the sampling rate. Battelle and EPA also held a meeting in Research Triangle Park, North Carolina, on June 17, 2002 to discuss the development details.

2.0 THE GENERAL DQO PROCESS

This section presents an overview of the seven steps in EPA's QA/G-4 DQO process as applied to one of the primary goals of the National Air Toxics Monitoring Network, namely to establish trends and evaluate the effectiveness of HAP reduction strategies (see *www.epa.gov/quality/qa_docs.html*). The purpose of this section is to provide general discussion on the specific issues that were used in developing the DQOs as they relate to the general DQO process.

The DQO process is a seven-step process based on the scientific method to ensure that the data collected by EPA meet the needs of its data users and decision makers in terms of the

information to be collected, in particular the desired quality and quantity of data. It also provides a framework for checking and evaluating the program goals to make sure they are feasible and that the data are collected efficiently. The seven steps are usually labeled as:

- State the Problem
- Identify the Decision
- Identify the Inputs to the Decision
- Define the Study Boundaries
- Develop a Decision Rule
- Specify Tolerable Limits on the Decision Errors
- Optimize the Design.

This section has general discussion for each of these items. The pollutant specific outcomes of the DQO process are contained in Section 3.

2.1 State the Problem

Characterize the ambient concentrations in the region represented by the monitor to establish any significant downward trend (measured by a percent change between successive 3-year means of the concentrations).

The ability to characterize the trends was statistically modeled. The statistical model was designed by starting with a model similar to the one used for $PM_{2.5}$ FRM data. The ambient concentrations are modeled as deviations from a sine curve, where the sine curve represents seasonality. This sine curve represents long-term daily averages of the concentrations that one would observe at the site. The form used is as follows:

$$A\left[1+\left(\frac{r-1}{r+1}\right)\sin\left(\frac{day}{365}2\ \pi\right)\right]$$

where

A = the long term annual average and
r = the ratio of the highest point on the sine curve to the lowest point. A value of r = 1 indicates no seasonality.)

The natural deviations from the sine curve are assumed to follow a lognormal distribution with a mean that is given by the particular point on the sine curve. (For example, the value of the

sine curve for Day 100 is the mean for all Day 100s across many years.) The coefficient of variation (CV) of the lognormal distribution is assumed to be a constant. The general model considered also allows for the day-to-day deviations from the sine curve to be correlated, but the current DQOs are based on a correlation of zero. (The correlation effectively measures how quickly the concentrations can change from one deviation from the sine curve to another. A correlation of zero indicates that it can change fast enough that values measured on consecutive days would be completely independent. A value of 0.2 would say that a positive deviation from the curve is somewhat more likely to be followed by another positive deviation than a negative deviation. A value of 0.9 would indicate that positive deviations are almost always followed by another positive deviation.) Finally, the measured values are modeled with a normally distributed random measurement error with a constant coefficient of variation (CV). The specific values for the various parameters are pollutant specific.

The population parameters (the degree of seasonality, the autocorrelation, and the CV of the deviations from the sine curve) were estimated from the Pilot City data (and in the case of benzene compared with estimates from the Air Toxics Data Archive). (See Appendix A.) A near worst-case choice was made for each of the parameters. The power curves and decision errors are established via Monte-Carlo simulation of the model with the particular parameters for various combinations of truth and observed percent changes in three-year mean concentrations. The power curves are plotted as functions of the true percent change in the three-year annual means for compound specific combinations of the sampling frequency, completeness, and precision. Decision errors are stated for these worst-case scenarios.

Note: It was decided by the workgroup from budgetary considerations that the proposed DQOs should be constrained to no more than one in six day sampling.

2.2 Identify the Decision

The decision statement should provide a link between the principal study question and possible actions. The potential actions associated with achieving or failing to achieve a particular percent decrease in the observed three-year mean concentration were not defined by the workgroup. However, it was decided that any decision would be based on whether or not a 15 percent decrease was observed. Hence the form of the decision was fixed, and may be specified as follows:

> *Significant decreases (15 percent or more) between successive three-year mean concentration levels will result in … Insignificant decreases, (increases, or decreases of less than 15 percent) will trigger alternate actions of .*

2.3 Identify the Inputs to the Decision

Only six HAPs (benzene, 1,3-butadiene, arsenic, chromium, acrolein, and formaldehyde) were considered in the DQO development. It is assumed that the other pollutants will be represented by at least one of these six. The statements included here apply implicitly to the other HAPs.

It is assumed that the analytical techniques used in the Pilot study will be used throughout the program. Most importantly for the DQOs the Method Detection Limits (MDLs) will not increase. The pollutant specific MDLs assumed are listed in Section 3. Those values were identified as pollutant-site maximums that were achieved by at least two of the pilot sites in each pollutant's case.

Among the key decisions made as a part of the DQO process was that each pollutant will need to be measured on a schedule of at least once every six days with a quarterly completeness of 85 percent for six consecutive years. The completeness criterion was checked against the pilot data, and was generally achieved. All valid measurements count toward the completeness goal, including non-detects. The analysis of the trends at the site level will be based on a percent difference between the mean of the first three annual concentrations and the mean of the last three annual concentrations. Hence for each year the annual average concentration, X_i, needs to be found, i = 1, 2, … 6. Next find the mean, X, for the first three years and the mean, Y, for years 4 through 6 as follows:

$$X = \frac{X_1 + X_2 + X_3}{3} \text{ and } Y = \frac{X_4 + X_5 + X_6}{3}.$$

Then the downward trend, T, is the percent decrease from the first three-year period to the second three-year period. Namely,

$$T = \frac{X - Y}{X} \cdot 100.$$

The Action Level is the cutoff point that separates different decision alternatives. Based on the assumed budgetary constraint of one in six day sampling and the natural variation exhibited by the six compounds considered, an action level of 15 percent was chosen. Hence at least a 15 percent decrease between the two distinct three-year mean concentrations will need to be observed in order to be considered a significant decrease. This assumes that the mean concentrations are above the health standards, and hence it makes sense to consider trends. (Note that characterizing the mean concentrations is a separate goal of the Air Toxics program that has not yet been considered and could result in different DQOs.)

2.4 Define the Study Boundaries

It is desired that the specific location of the monitors be constrained so that they represent neighborhood scale assessment for each of the two three-year periods under consideration. The details of how to ensure this goal have not yet been determined. Some guideline is provided by the Air Toxics Monitoring Concept Paper (see http://www.epa.gov/ttn/antic/airtxfil.html).

2.5 Develop a Decision Rule

The decision rule is an "if ... then" statement for how the various alternatives will be chosen. As noted above the specific alternative actions have not been formalized yet, just the form of the decision rule.

If the percent change between successive three-year average concentration levels is greater than or equal to 15 percent, then …Otherwise …

2.6 Specify Tolerable Limits on the Decision Errors

Since the program will not generate complete, error-free data, there will be some probability of making a decision error. The main goal of the DQO process is to find a workable balance between how complete and error free the data are with acceptable levels of decision errors. To find the balance, the possible errors need to be carefully defined. This usually needs to be done with the recognition that there will be a range, often called the gray zone, where it is impractical to control decision errors.

The QA/G-4 guidance recommends using 0.01 as the starting point for setting decision error rates. However, such a limit would generally require a sampling rate that is not feasible. The workgroup decided on the following limits:

If there is no true decrease in the three-year average concentrations, then the probability of observing a mean concentration for years four through six that is at least 15 percent below the observed mean concentration from years one through three should be no more than 10 percent.

If there is a true decrease in the three-year average concentrations of at least 30 percent, then the probability of observing a mean concentration for years four through six that is less than 15 percent below the observed mean concentration from years one through three should be no more than 10 percent.

Equivalently, the second statement could read that:

If there is a true decrease in the three-year average concentrations of at least 30 percent, then the probability of observing a mean concentration for years four through six that is at least 15 percent below the observed mean concentration from years one through three should be at least 90 percent.

The power curves shown in Section 3 show the probability of observing at least a 15 percent decrease as a function of the true decrease. In terms of the above goals this means that the power curve graphs should start below 10 percent for a true percent change of 0 and end above 90 percent for a true percent change of 30 percent. Since there is a particular interest in the error rates for no true change and for a true change of a 30 percent decrease, this associated x-axis (horizontal axis) range is shown for each curve. Also, it is sometimes useful to know when the two target error rates are achieved. The range of "truth" between these values is referred to as the gray zone, i.e., the range of true percent decreases that cannot be reliably detected by the sampling scheme. These are also given for each curve (and indicated with vertical dotted lines).

2.7 Optimize the Design

In each pollutant's case, a sampling schedule of once every six days is set forth with a quarterly completeness criteria of 85 percent. Pilot City study participants were surveyed and almost all were collecting and obtaining valid data values at a rate that exceeded 85 percent for each of the six compounds considered (valid non-detects counted toward completeness). Hence, the target rate of 85 percent was selected, instead of the more common 75 percent completeness goal. This should make the power curves more representative of the network's expected monitoring conditions.

3.0 DQOS FOR THE SIX STUDY COMPOUNDS

This section states the design values, namely it gives the expected maximum error rates, gray zones, and power curves for each of the six compounds considered explicitly. The parameters describing the natural state of the ambient conditions used to construct the power curves, error rates and gray zone are compound specific based on data from the Pilot Study. (See Appendix A.) In each case, the Pilot City data yielded a range of estimates. The specific values used were the extremes (or nearly so) that would make detecting a downward trend more difficult. Actual performance in almost all cases should be better than that indicated by the power curves, since specific sites would not be characterized by these extremes in each of these parameters. However, since the sensitivity to the different parameters is not the same, the DQOs need to protect against a combined set of extremes. Hence, the use of extremes for network design purposes is conservative.

Since the rural sites can be quite different from urban sites, separate DQOs are shown in those cases where there were sufficient data to support investigating a separate set of DQOs. In the case of formaldehyde, the urban and rural DQOs are essentially the same.

There are twelve input parameters shown in each section. They are:

1. T1. This is the target error rate for when there is no change. It is always 10 percent.

2. T2. This is the target error rate for when there is a 30 percent decrease. It is always 10 percent.

3. The action limit. This is the minimum observed percent change from the mean concentration of the first three years to the mean concentration from the last three years that would be used to indicate that the concentrations have decreased. Decreases less than this amount would not be considered significant decreases in the mean concentration.

4. The sampling rate. It is set to one in six day sampling in each case.

5. The quarterly completeness criterion. This was set to 85 percent based on the recommendation of ERG and a review of the Pilot Study data completeness.

6. Measurement error Coefficient of Variation (CV). This was assumed to be 15 percent for each compound. (A sensitivity analysis showed that the DQOs are robust to moderate changes in this value.)

7. Seasonality ratio. This is a measure of the degree of seasonality. Specifically, it is the ratio of the highest point on the seasonal curve to the lowest point. A value of 1 indicates no seasonality. Larger values make it more difficult to estimate an annual or three-year mean concentration, and hence larger values make it more difficult to measure the percent change.

8. Autocorrelation. This is a measurement of how quickly day-to-day deviation from the seasonal curve can occur. A value of 0 indicates that changes occur quickly enough that each day is independent of the preceding day. Values greater than 0 indicate that the changes are generally slower, so that days with concentrations above the seasonal curve are more likely to be followed by another day above the seasonal curve. Values greater than 0 increase the precision of the three-year means and the percent change between the three-year means. Hence, a value of 0 is the most conservative choice for the DQOs. Zero was used in all cases, because many daily measurements are required to obtain a reliable estimate of this parameter.

9. Population CV. This is a measurement of the natural variation about the seasonal curve. Larger values decrease the precision of the three-year mean concentration estimates and the percent change between them. The power curves are strongly dependent on this parameter, but the estimates can be strongly influenced by a few outlier values. Generally the 90^{th} percentile of the estimates from the Pilot study was used as a balance between these competing forces. This value was then rounded up to be a multiple of 5 percent for the urban DQOs. For the rural DQOs an additional 5 percent was added, since there were fewer rural sites on which to base the estimates.

10. MDL. This is the MDL used in the simulations. The value was chosen to be a reasonably attainable maximum for a site and compound.

11. Initial mean concentration. This is the mean concentration of the first three years in the simulations. Values closer to the MDL decrease the precision of the percent change estimate. The value chosen was approximately equal to the 25^{th} percentile of the site-compound means from the Pilot study.

12. Health Risk Standard. This value is shown for reference only. It was not used in the simulations.

In addition to the power curves, there are three sets of output values.

1. $Error_0$ is the percent of the simulations with no change in the true three-year means that in fact generated at least a 15 percent decrease in the observed three-year means.

2. $Error_{30}$ is the percent of the simulations with a 30 percent decrease in the true three-year means that generated less than a 15 percent decrease in the observed three-year means.

3. The gray zone is the interval of the true decreases that cannot be detected with confidence by the study design. In this range, the probability of observing at least a 15 percent decrease is greater than 10 percent, but less than 90 percent.

In summary, based on variability and uncertainty estimates from the ten-city Pilot Study, the following Sections 3.1 through 3.10 suggest that the specified air toxics trends DQOs will be met for monitoring sites that satisfy the goals of 1 in 6 day sampling, 85 percent completeness, and 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).

3.1 DQOs for Measuring the Percent Decrease of Benzene at Urban Locations

Table 3.1.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of benzene at urban locations. Table 3.1.2 shows the output values from the simulations. Figure 3.1.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.1.2 suggests that the specified air toxics trends DQOs will be met for benzene at urban monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See section 3.0 for definitions of the input parameters and output values.)

Table 3.1.1 DQO input parameters for benzene at urban locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration ($\mu g/m^3$)
10%	15%	1 in 6 day	4.5	85%	1.0
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL ($\mu g/m^3$)**	**Risk Standard ($\mu g/m^3$)**
10%	15%	85%	0	0.044	0.128

Table 3.1.2 DQO output parameters for benzene at urban locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
6%	97%	3% - 26%

Figure 3.1.1 Power curve for detecting a 15 percent decrease between successive three-year means of benzene concentrations based on the data variation found in urban locations of the Pilot Study

3.2 DQOs for Measuring the Percent Decrease of Benzene at Rural Locations

Table 3.2.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of benzene at rural locations. Table 3.2.2 shows the output values from the simulations. Figure 3.2.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.2.2 suggests that the specified air toxics trends DQOs will be met for benzene at rural monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See section 3.0 for definitions of the input parameters and output values.)

Table 3.2.1 DQO input parameters for benzene at rural locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration ($\mu g/m^3$)
10%	15%	1 in 6 day	4.0	60%	1.0
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL ($\mu g/m^3$)**	**Risk Standard ($\mu g/m^3$)**
10%	15%	85%	0	0.044	0.128

Table 3.2.2 DQO output parameters for benzene at rural locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
2%	99%	7% - 23%

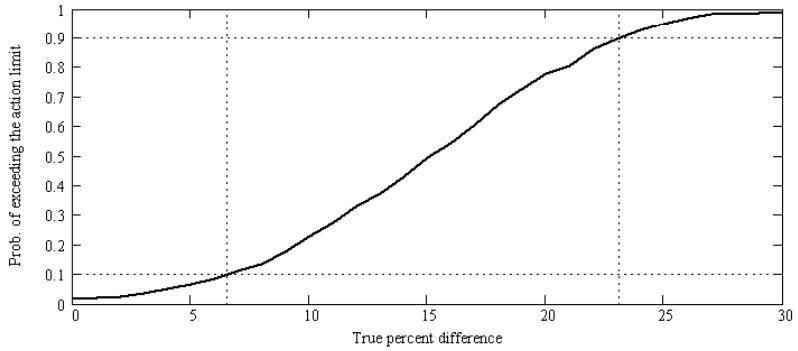


Figure 3.2.1 Power curve for detecting a 15 percent decrease between successive three-year means of benzene concentrations based on the data variation found in rural locations of the Pilot Study

3.3 DQOs for Measuring the Percent Decrease of 1,3-Butadiene at Urban Locations

Table 3.3.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of 1,3-butadiene at urban locations. Table 3.3.2 shows the output values from the simulations. Figure 3.3.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.3.2 suggests that the specified air toxics trends DQOs will be met for 1,3-butadiene at urban monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See section 3.0 for definitions of the input parameters and output values.)

Table 3.3.1 DQO input parameters for 1,3-butadiene at urban locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration ($\mu g/m^3$)
10%	15%	1 in 6 day	7.0	100%	0.1
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL ($\mu g/m^3$)**	**Risk Standard ($\mu g/m^3$)**
10%	15%	85%	0	0.02	10^{-5}

Table 3.3.2 DQO output parameters for 1,3-butadiene at urban locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
10%	94%	0% - 28%

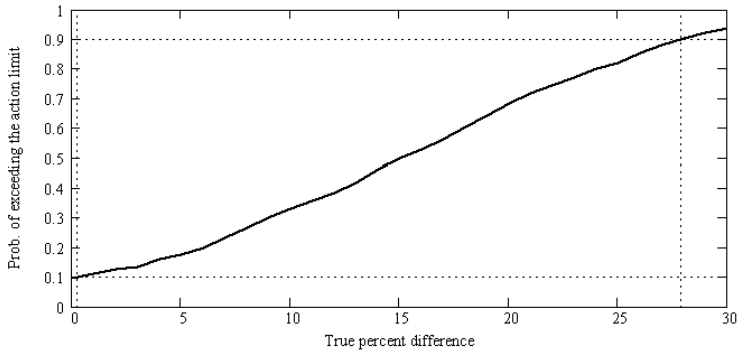


Figure 3.3.1 Power curve for detecting a 15 percent decrease between successive three-year means of 1,3-butadiene concentrations based on the data variation found in urban locations of the Pilot Study

3.4 DQOs for Measuring the Percent Decrease of 1,3-butadiene at Rural Locations

Table 3.4.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of 1,3-butadiene at rural locations. Table 3.4.2 shows the output values from the simulations. Figure 3.4.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.4.2 suggests that the specified air toxics trends DQOs will be met for 1,3-butadiene at rural monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See section 3.0 for definitions of the input parameters and output values.)

Table 3.4.1 DQO input parameters for 1,3-butadiene at rural locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration ($\mu g/m^3$)
10%	15%	1 in 6 day	6.0	75%	0.1
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL ($\mu g/m^3$)**	**Risk Standard ($\mu g/m^3$)**
10%	15%	85%	0	0.02	10^{-5}

Table 3.4.2 DQO output parameters for 1,3-butadiene at rural locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
4%	98%	4% - 25%

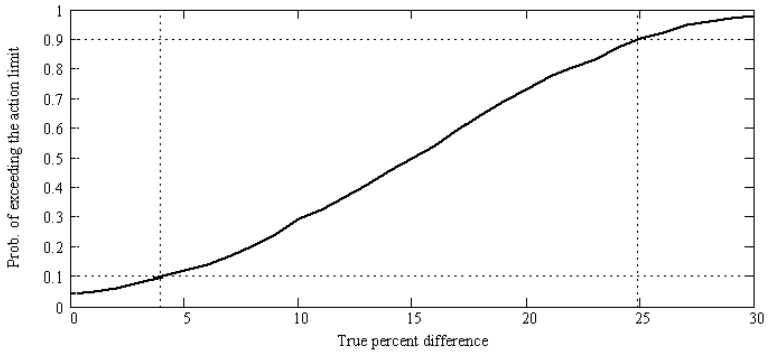


Figure 3.4.1 Power curve for detecting a 15 percent decrease between successive three-year means of 1,3-butadiene concentrations based on the data variation found in rural locations of the Pilot Study

3.5 DQOs for Measuring the Percent Decrease of Arsenic at Urban Locations

Table 3.5.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of arsenic at urban locations. Table 3.5.2 shows the output values from the simulations. Figure 3.5.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.5.2 suggests that the specified air toxics trends DQOs will be met for arsenic at urban monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See section 3.0 for definitions of the input parameters and output values.)

Table 3.5.1 DQO input parameters for arsenic at urban locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration ($\mu g/m^3$)
10%	15%	1 in 6 day	5.0	85%	0.002
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL ($\mu g/m^3$)**	**Risk Standard ($\mu g/m^3$)**
10%	15%	85%	0	0.000046	0.0043

Table 3.5.2 DQO output parameters for arsenic at urban locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
8%	95%	2% - 27%

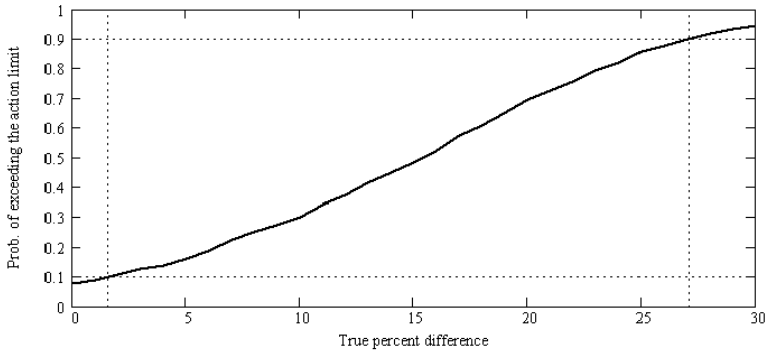


Figure 3.5.1 Power curve for detecting a 15 percent decrease between successive three-year means of arsenic concentrations based on the data variation found in urban locations of the Pilot Study

3.6 DQOs for Measuring the Percent Decrease of Arsenic at Rural Locations

Table 3.6.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of arsenic at rural locations. Table 3.6.2 shows the output values from the simulations. Figure 3.6.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.6.2 suggests that the specified air toxics trends DQOs will be met for arsenic at rural monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See section 3.0 for definitions of the input parameters and output values.)

Table 3.6.1 DQO input parameters for arsenic at rural locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration ($\mu g/m^3$)
10%	15%	1 in 6 day	4.0	65%	0.001
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL ($\mu g/m^3$)**	**Risk Standard ($\mu g/m^3$)**
10%	15%	85%	0	0.000046	0.0043

Table 3.6.2 DQO output parameters for arsenic at rural locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
3%	99%	5% - 24%

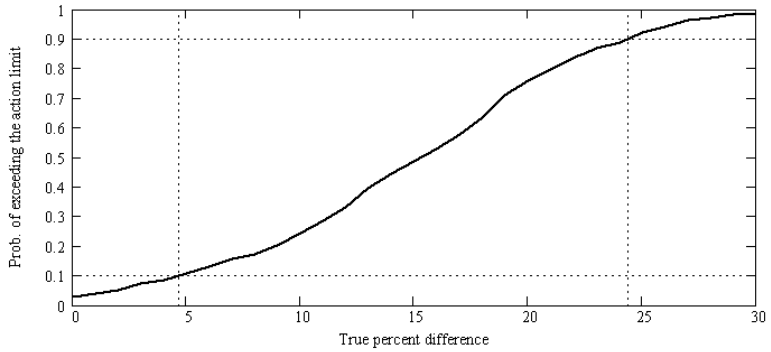


Figure 3.6.1 Power curve for detecting a 15 percent decrease between successive three-year means of arsenic concentrations based on the data variation found in rural locations of the Pilot Study

3.7 DQOs for Measuring the Percent Decrease of Chromium

Table 3.7.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of chromium. Table 3.7.2 shows the output values from the simulations. Figure 3.7.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.7.2 suggests that the specified air toxics trends DQOs will be met for chromium at monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See section 3.0 for definitions of the input parameters and output values.)

Table 3.7.1 DQO input parameters for chromium

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration ($\mu g/m^3$)
10%	15%	1 in 6 day	5.0	90%	0.0015
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL ($\mu g/m^3$)**	**Risk Standard ($\mu g/m^3$)**
10%	15%	85%	0	0.00018	0.012

Table 3.7.2 DQO output parameters for chromium

Error rate for no true change	Error rate for 30% decrease	Gray zone
7%	96%	2% - 27%

Figure 3.7.1 Power curve for detecting a 15 percent decrease between successive three-year means of chromium concentrations based on the data variation found in of the Pilot Study

3.8 DQOs for Measuring the Percent Decrease of Acrolein

Table 3.8.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of acrolein. Table 3.8.2 shows the output values from the simulations. Figure 3.8.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.8.2 suggests that the specified air toxics trends DQOs will be met for acrolein at monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See section 3.0 for definitions of the input parameters and output values.)

Table 3.8.1 DQO input parameters for acrolein

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration ($\mu g/m^3$)
10%	15%	1 in 6 day	4.0	105%	0.4
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL ($\mu g/m^3$)**	**Risk Standard ($\mu g/m^3$)**
10%	15%	85%	0	0.14	-

Table 3.8.2 DQO output parameters for acrolein

Error rate for no true change	Error rate for 30% decrease	Gray zone
10%	91%	0% - 29%

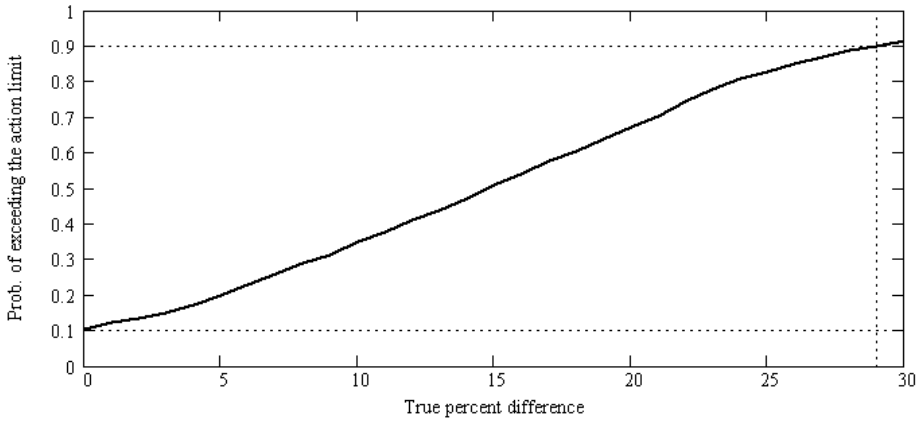


Figure 3.8.1 Power curve for detecting a 15 percent decrease between successive three-year means of acrolein concentrations based on the data variation found in the Pilot Study

3.9 DQOs for Measuring the Percent Decrease of Formaldehyde at Urban Locations

Table 3.9.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of formaldehyde at urban locations. Table 3.9.2 shows the output values from the simulations. Figure 3.9.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.9.2 suggests that the specified air toxics trends DQOs will be met for formaldehyde at urban monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See Section 3.0 for definitions of the input parameters and output values.)

Table 3.9.1 DQO input parameters for formaldehyde at urban locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration ($\mu g/m^3$)
10%	15%	1 in 6 day	7.0	90%	2.5
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL ($\mu g/m^3$)**	**Risk Standard ($\mu g/m^3$)**
10%	15%	85%	0	0.014	$1.3\ 10^{-3}$

Table 3.9.2 DQO output parameters for formaldehyde at urban locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
8%	95%	2% - 27%

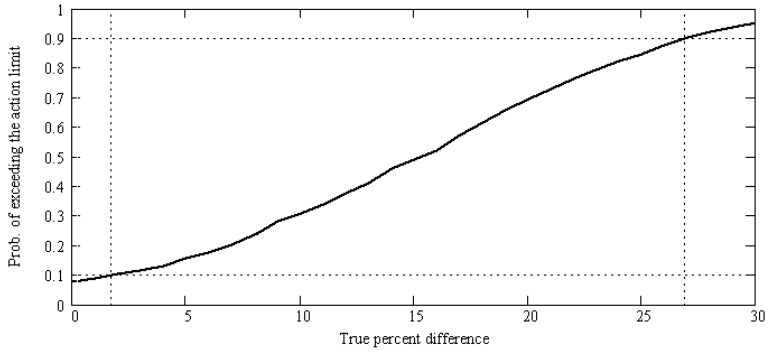


Figure 3.9.1 Power curve for detecting a 15 percent decrease between successive three-year means of formaldehyde concentrations based on the data variation found in urban locations of the Pilot Study

3.10 DQOs for Measuring the Percent Decrease of Formaldehyde at Rural Locations

Table 3.10.1 shows the input parameters used in the simulation model in developing the DQOs for measuring the percent decrease between three-year mean concentrations of formaldehyde at rural locations. Table 3.10.2 shows the output values from the simulations. Figure 3.10.1 shows the associated power curve, which is the probability of observing a 15 percent difference between successive three-year means as a function of the true percent difference in the distinct three-year means. In summary, based on variability and uncertainty estimates from the ten-city Pilot Study data, Table 3.10.2 suggests that the specified air toxics trends DQOs will be met for formaldehyde at rural monitoring sites that satisfy the goals of one in six-day sampling, 85 percent completeness, and 15 percent measurement CV. (See Section 3.0 for definitions of the input parameters and output values.)

Table 3.10.1 DQO input parameters for formaldehyde at rural locations

T1	Action Limit	Sampling Rate	Seasonality	Population CV	Initial Concentration ($\mu g/m^3$)
10%	15%	1 in 6 day	7.0	90%	2.1
T2	**Measurement CV**	**Completeness**	**Autocorrelation**	**MDL ($\mu g/m^3$)**	**Risk Standard ($\mu g/m^3$)**
10%	15%	85%	0	0.014	$1.3\ 10^{-3}$

Table 3.10.2 DQO output parameters for formaldehyde at rural locations

Error rate for no true change	Error rate for 30% decrease	Gray zone
8%	95%	1% - 27%

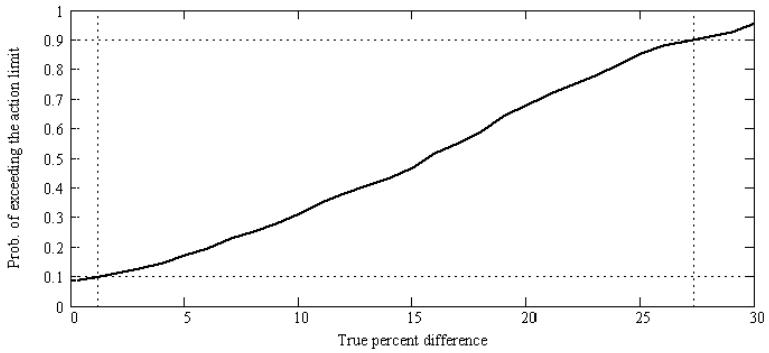


Figure 3.10.1 Power curve for detecting a 15 percent decrease between successive three-year means of formaldehyde concentrations based on the data variation found in rural locations of the Pilot Study

APPENDIX A:

ESTIMATES OF THE DQO PARAMETERS MEASURING ENVIRONMENTAL VARIABILITY

Appendix A: Estimates of the DQO Parameters Measuring Environmental Variability

The DQO parameters that measure the natural environmental variability of a pollutant are generally uncontrollable parameters that have a strong effect on the decision errors. The simulation model described in Section 2.1 uses these parameters. This appendix describes both the parameters and the method for estimating the parameters from the Pilot data. The basic simulation model is that the true concentration levels vary about a sinusoidal curve with one full oscillation in each year. Four parameters describe characteristics of the sine curve and the natural deviations from the sine curve.

Seasonality Ratio

The ratio parameter is a measure of the degree of seasonality in the data. It is the ratio of the high point to the low point on the sine curve. The model assumes that the amplitude of the sine curve is proportional to the mean. The parameter was estimated by finding the monthly averages and taking the ratio of the highest average to the lowest average. The site estimates are restricted to those sites that had at least 3 measurements in each of at least six months.

Population CV

This parameter measures the amount of random, day-to-day variation of the true concentration about the sine curve. This parameter was estimated as follows. Starting with every 6^{th} day measurements (deleting if needed), the natural log of each measurement was found. Next, a new sequence of numbers was created equal to the differences of successive pairs in the sequence of the log-concentrations that were from measurements taken six days apart. Finally, terms were removed from this sequence so that each term in the remaining sequence was based on distinct numbers. Let S be the standard deviation of this set of numbers. The estimate for the population CV is $\sqrt{(\exp(S^2/2)-1)}$. The site estimates are restricted to those with at least ten terms being used in the estimates.

Autocorrelation

The final parameter describing the natural variation of the true concentrations is autocorrelation. This is a measurement of the similarity between successive days. Consider two sets of measurements. First, suppose you had measured the concentrations on every July 15^{th} for the p ast five years. You would expect those five values to be rather spread out. The population CV should capture how different these measurements are from each other. On the other hand, suppose instead you measure the concentrations each day from July 15, 2002, to July 20, 2002. These values may not be as spread out as the other set, simply because they are nearer in time to each other. Autocorrelation measures this effect. A good way to think of autocorrelation is it measures how quickly the local concentrations can change. The value of the autocorrelation ranges between 0 and 1. A value of 0 means that the local concentrations can change very rapidly from day-to-day. A value of 1 means that the local concentrations are constant.

Estimating autocorrelation is more difficult than estimating the population CV. Unless a site had daily measurements, a value of 0 was used. Realistically, 0 is the most conservative case and can always be used. Assuming a site had daily measurements, let S6 be the standard deviation computed as in the section on population CV, based on differences of the logs from every 6th day measurements. Let *S*1 be the same thing using differences of logs from daily measurements. If *S*6 > *S*1, then the autocorrelation was estimated with $\left(S6^2 - S1^2\right)/S6^2$. This method adjusts for seasonality, but still tends to slightly over estimate the truth. There were too few sites with sufficient daily measurements to obtain distributions of the pollutant autocorrelations, so a value of 0 was used for all pollutants.

Initial concentration.

This is simply the mean concentration for the site.

Table A-1 gives the pollutant and site estimates for the seasonality ratio and the initial mean concentrations. Table A-2 gives the pollutant and site population CV estimates.

Table A-1. Estimates of the seasonality ratio and initial mean by pollutant and site

Pollutant	Site ID	Urban / Rural	Mean ($\mu g/m^3$)	Seasonality Ratio
1,3-BUTADIENE	2616300051	Urban	0.3190	3.60
1,3-BUTADIENE	4400700261	Urban	0.2600	3.15
1,3-BUTADIENE	2616300331	Urban	0.2067	2.65
1,3-BUTADIENE	2616300271	Urban	0.2032	2.03
1,3-BUTADIENE	2612500101	Urban	0.2027	1.36
1,3-BUTADIENE	4400700221	Urban	0.1789	5.86
1,3-BUTADIENE	1210300181	Urban	0.1732	4.41
1,3-BUTADIENE	4400700251	Urban	0.1431	4.07
1,3-BUTADIENE	1205710751	Urban	0.1382	5.43
1,3-BUTADIENE	1210310081	Urban	0.1272	3.31
1,3-BUTADIENE	5303300321	Urban	0.1250	6.51
1,3-BUTADIENE	1210350021	Urban	0.1164	2.50
1,3-BUTADIENE	5303300801	Urban	0.1148	5.76
1,3-BUTADIENE	5303300241	Urban	0.1141	7.10
1,3-BUTADIENE	4400700241	Urban	0.1041	4.64
1,3-BUTADIENE	4400710101	Urban	0.1019	5.35
1,3-BUTADIENE	5303300201	Urban	0.1010	10.03
1,3-BUTADIENE	5303300101	Urban	0.0916	10.39
1,3-BUTADIENE	5303300381	Urban	0.0809	5.51
1,3-BUTADIENE	4400300021	Urban	0.0358	5.38
1,3-BUTADIENE	0807700131	Rural	0.2192	6.00
1,3-BUTADIENE	0807700161	Rural	0.1810	4.06
1,3-BUTADIENE	1311300391	Rural	0.1182	3.23
1,3-BUTADIENE	1311300371	Rural	0.0886	1.22
ACROLEIN	4400700261	Urban	0.5904	2.04
ACROLEIN	4400700221	Urban	0.5866	3.36
ACROLEIN	4400700241	Urban	0.5366	2.36
ACROLEIN	4400700251	Urban	0.5366	2.18
ACROLEIN	4400710101	Urban	0.3637	3.34
ACROLEIN	4400300021	Urban	0.3509	3.69
ARSENIC TSP	1205710751	Urban	0.0038	5.01
ARSENIC TSP	2616300271	Urban	0.0033	2.06
ARSENIC TSP	2616300331	Urban	0.0028	3.13
ARSENIC TSP	1210350021	Urban	0.0027	2.94
ARSENIC TSP	1205700811	Urban	0.0027	1.59
ARSENIC TSP	1205710651	Urban	0.0026	1.40
ARSENIC TSP	2616300151	Urban	0.0024	2.68
ARSENIC TSP	1210300181	Urban	0.0024	2.41
ARSENIC TSP	2616300051	Urban	0.0023	2.82
ARSENIC TSP	1210310081	Urban	0.0022	1.56
ARSENIC TSP	2616300011	Urban	0.0021	4.50
ARSENIC TSP	2616300191	Urban	0.0019	2.97
ARSENIC TSP	5303300241	Urban	0.0015	4.48
ARSENIC TSP	2612500101	Urban	0.0014	14.99

Table A-1. Estimates of the seasonality ratio and initial mean by pollutant and site (Cont'd.)

Pollutant	Site ID	Urban / Rural	Mean µg/m^3)	Seasonality Ratio
ARSENIC TSP	5303300201	Urban	0.0010	3.80
ARSENIC TSP	5303300381	Urban	0.0009	3.13
ARSENIC TSP	5303300101	Urban	0.0008	4.94
ARSENIC TSP	0807700161	Rural	0.0016	2.11
ARSENIC TSP	0807700131	Rural	0.0008	3.54
BENZENE	2616300271	Urban	18.8411	12.42
BENZENE	2616300051	Urban	2.2038	1.92
BENZENE	2612500101	Urban	2.0860	1.59
BENZENE	2616300331	Urban	2.0710	1.55
BENZENE	5303300321	Urban	1.7124	3.97
BENZENE	5303300241	Urban	1.6500	2.76
BENZENE	4400700261	Urban	1.4416	2.43
BENZENE	1210300181	Urban	1.2763	3.09
BENZENE	4400700221	Urban	1.2648	3.49
BENZENE	5303300801	Urban	1.1697	1.71
BENZENE	5303300101	Urban	1.1466	2.08
BENZENE	5303300381	Urban	1.1161	2.30
BENZENE	4400700251	Urban	1.1123	3.30
BENZENE	1205710751	Urban	1.0364	2.98
BENZENE	5303300201	Urban	1.0229	2.03
BENZENE	1210310081	Urban	0.9283	2.62
BENZENE	1210350021	Urban	0.8940	1.94
BENZENE	4400700241	Urban	0.8849	3.06
BENZENE	1205710651	Urban	0.8791	2.47
BENZENE	4400710101	Urban	0.8006	4.15
BENZENE	1205700811	Urban	0.6451	2.37
BENZENE	4400300021	Urban	0.4190	5.05
BENZENE	0807700131	Rural	2.7088	2.36
BENZENE	0807700161	Rural	1.8649	3.16
BENZENE	1311300391	Rural	1.1701	2.68
BENZENE	0606530111	Rural	1.0166	3.10
BENZENE	1311300371	Rural	0.9221	1.66
BENZENE	0606530121	Rural	0.7622	2.71
CHROMIUM TSP	2616300271	Urban	0.0075	1.70
CHROMIUM TSP	2616300331	Urban	0.0061	1.68
CHROMIUM TSP	2616300151	Urban	0.0059	2.09
CHROMIUM TSP	2616300051	Urban	0.0049	1.90
CHROMIUM TSP	2616300011	Urban	0.0036	2.31
CHROMIUM TSP	2612500101	Urban	0.0034	1.79
CHROMIUM TSP	2616300191	Urban	0.0031	2.45
CHROMIUM TSP	1205710651	Urban	0.0019	1.62
CHROMIUM TSP	1210350021	Urban	0.0017	3.68
CHROMIUM TSP	5303300201	Urban	0.0017	6.25
CHROMIUM TSP	1210300181	Urban	0.0016	2.51

Table A-1. Estimates of the seasonality ratio and initial mean by pollutant and site (Cont'd.)

Pollutant	Site ID	Urban / Rural	Mean ($\mu g/m^3$)	Seasonality Ratio
CHROMIUM TSP	1205700811	Urban	0.0014	1.87
CHROMIUM TSP	1210310081	Urban	0.0014	2.99
CHROMIUM TSP	1205710751	Urban	0.0014	1.88
CHROMIUM TSP	5303300241	Urban	0.0011	4.23
CHROMIUM TSP	5303300381	Urban	0.0009	3.02
CHROMIUM TSP	5303300101	Urban	0.0009	3.17
FORMALDEHYDE	2616300331	Urban	7.2980	70.55
FORMALDEHYDE	1210300181	Urban	4.1605	2.36
FORMALDEHYDE	4400710101	Urban	4.0325	2.80
FORMALDEHYDE	1205710651	Urban	3.8291	2.25
FORMALDEHYDE	4400700251	Urban	3.6958	2.53
FORMALDEHYDE	2616300271	Urban	3.5940	1.64
FORMALDEHYDE	4400700261	Urban	3.4373	2.36
FORMALDEHYDE	1205700811	Urban	3.4311	2.38
FORMALDEHYDE	4400700221	Urban	3.3888	2.01
FORMALDEHYDE	1210310081	Urban	3.2569	2.56
FORMALDEHYDE	1205710751	Urban	2.9991	2.73
FORMALDEHYDE	2612500101	Urban	2.8279	2.21
FORMALDEHYDE	1210350021	Urban	2.8150	2.31
FORMALDEHYDE	2616300191	Urban	2.7887	4.43
FORMALDEHYDE	4400700241	Urban	2.6769	3.25
FORMALDEHYDE	2616300011	Urban	2.4937	2.98
FORMALDEHYDE	5303300801	Urban	1.7148	2.97
FORMALDEHYDE	5303300321	Urban	1.4839	3.56
FORMALDEHYDE	5303300381	Urban	1.3536	2.53
FORMALDEHYDE	5303300201	Urban	1.3236	3.78
FORMALDEHYDE	5303300241	Urban	1.1373	2.48
FORMALDEHYDE	5303300101	Urban	1.0165	9.43
FORMALDEHYDE	0807700131	Rural	7.3046	6.72
FORMALDEHYDE	0807700161	Rural	7.0664	2.15
FORMALDEHYDE	1311300371	Rural	2.3401	5.10
FORMALDEHYDE	1311300391	Rural	2.1613	3.02
FORMALDEHYDE	0606530121	Rural	2.1246	2.83
FORMALDEHYDE	0606530111	Rural	1.6840	1.90

Table A-2. Population CV estimates by pollutant and site

Pollutant	SITE_ID	Urban / Rural	State	County	Population CV
1,3-BUTADIENE	530330032	Urban	WA	King County	109.2%
1,3-BUTADIENE	530330024	Urban	WA	King County	106.7%
1,3-BUTADIENE	530330010	Urban	WA	King County	97.4%
1,3-BUTADIENE	530330038	Urban	WA	King County	85.8%
1,3-BUTADIENE	440070025	Urban	RI	Providence County	84.2%
1,3-BUTADIENE	530330020	Urban	WA	King County	79.6%
1,3-BUTADIENE	261630027	Urban	MI	Wayne County	78.0%
1,3-BUTADIENE	261250010	Urban	MI	Oakland County	74.7%
1,3-BUTADIENE	440071010	Urban	RI	Providence County	74.1%
1,3-BUTADIENE	530330080	Urban	WA	King County	72.4%
1,3-BUTADIENE	261630033	Urban	MI	Wayne County	67.8%
1,3-BUTADIENE	121030018	Urban	FL	Pinellas County	67.5%
1,3-BUTADIENE	440070024	Urban	RI	Providence County	64.5%
1,3-BUTADIENE	440070022	Urban	RI	Providence County	63.8%
1,3-BUTADIENE	120571075	Urban	FL	Hillsborough County	62.9%
1,3-BUTADIENE	440070026	Urban	RI	Providence County	61.7%
1,3-BUTADIENE	261630005	Urban	MI	Wayne County	59.5%
1,3-BUTADIENE	121031008	Urban	FL	Pinellas County	57.9%
1,3-BUTADIENE	120571065	Urban	FL	Hillsborough County	57.6%
1,3-BUTADIENE	121035002	Urban	FL	Pinellas County	55.7%
1,3-BUTADIENE	440030002	Urban	RI	Kent County	54.1%
1,3-BUTADIENE	120570081	Urban	FL	Hillsborough County	32.7%
1,3-BUTADIENE	080770013	Rural	CO	Mesa County	69.8%
1,3-BUTADIENE	080770016	Rural	CO	Mesa County	67.1%
1,3-BUTADIENE	131130039	Rural	GA	Fayette County	34.5%
1,3-BUTADIENE	131130037	Rural	GA	Fayette County	13.4%
ACROLEIN	440030002	Urban	RI	Kent County	100.3%
ACROLEIN	440071010	Urban	RI	Providence County	80.7%
ACROLEIN	440070024	Urban	RI	Providence County	66.4%
ACROLEIN	440070022	Urban	RI	Providence County	58.7%
ACROLEIN	440070026	Urban	RI	Providence County	53.4%
ACROLEIN	440070025	Urban	RI	Providence County	39.9%
ARSENIC TSP	530330024	Urban	WA	King County	99.6%
ARSENIC TSP	261630001	Urban	MI	Wayne County	83.8%
ARSENIC TSP	261630019	Urban	MI	Wayne County	78.2%
ARSENIC TSP	261630033	Urban	MI	Wayne County	74.3%
ARSENIC TSP	530330010	Urban	WA	King County	72.1%
ARSENIC TSP	261630005	Urban	MI	Wayne County	68.4%
ARSENIC TSP	530330038	Urban	WA	King County	67.2%
ARSENIC TSP	530330020	Urban	WA	King County	64.0%
ARSENIC TSP	261630027	Urban	MI	Wayne County	64.0%
ARSENIC TSP	261630015	Urban	MI	Wayne County	61.1%
ARSENIC TSP	121035002	Urban	FL	Pinellas County	47.3%
ARSENIC TSP	120571075	Urban	FL	Hillsborough County	44.3%

Table A-2. Population CV estimates by pollutant and site (Cont'd.)

Pollutant	SITE_ID	Urban / Rural	State	County	Population CV
ARSENIC TSP	120570081	Urban	FL	Hillsborough County	27.9%
ARSENIC TSP	121031008	Urban	FL	Pinellas County	27.2%
ARSENIC TSP	121030018	Urban	FL	Pinellas County	26.5%
ARSENIC TSP	120571065	Urban	FL	Hillsborough County	22.7%
ARSENIC TSP	080770016	Rural	CO	Mesa County	56.4%
ARSENIC TSP	080770013	Rural	CO	Mesa County	37.0%
BENZENE	261630027	Urban	MI	Wayne County	221.2%
BENZENE	530330032	Urban	WA	King County	93.5%
BENZENE	530330020	Urban	WA	King County	82.2%
BENZENE	530330010	Urban	WA	King County	66.2%
BENZENE	530330024	Urban	WA	King County	64.7%
BENZENE	261630005	Urban	MI	Wayne County	55.1%
BENZENE	121031008	Urban	FL	Pinellas County	49.8%
BENZENE	121030018	Urban	FL	Pinellas County	49.6%
BENZENE	261250010	Urban	MI	Oakland County	48.7%
BENZENE	261630033	Urban	MI	Wayne County	46.2%
BENZENE	440071010	Urban	RI	Providence County	45.8%
BENZENE	121035002	Urban	FL	Pinellas County	41.9%
BENZENE	440070024	Urban	RI	Providence County	41.6%
BENZENE	120571075	Urban	FL	Hillsborough County	41.6%
BENZENE	530330080	Urban	WA	King County	40.1%
BENZENE	530330038	Urban	WA	King County	39.4%
BENZENE	440070025	Urban	RI	Providence County	37.7%
BENZENE	120571065	Urban	FL	Hillsborough County	36.1%
BENZENE	120570081	Urban	FL	Hillsborough County	35.8%
BENZENE	440030002	Urban	RI	Kent County	34.6%
BENZENE	440070022	Urban	RI	Providence County	33.9%
BENZENE	440070026	Urban	RI	Providence County	29.1%
BENZENE	131130037	Rural	GA	Fayette County	54.2%
BENZENE	060653011	Rural	CA	Riverside County	53.7%
BENZENE	131130039	Rural	GA	Fayette County	52.1%
BENZENE	060653012	Rural	CA	Riverside County	49.1%
BENZENE	080770016	Rural	CO	Mesa County	45.8%
BENZENE	080770013	Rural	CO	Mesa County	32.2%
CHROMIUM TSP	530330010	Urban	WA	King County	98.5%
CHROMIUM TSP	530330020	Urban	WA	King County	87.0%
CHROMIUM TSP	530330038	Urban	WA	King County	84.9%
CHROMIUM TSP	530330024	Urban	WA	King County	84.6%
CHROMIUM TSP	121035002	Urban	FL	Pinellas County	61.5%
CHROMIUM TSP	120571065	Urban	FL	Hillsborough County	51.2%
CHROMIUM TSP	120571075	Urban	FL	Hillsborough County	44.6%
CHROMIUM TSP	261630033	Urban	MI	Wayne County	43.9%
CHROMIUM TSP	261630019	Urban	MI	Wayne County	42.7%
CHROMIUM TSP	261630005	Urban	MI	Wayne County	42.0%

Table A-2. Population CV estimates by pollutant and site (Cont'd.)

Pollutant	SITE_ID	Urban / Rural	State	County	Population CV
CHROMIUM TSP	261630015	Urban	MI	Wayne County	39.8%
CHROMIUM TSP	121031008	Urban	FL	Pinellas County	39.5%
CHROMIUM TSP	121030018	Urban	FL	Pinellas County	35.6%
CHROMIUM TSP	120570081	Urban	FL	Hillsborough County	34.5%
CHROMIUM TSP	261630027	Urban	MI	Wayne County	33.0%
CHROMIUM TSP	261630001	Urban	MI	Wayne County	31.8%
FORMALDEHYDE	121031008	Urban	FL	Pinellas County	84.9%
FORMALDEHYDE	120570081	Urban	FL	Hillsborough County	80.1%
FORMALDEHYDE	261630033	Urban	MI	Wayne County	78.0%
FORMALDEHYDE	530330032	Urban	WA	King County	72.2%
FORMALDEHYDE	530330024	Urban	WA	King County	59.7%
FORMALDEHYDE	530330020	Urban	WA	King County	57.9%
FORMALDEHYDE	120571075	Urban	FL	Hillsborough County	55.8%
FORMALDEHYDE	530330010	Urban	WA	King County	53.9%
FORMALDEHYDE	440070024	Urban	RI	Providence County	52.3%
FORMALDEHYDE	530330080	Urban	WA	King County	52.2%
FORMALDEHYDE	261630019	Urban	MI	Wayne County	52.0%
FORMALDEHYDE	530330038	Urban	WA	King County	48.9%
FORMALDEHYDE	261630001	Urban	MI	Wayne County	44.0%
FORMALDEHYDE	121035002	Urban	FL	Pinellas County	40.9%
FORMALDEHYDE	120571065	Urban	FL	Hillsborough County	38.2%
FORMALDEHYDE	440070022	Urban	RI	Providence County	37.4%
FORMALDEHYDE	261630027	Urban	MI	Wayne County	35.8%
FORMALDEHYDE	121030018	Urban	FL	Pinellas County	32.7%
FORMALDEHYDE	261250010	Urban	MI	Oakland County	31.1%
FORMALDEHYDE	440070026	Urban	RI	Providence County	28.3%
FORMALDEHYDE	440071010	Urban	RI	Providence County	26.6%
FORMALDEHYDE	440070025	Urban	RI	Providence County	26.6%
FORMALDEHYDE	060653011	Rural	CA	Riverside County	84.3%
FORMALDEHYDE	131130037	Rural	GA	Fayette County	57.2%
FORMALDEHYDE	060653012	Rural	CA	Riverside County	39.3%
FORMALDEHYDE	131130039	Rural	GA	Fayette County	35.1%
FORMALDEHYDE	080770013	Rural	CO	Mesa County	27.6%
FORMALDEHYDE	080770016	Rural	CO	Mesa County	23.7%

APPENDIX B

NATTS AQS REPORTING GUIDANCE FOR QUALITY ASSURANCE SAMPLES

BLANKS AND PRECISION SAMPLES (COLLOCATED, DUPLICATE, AND REPLICATE REPORTING)

NATTS QA Data Reporting to AQS

Blanks and Precision Samples (Collocated, Duplicate, and Replicate reporting)

Blank Sample Reporting

Blank samples in the NATTS program consist of field blanks, trip blanks, lot blanks, laboratory method blanks, and exposure blanks. Monitoring agencies are required to report field blank, trip blank, and lot blank data to AQS. Optionally, monitoring agencies may also report laboratory method blanks and exposure blanks.

To report blank data, submit a raw blank (RB) transaction for each blank sample. The Blank Type for the various blanks are:

Field blank:	FIELD
Trip blank:	TRIP
Lot blank:	LOT
Laboratory Method Blank:	LAB
Exposure Blank:	FIELD 24HR

To create an RB transaction for a field blank, the Blank Type field is entered as "FIELD" (bold below) as in the following example:

RB|I|11|222|3333|44444|9|7|454|888|**FIELD**|20150101|00:00|0.0463|||||||||||0.0001|

Precision Sample Background

Duplicate and replicate analyses are defined and reported in the NATTS program. Collocated data reporting is used in both the SLAMS and NATTS programs. The purpose of this section is to clarify how data from these assessments should be reported to AQS using the new QA transaction formats. (Please note, the old AQS "RA" and "RP" transactions have been retired and can no longer be used to report data.) The goal is to provide consistent reporting terms and procedures to allow the data to be universally understood.

Simplified schematics are included in this article for illustrative purposes and do not address specifics related to different sampling approaches or methodologies.

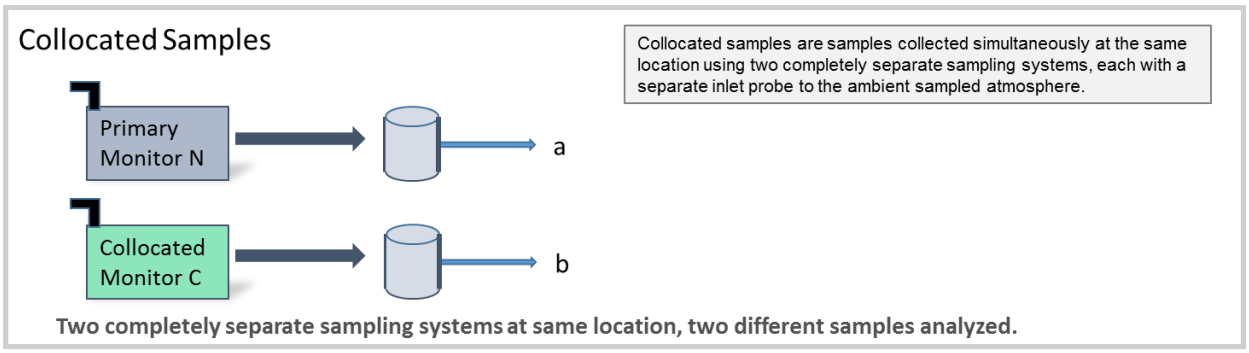
The AQS transaction formatting descriptions are not repeated herein this document. Please refer to the, but may be found on the AQS web site for those (accessed October 19, 2016):

https://aqs.epa.gov/aqsweb/documents/TransactionFormats.html

Collocated Samples

Collocated samples are samples collected simultaneously at the same location using two completely separate sampling systems, each with a separate inlet probe to the ambient sampled atmosphere. The allowable distance between inlet probes is defined in regulations or in program guidance. Both of the monitors (each designated by a separate AQS Parameter Occurrence Code - POCs) have been established in AQS already. The samples are collected and analyzed separately. Each is reported as a sample value for the appropriate monitor.

Schematic



Collocated Sample Reporting Instructions

For AQS to automatically create the 'precision pair' for the primary and collocated samples, the monitors must be identified to the system as QA collocated. One monitor must be designated as the QA primary. If using transactions, the Monitor Collocation Period (MJ) transaction is used. (If using the AQS application, the "QA Collocation" tab on the Maintain Monitor form may be used to enter thesis data). The collocation data must be entered for **both** monitors, with one indicated as the primary, and the other indicated as the collocated (not the primary). In the example below, the primary monitor is indicated by the bolded 'Y' (yes, this is the primary) in the Primary Sampler Indicator in the first MJ string and the collocated monitor by the bolded 'N' (no, this is not the primary) in the Primary Sampler Indicator in the second MJ string.

Once the monitors have been identified as collocated this is done, there are no additional reporting requirements; simply report the raw data from each monitor (From the schematic, value 'a' from the primary monitor 'N' and value 'b' from the collocated monitor 'C'). Once this is done, AQS will know to pair data from these two monitors for the date range specified.

A set of transactions must be created for each time period the monitors are operating together. The transactions have a begin date and end date for the operational period. The end date may be left blank if the collocation period is still active (as indicated in the example below). To define a collocation, submit two MJ transactions (example below with differences bolded and where primary monitor 'N' is POC 5 and collocated monitor 'C' is POC 9):

```
MJ|I|11|222|3333|44444|5|20150101||3|Y
MJ|I|11|222|3333|44444|9|20150101||3|N
```

Report two Raw Data (RD) transactions for each time sample data are to be reported from both monitors; one for each monitor (POC). (In this example, sample 'a' is 0.0463 from monitor 'N' (POC 5) and sample 'b' from monitor 'C' (POC 9) is 0.0458):

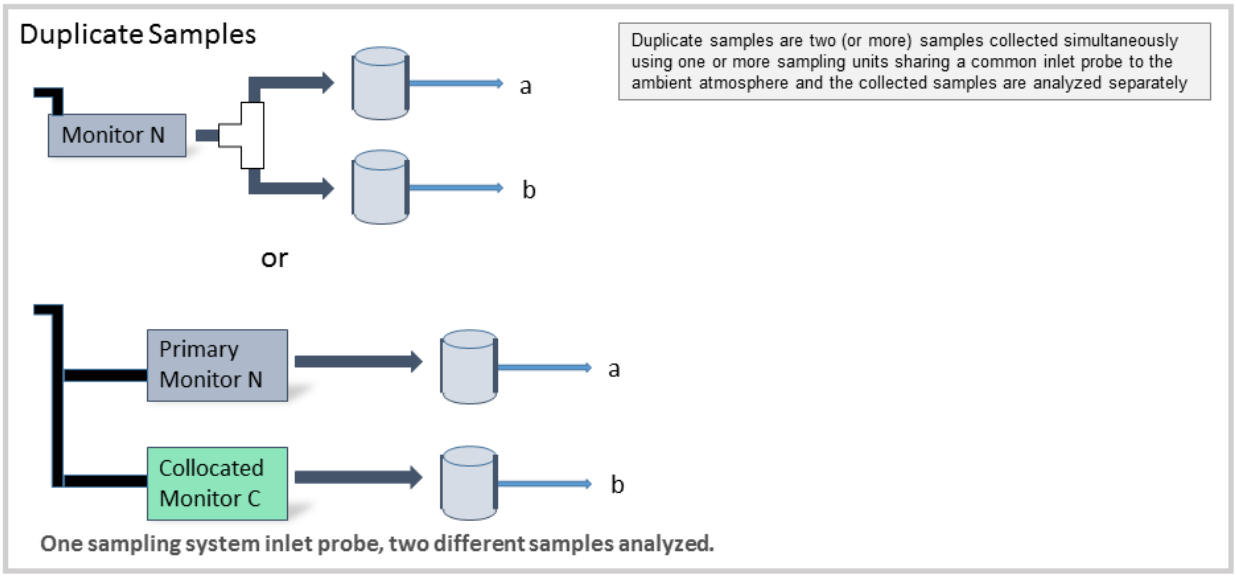
```
RD|I|11|222|3333|44444|5|7|454|888|20150101|00:00|0.0463||6|||||||||||0.0001|0. 0005
RD|I|11|222|3333|44444|9|7|454|888|20150101|00:00|0.0458||6|||||||||||0.0001|0.0005
```

Since there are two monitors involved, each sample is reported for its appropriate POC and there will be an RD transaction for every time there is a valid sample from each monitor (e.g., two per day in this scenario). If the sample value from one POC is not available, report a null data code for that monitor (that is, do not report the sample value from the collocated monitor as being from the primary POC).

Duplicate Samples

Duplicate samples are two (or more) samples collected simultaneously using one or more sampling units sharing a common inlet probe to the ambient atmosphere and the collected samples are analyzed separately. This simultaneous collection may be accomplished by "teeing" the line from the flow control device (sampling unit) to the media (e.g. canisters), and then doubling the collection flow rate, or may be accomplished by collecting one discrete sample via two separate flow control devices (sampling units) connected to the same inlet probe.

Schematic



Duplicate Sample Reporting Instructions

In this case, there is only one inlet probe involved but with multiple samples. Since only one inlet probe is involved, all data should be reported for the same POC.

First, report the raw data as you normally would via the RD transaction. Report just one value, the one for the sample obtained through the 'primary' hardware (the normal flow path or normal canister, etc. as defined by the monitoring organization convention – typically this would be sample 'a'). In this case, if sample 'a' comes from the primary hardware and has a value of 54.956, you would report:

RD|I|11|222|3333|44444|**5**|7|454|888|20150101|00:00|**54.956**||6|||||||||||0.0001|0.0005

If the primary value is null for some reason, the duplicate value may be reported as the sample value for this POC in the RD transaction. In this case, there is not a valid duplicate assessment to report. If all duplicates are null, an RD transaction with no sample value and a null data code should be reported.

Each of the duplicate sample values is then also reported via the QA – Duplicate transaction. This transaction has room for up to 5 duplicate sample values. Report them in any order, starting with 1 and proceeding through the number of samples. In the schematic, there are two samples (a 'primary' and a 'duplicate') so sample value 'a' would be reported as Duplicate Value 1 and sample value 'b' would be reported as Duplicate Value 2. The same value reported on the Raw Data transaction must be one of the values reported on the QA – Duplicate transaction.

Note that there is no sampling time reported on the QA – Duplicate transaction. Instead, there is an Assessment Date and an Assessment Number. If multiple duplicate samples are performed on the same day, label the first with Assessment Number = 1, the second with Assessment Number = 2, and so on. Also note that all values must be reported in the same units of measure.

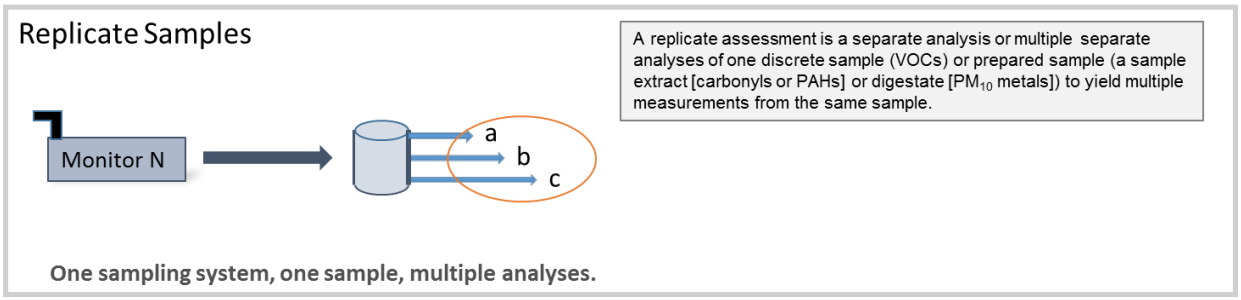
Here is an example QA – Duplicate transaction (with sample 'a' = 54.956 and sample 'b' = 51.443 – Assessment Number '1' bolded):

QA|I|Duplicate|999|11|222|3333|44444|5|20150101|**1**|454|888|54.956|51.443||||

Replicate Analysis

A replicate assessment is a separate analysis or multiple separate analyses of one discrete sample (VOCs) or prepared sample (a sample extract [carbonyls or PAHs] or digestate [PM_{10} metals]) to yield multiple measurements from the same sample.

Schematic



Replicate Sample Reporting Instructions

Again in this case, there is only one AQS monitor (POC) involved and one single sample, however multiple analyses of the sample.

First, report the raw data as you normally would via an RD transaction. Report just one value, according to your laboratory's convention for reporting replicate data (e.g. the first replicate). In this case, if you have chosen replicate 'a' as your raw data value and it has a value of 0.844, you would report:

```
RD|I|11|222|3333|44444|5|7|454|888|20150101|00:00|0.844||6|||||||||||0.0001|0.0005
```

If the normally reported value is null for some reason, one of the other replicate values may be reported as the sample value for this POC in the RD transaction. If only one of the replicate values remains valid, there is not a valid replicate assessment to report. If all replicates are null, an RD transaction with no sample value and a null data code should be reported.

Once the RD transaction is completed, if two or more replicates are valid, these are reported via the QA – Replicate transaction. This transaction has room for up to 5 replicate sample values. Report them in any order, starting with 1 and proceeding through the number of samples. In the schematic above there are three replicates 'a', 'b', and 'c', thus analytical value 'a' would be reported as Replicate Value 1, analytical value 'b' would be reported as Replicate Value 2, and analytical value 'c' would be reported as Replicate Value 3.

Note that there is no sampling time reported on this transaction. Instead, there is an Assessment Date and an Assessment Number. If multiple replicate samples are collected on the same day, label the first with Assessment Number = 1 (indicated below in bold), the second with

Assessment Number = 2, and so on. Also note that all values must be reported in the same units of measure.

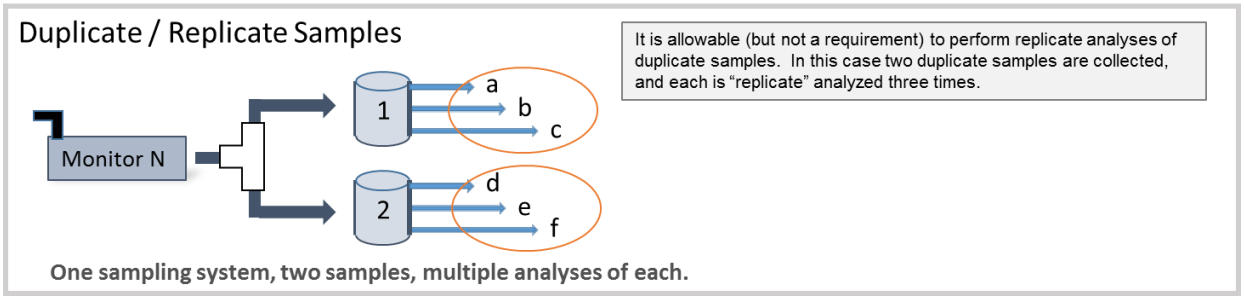
Here is a sample QA – Replicate transaction (if sample values ‘a’, ‘b’, and ‘c’ are 0.844, 0.843, and 0.792, respectively):

```
QA|I|Replicate|999|11|222|333|44444|5|20210101|1|454|888|0.844|0.843|0.792|||
```

Combining Duplicates and Replicate Analysis

It is possible to collect duplicate samples simultaneously and perform replicate analyses of these duplicate samples. This is often referred to as a duplicate/replicate sample. In this case (see schematic below), there are two duplicate samples, ‘1’ and ‘2’. Duplicate Sample ‘1’ has three replicates: ‘a’, ‘b’, and ‘c’. Duplicate Sample ‘2’ has three replicates: ‘d’, ‘e’, and ‘f’.

Schematic



Duplicate/Replicate Reporting Instructions

This scenario requires the reporting of an RD transaction, a QA – Duplicate transaction, and a QA – Replicate transaction to AQS.

For the RD transaction, follow the same rules to report the value from the primary (normal) hardware (this would typically be sample ‘1’, replicate ‘a’) and operations procedure path if possible; follow the convention established by the laboratory. If the normal hardware path yields sample ‘1a’ you would report (in this case the value is represented by the “a” in the appropriate place, with spaces for clarity):

```
RD|I|11|222|3333|44444|5|7|454|888|20150101|00:00| a ||6|||||||||||||0.0001|0.0005
```

For the QA - Duplicate transaction: select one of the replicate analyses each from the primary and duplicate sample (using the convention established by the laboratory) and report those on the QA – Duplicate transaction. If the values to be reported are ‘1a’ and ‘2d’, the record would look like this (again, values are represented by ‘a’ and ‘d’, spaces added for clarity):

```
QA|I|Duplicate|999|11|222|333|44444|5|20210101|1|454|888| a | d ||||
```

There are only two duplicate samples (one pair) in this case because only two paths were assessed. (That is, you are not allowed to cross-multiply the replicate analyses to create additional duplicate assessments [pairs].)

For the replicate transaction: report this as two assessments. Assessment Number 1 for the day would include the values for replicates ‘a’, ‘b’, and ‘c’. Assessment Number 2 for the day would include values for replicates ‘d’, ‘e’, and ‘f’.

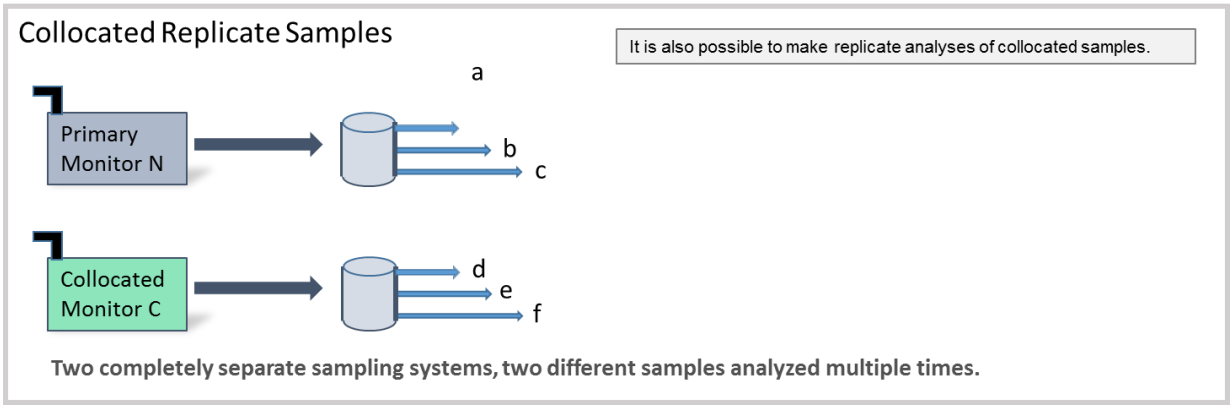
The example transactions, using letters in place of the values:

```
QA|I|Replicate|999|11|222|333|44444|5|20210101|1|454|888| a | b | c |||
QA|I|Replicate|999|11|222|333|44444|5|20210101|2|454|888| d | e | f |||
```

Combining Collocated Samples and Replicate Analysis

It is also possible to make replicate analyses of collocated samples. Theseis is are sometimes referred to as collocated replicate samples.

Schematic



Collocated Replicate Reporting Instructions

Since collocated monitors report all data independently, report these data for each monitor (e.g., under its own POC) according to the replicate reporting instructions.

APPENDIX C

EPA ROUNDING GUIDANCE

Provided by EPA Region IV

Rounding Policy for Evaluating NAAQS QA/QC Acceptance Criteria

The following outlines EPA's Rounding Policy for evaluating Quality Assurance / Quality Control (QA/QC) acceptance criteria. This policy is being provided to air monitoring organizations in order to ensure consistency across the country in the validation of monitoring data that is used for demonstrating compliance with the National Ambient Air Quality Standards (NAAQS).

EPA's interpretation of standard rounding conventions is that the resolution of the measurement device or instrument determines the significant figures used for rounding. The acceptance criteria promulgated in the appendices of 40 CFR Part 50, or otherwise established in EPA guidance documents, are not physical measurements. As an example, the quality control (QC) acceptance criterion of ±5% stated in the fine particulate matter regulations (40 CFR Part 50, Appendix L, Section 7.4.3.1) is not a measurement and, as such, does not directly contribute to either the significant figures or to rounding. However, the flow rate of the sampler – measured either internally by the flow rate control system or externally with a flow rate audit standard – is a measurement, and as such, will contribute to the significant figures and rounding. EPA's position is that it is not acceptable to adjust or modify acceptance criteria through rounding or other means.

Example using $PM_{2.5}$ Sampler Design Flow Rate

40 CFR Part 50, Appendix L, Section 7.4.3.1 defines the 24-hour sample flow rate acceptance criterion as ±5% of the design flow rate of the sampler (16.67 liters per minute, LPM). The QC acceptance criterion of ±5% stated in regulation is not a measurement and, therefore, does not contribute towards significant figures or rounding. The measurement in this example is the flow rate of the sampler. $PM_{2.5}$ samplers display flow rate measurements to the hundredths place (resolution) – e.g., 16.67 LPM, which has 4 significant figures. Multiplying the design flow rate (16.67 LPM) by the ±5% acceptance criterion defines the acceptable flow regime for the sampler. By maintaining 4 significant figures – with values greater than 5 rounding up – the computations provide the following results:

- The low range is -5% of the design flow: $0.95 \times 16.67 = 15.8365 \approx 15.84$
- The upper range is +5% of the design flow: $1.05 \times 16.67 = 17.5035 \approx 17.50$

Rounding in this manner, the lower and upper acceptance limits for the flow rate measurement are defined as 15.84 and 17.50 LPM, respectively.

40 CFR Part 58, Appendix A, Section 3.2.1 requires monthly $PM_{2.5}$ flow rate verifications. The verification is completed with an independent audit standard (flow device). The monthly check includes a calculation to ensure the flow rate falls within ±5% of the design flow rate (see

Method 2.12, Section 7.4.7). Therefore, flow rates obtained during monthly flow rate verification checks should measure between 15.84 – 17.50 LPM, as defined above.

Measurements, in general, are approximate numbers and contain some degree of error at the outset; therefore, care must be taken to avoid introducing additional error into the final results. With regards to the $PM_{2.5}$ sampler's design flow rate, it is not acceptable to round the ±5% acceptance criterion such that any calculated percent difference up to ±5.4% is acceptable – because rounding the acceptance criterion increases the error in the measurement. It is important to note that the $PM_{2.5}$ sampler must maintain a volumetric flow rate of approximately 16.67 LPM in order for its inertial separators to appropriately fractionate the collected ambient air particles. Flow rates greater than 5% of the nominal 16.67 LPM will shift the cut point of the inertial separator lower than the required aerodynamic diameter of 2.5 microns and, thus, block the larger fraction of the $PM_{2.5}$ sample from being collected on the sample filter. Conversely, as the sampler's flow rate drops below -5% of the nominal 16.67 LPM, the inertial separator will allow particulate matter with aerodynamic diameters unacceptably larger than 2.5 microns to be passed to the sample filter. Therefore, it is imperative that the flow rate of the sampler fall within the ±5% acceptance criterion.

A Note on Resolution and Rounding

Measurement devices will display their measurements to varying degrees of resolution. For example, some flow rate devices may show measurements to tenths place resolution, whereas others may show measurements to the hundredths place. The same holds true for thermometers, barometers, and other instruments. With this in mind, rounding should be based on the measurement having the least number of significant figures. For example, if a low-volume PM_{10} sampler displays flow rate measurements to the tenths place (3 significant figures), but is audited with a flow device that displays measurements to the hundredths place (4 significant figures), the rounding in this scenario will be kept to 3 significant figures.

Table 1 below lists some examples of NAAQS regulatory QA/QC acceptance criteria with EPA's interpretation of the allowable acceptance ranges, as well as a column that identifies results that **exceed** the stated acceptance limits. Table 1 is not a comprehensive list of ambient air monitoring QA/QC acceptance criteria. Rather, Table 1 is provided to demonstrate how EPA evaluates acceptance criteria with respect to measurement resolution.

The validation templates in the QA Handbook Vol II will be revised to meet this policy.

If you have any questions regarding this policy or the rounding conventions described, please contact your EPA Regional Office for assistance.

Table 1: Examples of Quality Control Acceptance Criteria

Regulatory Method Requirement	Method Acceptance Criteria	Typical Measurement Resolution	Acceptance Range (Passing Results)			Exceeding QA/QC Check
Shelter Temperature	20 to 30°C or FEM op. range	1 Decimal, 3 SF*	20.0 to 30.0°C or FEM op. range			≤ 19.9°C ≥ 30.1°C
PM2.5 Design Flow (16.67 lpm)	±5%	2 Decimal, 4 SF	15.84 to 17.50 lpm			≤ -5.1% ≥ +5.1%
PM2.5 Transfer Standard Tolerance	±4%	2 Decimal, 4 SF	-4% Audit Std	Sampler Display	+4% Audit Std	≤ -4.1% ≥ +4.1%
				15.84	16.47	
			16.00	16.67	17.34	
			16.80	17.50		
PM2.5 Lab: Mean Temp 24-hr Mean	20 to 23°C	1 Decimal, 3 SF	20.0 to 23.0°C			≤ 19.9°C ≥ 23.1°C
PM2.5 Lab: Temp Control SD over 24-hr	±2°C	1 Decimal, 3 SF	±2.0°C			≤ -2.1°C ≥ +2.1°C
PM2.5 Lab: Mean RH 24-hr Mean	30% to 40%	1 Decimal, 3 SF	30.0% to 40.0%			≤ 29.9% ≥ 40.1%
PM2.5 Lab: RH Control SD over 24-hr	±5%	1 Decimal, 3 SF	±5.0%			≤ -5.1% ≥ +5.1%
PM2.5 Lab: Difference in 24-hr RH Means	±5%	1 Decimal, 3 SF	±5.0%			≤ -5.1% ≥ +5.1%

*SF = Significant Figures