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AIR

Pilot City Air Toxics Measurements Summary

This document is intended only for use by the participants in the FY2000 and FY2001 Ambient Air Toxics Pilot Monitoring Program and does not constitute guidance which is generally applicable to State and local agencies. Its purpose is to ensure consistency among Pilot monitoring project measurements so that analyses of the resulting data can be evaluated based on minimal variables.

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Foreword

In order to provide consistency in the data set generated by the Pilot Toxics Monitoring network, a laboratory measurements work group was formed to discuss the procedures to be used for measurements. This group of laboratory, State, local, Regional and EPA representatives had a series of discussions to define critical details of the measurement procedures needed to provide data to meet the needs of the NATA, the data users, and the national air toxics Pilot City monitoring program. The purpose of this document is to outline the procedures that the laboratory work group have defined. The document is to be used as a supplement to the EPA Compendium of Methods identified for use by the Pilot City network. Specifically, Method TO-15A, "Determination of Volatile Organic Compounds in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry, GC/MS."; TO-11A, "Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography, HPLC"; and IO-3.5, "Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma/Mass Spectrometry, ICP/MS".

Although the details of the procedures described below are not entirely consistent with the Compendium of Methods, items called out in this document are specific to the data quality goals of the Pilot monitoring program. This guideline is provided to assist states in implementation of the Pilot monitoring network. This document is not policy and does not contain legally binding requirements, nor is it regulation. It is intended only for use by the participants in the FY2000 and FY2001 Ambient Air Toxics Pilot Monitoring Program and does not constitute guidance which is generally applicable to State and local agencies. Its purpose is to ensure consistency among Pilot monitoring project measurements so that analyses of the resulting data can be evaluated based on minimal variables. This document is intended for use by those already familiar with the analysis of field samples for volatile organic compounds (VOCs), carbonyl compounds and metals.

As this document is being issued, a Data Management work group is being convened to identify and resolve issues related to reporting of data (e.g., concentration data reporting units, AIRS method codes, etc.). Please refer to the reports of this group for clarification of data management issues.

1.0 Background

To address the concerns about the prevalence of air toxics emissions and to meet EPA's strategic goals, a national air toxics program has been designed to characterize, prioritize, and equitably address the impacts of HAPs on the public health and environment. The national air toxics program seeks to address air toxics problems through a combination of activities and authorities, including regulatory approaches and voluntary partnerships. One of the key activities is the National Air Toxics Assessment (NATA). NATA activities will help EPA identify areas of concern, characterize human health and ecosystem risks and track progress of trends.

As outlined in the air toxics monitoring "Concept Paper", posted at http://www.epa.gov/ttn/amtic/files/ambient/airtox/cncp-sab.pdf, the role of ambient monitoring to support NATA activities includes:

- characterization of ambient concentrations and deposition in representative monitoring areas;
- provide data to support and evaluate dispersion and deposition models; and
- establish trends and evaluate the effectiveness of HAP reduction strategies.

In addition, initial pilot monitoring together with data analysis of existing measurements will be needed to provide information on spatial and temporal variability of ambient air toxics. This information will aid in providing state and local air agencies important information about their particular network needs. The pilot monitoring program will also provide very useful information to help the EPA design a long-term national air toxics monitoring network.

In order to provide consistency in the data set generated by the Pilot City Program, a laboratory work group was formed to discuss the details regarding procedures to be used for measurements. This group of laboratory, State, local, Regional and EPA representatives met to define critical details of the measurement procedures needed to provide data that will meet the needs of the NATA, the data users, and the national air toxics monitoring program. The primary goal of the laboratory work group was to develop consistent procedures for use by all cities participating in the Pilot Study in order to maximize the data comparability. Consistency and comparability of data is very

important due to differences in data reporting procedures, method detection limit determination, and other issues that may create an artificial bias in the data base as a result of the preponderance of values not detected.

The purpose of this document is to outline the procedures that the laboratory measurements work group have defined. The document is to be used as a supplement to the EPA Compendium of Methods identified for use by the Pilot City network. Specifically, Method TO-15A, "Determination of Volatile Organic Compounds in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry, GC/MS."; TO-11A, "Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography, HPLC"; and IO-3.5, "Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma/Mass Spectrometry, ICP/MS". This document is intended to provide guidance to those who are already familiar with the analysis of field samples for VOCs, carbonyls and metals.

Although the details described below are not entirely consistent with the Compendium of Methods, items called out in this document are specific procedures needed to meet the data quality goals of the Pilot monitoring program. This guideline is provided to assist states in implementation of the Pilot monitoring network. This document is not policy and does not contain legally binding requirements, nor is it regulation. While it presents recommendations and suggestions regarding techniques for the measurement of toxic air pollutants for the Pilot Air Toxics Monitoring network, it may not be appropriate for other situations.

2.0 Method Detection Limit (MDL)

It is recognized that laboratories may obtain varying detection limits based on the procedure used and level of the standard chosen for the method detection limit (MDL) study. It is also recognized that data measured below the detection limit has a high level of uncertainty and in theory cannot be reliably measured or quantitatively distinguished from zero or instrument noise. One of the key goals of this pilot program is to gather measurement data for use in evaluating the issue of calculating annual averages with data sets containing several observations less than the MDL. Annual-average concentrations and comparisons to modeled estimates can be highly uncertain when a large percentage of the measurements are below the MDL. To estimate annual average concentrations from monitoring data, the data user generally substitutes ½ MDL for those observations reported as less than MDL. In

order to gather additional data to help improve the annual average determinations and shed light on the quality of data at and below the MDL, "uncensored" data will be reported by the Pilot City laboratories. An important facet of this "uncensored" data set will be the determination and reporting of the uncertainty associated with data. The uncertainty estimates will be determined from data generated by collocated monitors for precision.

A quote from the recent Science Advisory Board (SAB) review: "*Just because an analytical result is below the MDL does not mean that the laboratory has not been able to measure a value, but rather that the measurement has less reliability than others that are above the MDL. Subcommittee members stated that it is more useful to have laboratories report all data with associated uncertainties than to have laboratories censor the data."* Although the values less than the MDL cannot be reliably measured or quantitatively distinguished from zero, they have potential value in computation of certain summary statistics (e.g. annual average concentration). The SAB review can be obtained from the SAB web site under FY2000 full reports at http://www.epa.gov/sab/fiscal00.htm

The guidance given in 40 CFR Appendix B to Part 136, "Definition and procedure for determination of the method detection limit"(See Appendix H of this document), will be used. Method detection limit is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

2.1 Volatile Organic Compound (VOC) HAPs

Estimates of the method detection limits for the volatile organic compound (VOC) HAPs will be determined in the following manner:

- A minimum of seven aliquots of the sample (individual canister samples) will be prepared and each processed through the entire analytical method.
- The MDL should be determined on an annual basis, as a minimum, and when significant instrument changes or maintenance occurs.
- Canisters should be humidified prior to MDL determination; refer to section on humidification contained in this document.
- Individual canisters will be analyzed over a minimum period of 2 days (no maximum period is specified).

- All computations are made according to the defined method with the final results in the method reporting units (ppbv for VOC).
- The guidance in 40CFR will be used to determine the suggested concentration ranges for the individual canister (1 to 5 times the estimated detection limit), which should correspond to approximately 0.1 to 0.5 ppbv.
- Reasonableness of the calculated MDL will be determined using the iterative procedure as described in 40 CFR Appendix B, section 7, which involves preparing additional standards at the calculated MDL and analyzing. This may be difficult to implement with calculated MDLs as low as 0.02 ppbv. Laboratory managers will be using the iterative procedure along with their technical expertise and judgement to determine whether the calculated MDL is adequately representative of the instrument capabilities.

2.2 Carbonyl Compounds

Estimates of the method detection limits for the carbonyl HAPs (formaldehyde and acetaldehyde) will be determined in the following manner:

- A minimum of seven cartridges are spiked with derivatized compounds. Underivatized compounds may be used at the discretion of the laboratory.
- The MDL should be determined on an annual basis, as a minimum, and when significant instrument changes or maintenance occurs.
- Individual spiked cartridges are extracted and analyzed no sooner than 24 hours after spiking.
- Each cartridge is processed through the entire analytical method. All computations are made according to the defined method with the final results in the method reporting units (total ug converted to ppbv based on typical sample volume in L for a 24-hr sample).
- The guidance in 40CFR will be used to determine the suggested concentration ranges for the individual cartridges (1 to 5 times the estimated detection limit), which should correspond to about 0.03 to 0.15 µg per cartridge for formaldehyde and 0.05 to 0.25 :g per cartridge for acetaldehyde (based on 500-L sample volume).
- Reasonableness of the calculated MDL will be determined using the iterative procedure as described in 40 CFR Appendix B, section 7, which involves preparing additional standards at the calculated MDL and analyzing. Laboratory managers will be using the iterative procedure along with their technical expertise and judgement to determine whether the calculated MDL is

adequately representative of instrument capabilities.

2.3 Metals and Compounds

The detection limits stated in Table 1 of IO-3 for ICP/MS are sufficient to meet the needs of the Toxics Pilot Monitoring program. Estimates of the method detection limits for the HAP metals will be determined using 40 CFR Part 136, Appendix B and in a similar manner as described for the VOCs and carbonyls. A minimum of seven strips from seven individual filters will be spiked with solutions containing the core metal compounds at a level of 3 to 5 times the expected detection limit. Using the detection limits given in IO-3, this corresponds to about 0.03 to 0.05 ng/L.

3.0 Uncertainty (Precision)

The SAB recommends that uncensored data be reported with an associated level of uncertainty. For the Pilot monitoring program, this uncertainty will be determined from data collected for precision estimates; however, a measure of uncertainty will not be established or reported with each individual measurement. Procedures available to provide data for uncertainty and estimates of precision include the use of collocated samples and replicate analyses. Precision is a measurement of mutual agreement among individual measurements made under prescribed similar conditions. No special adjustments, calibrations, or maintenance of the instruments should be made. Precision checks should be made prior to any routine or special adjustments, calibrations or maintenance.

The types of precision determinations that will be made for the HAPs include:

- replicate analyses;
- collocated samples; and
- inter- laboratory precision checks or "round-robin" analyses.

A minimum of 10% of the total number of samples will be collected in duplicate (collocated) during the Pilot monitoring program for the urban area networks. For the small city/rural component, collocated samples will be collected on a 1 in 12 day schedule for a minimum of 30 samples, as resources allow. Replicate analyses will be performed on all collocated samples to provide "nested duplicates" in order to provide an assessment of sampling and analytical precision for the study.

Measures of precision will also be fulfilled using collocated samples that are processed and analyzed by different organizations to provide inter-laboratory precision information for the

measurement process. A sample exchange program that involves inter-laboratory precision gives important information concerning inconsistencies that may exist. Interpretation of these data must be based on clear understanding and knowledge of how the data were obtained. Any differences in the methodologies (i.e., detection limits, analytical column, calibration procedures, etc.) used to analyze the exchange sample must be clarified in order to interpret and resolve any inconsistencies in the results. Precision for inter-laboratory exchange samples is calculated in the same manner as precision for replicate analyses or collocated samples. Round-robin sample analysis will occur twice over the course of the Pilot program around the March and November time frame for VOCs and metals. Region 2, Wisconsin, Michigan and South Coast Air Quality Management District (AQMD) have volunteered and agreed to provide round-robin samples at this time.

A mechanism for providing round-robin samples for carbonyls has not been identified. Technical limitations of sampling exist in relationship to collecting multiple, simultaneous ambient air DNPH cartridges for this purpose. During the Pilot monitoring program, a round-robin comparison for carbonyls will not be performed.

When evaluating the precision measurements, laboratories must consider each individual target compound because precision will be compound-dependent with an influence of physical and chemical properties (such as vapor pressure and reactivity). At very low concentrations, those at or below the detection limit, agreement between measurements are expected to be poor.

Data pairs where the compound is detected in both samples can be evaluated for percent difference. To make a comparison of two values (i.e., duplicates or replicates) for precision, the Relative Percent Difference (RPD) is a more meaningful statistic than relative standard deviation (RSD), since the number of available measurements is only two.

$$RPD = \frac{Y_i - X_i}{(Y_i + X_i)/2} \times 100$$

Where:

$\mathbf{Y_i}$ = larger of the two observed values

$\mathbf{X_i}$ = smaller of the two observed values

Measures of precision are to be reported with the measurement data, in order to provide the data users with information to evaluate the uncertainty. If precision is calculated from three or more values (e.g., annual precision), RSD should be used.

$$\mathbf{RSD = (s / x) \times 100}$$

Where:

S = standard deviation of replicate values

X = mean of replicate values

The results from the various components of the quality assurance program are a vital part of the database generated by the pilot projects. Unfortunately, AIRS does not currently accept this type of information. It is the recommendation of the laboratory measurements work group that another group be created to address data management issues and determine the components of the data package that will be submitted by the Pilot City laboratories to the data analysis contractor.

4.0 National Performance Audit Program (NPAP) - Bias

The NPAP will be unable to provide any audit or "check" samples due to reduction in budget for FY2001. The option does exist to allow agencies to "buy in" to the program. If an agency has resources for audit samples for carbonyl and VOC audits, contact the NPAP coordinator ***Mark Shanis, EPA, OAQPS at 919-541-1323***

5.0 Stability and Hold Times

5.1 Volatile Organic Compound (VOC) HAPs

The guidance given in TO-15 and data from the Office of Research and Development (ORD) obtained as part of another toxics subcommittee are used to support the hold time for the core and max pollutants at 30 days. The ORD data below gives the percent change over a 30 day period for each pollutant. The concentration tested is given in parentheses. Methylene chloride seemed to be the least stable in this data set.

Core List	% Change (concentration)	*Max. List*	% Change (concentration)
benzene	5% (0.6 ppbv)	1,2-dibromoethane	8% (1.2 ppbv)
1,3-butadiene	17% (2.5 ppbv)	1,3-dichloropropene	8% (0.5 ppbv)
carbon tetrachloride	12% (0.9 ppbv)	1,2-dichloroethane	9% (0.9 ppbv)
chloroform	9% (1.2 ppbv)	1,1,2,2-tetrachloroethane	12% (2.1 ppbv)
1,2-dichloropropane	15% (2.4 ppbv)		
methylene chloride	27% (3.6 ppbv)		
tetrachloroethylene	12% (1 pbbv)		
trichloroethylene	13% (1 ppbv)		
vinyl chloride	18% (0.8 ppbv)		

5.2 Carbonyl Compounds

The specified hold time in TO-11A will be used for the Pilot program. DNPH-coated cartridges will be extracted within 2 weeks and the extracts should be analyzed within 30 days.

5.3 Metal Compounds

The hold time of 180 days as specified in IO-3 for filters will be used. Metals should be very stable as long as the filters are handled and stored properly.

6.0 Measurement Procedures

6.1 Volatile Organic Compounds (VOCs)

Table 1 provides an outline of the specific procedures to be followed for the analysis of VOCs by Compendium Method TO-15, "Determination of Volatile Organic Compounds in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry, GC/MS." A copy of this document is given in Appendix A. The procedures outlined in Table 1 also apply to the use of Compendium Method TO-14A, "Determination of VOCs in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography."

Table 1. VOC Analysis via TO-15A GC/MS for Air Toxics Pilot Monitoring Program

Item	Description
Canister Type	SUMMA or equivalent
Canister Certification	No target analyte > MDL; 1 canister selected per batch (batch size determined by laboratory)
Canister Transport	Ambient conditions
Canister Storage	Ambient conditions
Canister Hold Time	30 days
Method Detection Limit	40 CFR Appendix B to Part 136 Minimum of 7 low level canister standards analyzed over minimum of 2 day period; MDL to be determined on annual basis at minimum
Field Duplicates or Collocated Samples	10% of total samples for urban network or 1/12 for small city; 30 minimum per network
Analytical Instrumentation	**GC/MS or GC**
Blanks • Instrument blank	 Performed after instrument calibration
Replicate Analyses	Performed on collocated (duplicate) samples

6.1.1 Humidification of VOC Canister Calibration Standards

The guidance on humidification is given in the PAMS Technical Assistance Document (TAD), EPA/600-R-98/161, Section 2.3.4.3.1. This guidance (Appendix B) will be adopted for the toxics program. The TAD gives information on procedures for determining the appropriate amount of water to attain an adequate level of humidity in the sample canister without condensation. As stated in the TAD, low pressure (30 psig) calibration standards prepared in canisters ideally should have a minimum amount of water vapor ($20% relative humidity) to ensure sample integrity, but not enough water to cause condensation of water vapor in the canister ($33% relative humidity). To achieve these conditions in a 6-liter canister at 70°F, between 66 and 110 µL should be added. Calculations are included in the guidance in order to determine the amount of water needed at varying pressures and temperatures.

6.1.2 Canister Certification

Canisters will be cleaned in accordance with the laboratory's normal procedures and TO-15. Canisters will be acceptable for use if no target analyte is present at a level greater than the specified MDL as determined in accordance with 40 CFR Part 136, Appendix B. One canister will be randomly selected, or the canister known to be the "dirtiest" will be selected from each batch of canisters cleaned. If the canister meets the acceptance criteria, the entire batch is considered acceptable and therefore, ready for use. No additional flags or blank subtraction will be applied to the reported data.

6.2 Carbonyl Analysis

Table 2 outlines the specific procedures to be followed for the analysis of VOCs by Compendium Method TO-11A, "Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography, HPLC" (Appendix C). Considerations were given to procedures also outlined in the compendium method, as well as those provided in the Section 5, "Methodology for Determining Carbonyl Compounds in Ambient Air"(Appendix D), of the PAMS Technical Assistance Document for the Sampling and Analysis of Ozone Precursors, EPA/600-R-98/161; and draft guidance given in the "Guidance for Carbonyl Measurements at PAMS" (Appendix E).

Table 2. Carbonyl Analysis via TO-11A HPLC for Air Toxics Pilot Monitoring Program

Item	Description
Cartridge Type	DNPH-coated silica gel with ozone scrubber
Cartridge Lot Certification	Minimum of 3 selected per Lot. Formaldehyde not > 0.15 µg per cartridge Acetaldehyde not > 0.10 µg per cartridge
Cartridge Sample Transport	Ambient conditions
Cartridge Storage	Refrigerated conditions
Hold Time	Cartridges extracted within 2 weeks; extracts analyzed within 30 days

Field Blanks	Frequency = (N)½; where N is the number of field samples. < 0.15 µg formaldehyde and < 0.10 µg acetaldehyde
Trip Blanks	Optional - normally used to resolve issues identified from field blanks.
Method Detection Limit	40 CFR Appendix B to Part 136 Minimum of 7 derivatized spiked cartridges; extracted no sooner than 24 hours after spiking; MDL must be determined on annual basis at a minimum. If labs successful spiking underivatized components then - OK
Field Duplicates or Collocated Samples	10% of total samples for urban network or 1/12 for small city; 30 minimum per network

Analytical Instrumentation	**HPLC (High performance liquid chromatography)**
Blanks	
• Instrument blank	Performed after instrument calibration
• Reagent blank	Performed for each new Lot of reagent
Replicate Analyses	Performed on duplicate (collocated) samples

6.3 Metals Analysis

Table 3 outlines the specific procedures to be followed for the analysis of TSP (total suspended particulate) filters by Inorganic Compendium Method IO-3.5, "Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma/Mass Spectrometry, ICP/MS" (Appendix F). Considerations were also given to procedures outlined in 40 CFR, Part 50 Appendix G, "Reference method for the determination of lead in suspended particulate matter collected from ambient air". Consistency between Part 50, Appendix G and IO-3.5 were maintained where appropriate for filter handling and other sampling-related procedures. For guidance related to the preparation of filter material, Inorganic Compendium Method IO-3.1, "Selection, Preparation and Extraction of Filter Material" is included in Appendix G.

6.3.1 Extractable versus Total Metals

Total metals (dissolution) indicates that the particulate and its matrix, as well as the filter, are completely dissolved and results in a clear solution. This usually results in a fairly high level of solids in solution and is often more difficult to analyze. Glass and quartz fiber filters would required the use of hydrofluoric acid (HF) which means a more difficult and dangerous extraction process. "Extractables" are just the compounds of the metal that dissolve into the solution you use for extraction. Different metal compounds are extracted with nitric acid than with hydrochloric acid, or combinations, and the amounts will vary depending on whether a hot plate, microwave or ultrasonic bath is used. Using different extraction methods can complicate the interpretation of the data. Total metals determination is considered more costly, difficult to perform and subject to greater background interference. Hot acid extraction with HNO_3 / HCl to determine "extractable" metals will be the procedure used for the Toxics Pilot Monitoring Program.

Table 3. TSP Analysis via IO-3.5 ICP/MS for Air Toxics Pilot Monitoring Program

Item	Description
Filter type	Quartz Filters. Based on results from filter contamination study - glass fiber are also acceptable for the "core" pollutant list of metals only
Filter QC	per Method IO-3.1, Table 7 and Part 50, Appendix G
• Method (reagent) Blank • Filter Lot Blank • Matrix Spike • Lab control (LC) blank • Lab control sample (LCS)	1 per 24 samples; reagents only Lots >500 (20-30 selected at random); Lots <500 (lesser number can be taken) Filters analyzed for target species 1 per 20 samples; spiked filter 1 per extraction day; manufactured filter blank certified below NIST traceable detection limits 1 per extraction day
Filter cutting procedure	Pizza cutter preferred (as represented in IO-3.1, Figures 1 and 2). Strip width of 1 inch. **Do not unfold filter as specified in IO-3.**
Filter Transport	Ship under ambient conditions in protective envelope
Filter Storage	15-30°C
Filter Hold Time	180 days
Field Blanks	1/10 filters or 10%
Extraction procedure	Hot acid extraction with HNO_3 / HCl - extractable metals
Extraction Efficiency	Target 75-125% using NIST SRM 3087a, 2677a, or 1648 as appropriate
Method Detection Limit	40 CFR Appendix B to Part 136 Minimum of 7 filters; MDL must be determined on annual basis as a minimum
Duplicate Filter Strips (Precision)	10 % of total samples for urban network or 1/12 for small city; 30 minimum per network

Analytical Instrumentation	**ICP/MS**
Blanks • Instrument Blank • Reagent Blank • Rinse Blank	As outlined in IO-3.5, page 3.5-11
Interferences - ICP/MS • As interference by Argon on ICP/MS • Isobaric elemental interference • Abundance sensitivity • Isobaric polyatomic Ion interference • Physical interferences • Memory interferences	Several identified in IO-3.5, pages 3.5-4 for ICP/MS and recommendations that labs should be aware of

7.0 Data Reporting

All data for the pilot study will be reported without "screening" or “censoring” the data below detection or reporting limits. All measurements detected by the instrument will be reported with a qualifying flag for those values below the lowest calibration level (LCL) - see below. The “7" data qualifying flag has been established in the AIRS-AQS for this purpose. Only flag 7 will be used, which also covers those values below the calculated MDL. Values analyzed for, but not detected, will be reported as ND. Measures of precision as defined under the “Uncertainty” section of this document will be reported along with the data set. Data reporting units to be defined by the Data Management work group. A Data Management work group is being convened to discuss and clarify issues related to data reporting. Please refer to the discussions and outcome of this work group for guidance on these issues.

7.1 Lowest Calibration Level (LCL)

Also often referred to as the minimum reporting level (MRL). Defined as the minimum concentration that can be reported as a quantitated value for a target analyte in a sample following analysis. For the purposes of the Pilot City study, data will be quantitated and reported below this level. This will be the level at which the data below will be flagged indicating a level of uncertainty and still

useful for certain statistical purposes. This will be equivalent to the concentration of the lowest calibration standard which can only be used if acceptable quality control criteria for this standard are met. This is established at a level 3 times the MDL. Reference: Perchlorate in drinking water method http://www.epa.gov/OGWDW/methods/met314.pdf.

8.0 Clarification of Terminology

There appear to be many different acronyms in use for the quantitation of instrument sensitivity and reporting of data. A sampling: PQL, MDL, LOD, LOQ, IDL, ... Many of the terms are used to refer to the same thing and typically are used for water quality analyses; however, there are generally 2 distinct classes: detection limits and quantitation limits. For use in our discussions I decided to compile some information from a variety of sources which describes some of the terminology (acronyms) used. However, I do not try to address the issue of the variety of methods that can be used to determine these detection or quantitation limits and how that impacts the values obtained by a specific laboratory. ***Clarification: For the purposes of the Pilot Toxics monitoring network, we are using the terms method detection limit (MDL) and lowest calibration level (LCL), which is very similar to the MRL given below.***

8.1 Detection Limits

8.1.1 Method Detection Limit (MDL)

EPA definition: the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. (Part 136, App. B) Determined by taking a minimum of seven aliquots of the sample (in case of air sample analysis we are using individual canister samples) to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with the final results in the method reporting units (ppbv).

Compendium Method TO-15 and TO-11A; Method 314.0 and 1631 (Bob Avery) also refer to 40 CFR, Part 136, Appendix B

8.1.2 Limit of Detection (LOD)

Lowest concentration of an analyte that the analytical process can reliably detect. (Anal. Chem., Vol. 52, No. 14, December 1980)

A number, expressed in units of concentration (or amount), that describes the lowest concentration level (or amount) of the element that an analyst can determine to be statistically different from the analytical blank. (Anal. Chem., Vol. 55, No. 7, June 1983 in reference to IUPAC definition in Spectrochem. Acta B 1978, 33B, 242)

The lowest concentration of an analyte in a sample that can be detected but not necessarily quantitated. Approximately 2 or 3 times the signal-to-noise (S/N) ratios. (LC/GC Vol. 16, No. 10, October 1998 take from U.S. Pharmacopeia Conference, 1995)

The smallest observed signal (x) that with a reliability 1-" can be considered as being a signal caused by the component to be measured. When the observed signal is smaller than x, however, it cannot be stated that the component is absent. It can only be said with a reliability 1-$ that the concentration of the component will be less than a certain value. (Quality Control in Analytical Chemistry, Vol. 60, Kateman and Pijpers, John Wiley & Sons, 1981)

8.1.3 Detection Limit (DL)

Minimum concentration of an analyte that can be measured above instrument background.

Estimates of concentrations at which one can be fairly certain that the compound is present. Concentrations below this limit may not be detected. Concentrations above this limit are almost certainly detected. http://www.wcaslab.com/TECH/DETLIM.HTM

8.1.4 Instrument Detection Limit (IDL)

Lowest concentration that can be detected by an instrument without correction for the effects of the sample matrix or method-specific parameters such as sample preparation. (Web reference dated 1/27/999 - www.pw1.netcom.com/~qaa/DETLIM.html- appears to be no longer available)

8.2 Quantitation Limits

8.2.1 Minimum Level (ML)

The lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specific sample weights, volumes, and cleanup procedures have been employed. Calculated by multiplying the MDL by 3.18 and rounding the result to the number nearest to (1,2, or 5) x 10^n, where n is an integer. Method 1631 (from Bob Avery at http://www.epa.gov/ost/methods/1631final2.pdf)

8.2.2 Limit of Quantitation (LOQ)

A minimum criterion or region for quantitation that should be clearly above the detection limit. The lowest concentration of an analyte in a sample that can be determined (quantitated) with acceptable precision and accuracy under the stated operational conditions of the method. Approximately 10 times the signal-to-noise (S/N) ratios. (LC/GC Vol. 16, No. 10, October 1998 take from U.S. Pharmacopeia Conference, 1995)

8.2.3 Practical Quantitation Limit (PQL)

The lowest concentration of an analyte that can be reliably measured within specified limits of precision and accuracy during routine laboratory operating conditions. The Agency has used the PQL to estimate or evaluate the minimum concentration at which most laboratories can be expected to reliably measure a specific chemical contaminant during day-to-day analyses of drinking water samples. (EPA Office of Water web site www.epa.gov/ogwdw000/standard/review/methods.html)

Normally determined as 3 to 10 times the MDL and is considered the lowest concentration that can be accurately measured , as opposed to just detected.
http://www.wcaslab.com/TECH/DETLIM.HTM

8.2.4 Minimum Reporting Level (MRL)

The minimum concentration that can be reported as a quantitated value for a target analyte in a sample following analysis. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met. Established at a level either 3 times the MDL or at a concentration which would yield a response greater than a signal-to-noise ratio of five. (Perchlorate in drinking water method http://www.epa.gov/OGWDW/methods/met314.pdf)

Appendix A

Compendium Method TO-15A, "Determination of Volatile Organic Compounds in Air Collected in Specially-prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry, GC/MS

See: http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-15r.pdf

Appendix B

Procedure for Humidification, Section 2.3.4.3.1 taken from the PAMS Technical Assistance Document for the Sampling and Analysis of Ozone Precursors, EPA/600-R-98/161

See: http://www.epa.gov/ttn/amtic/files/ambient/pams/newtad.pdf

Appendix C

Compendium Method TO-11A, "Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography, HPLC"

See: http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-11ar.pdf

Appendix D

DRAFT

Guidance for Carbonyl Measurements at PAMS

prepared for EPA under contract 68-D-98-030

February 2001

DRAFT
Guidance for Carbonyl Measurements at Photochemical Assessment Monitoring Stations (PAMS)

September 30, 1999

Prepared for EPA under
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Emissions, Monitoring, and Analysis Division
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency

EPA Disclaimer

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Acknowledgment

We thank the many participants for their time in reviewing our outline and the draft document. The participants were staff involved in a previous work assignment involving a series of conference calls to assess carbonyl measurements at PAMS. Their enthusiasm and willingness to share experiences and knowledge were quite evident during the review process.

Guidance for Carbonyl Measurements at Photochemical Assessment Monitoring Stations (PAMS)

The determination of ambient concentrations of carbonyl compounds is a requirement of 40 CFR Part 58, Subpart E, enhanced ozone network monitoring programs.[1] The U.S. Environmental Protection Agency (EPA) has established a Photochemical Assessment Monitoring Stations (PAMS) program to provide routine measurements of selected volatile organic compounds (VOCs) and carbonyl species. The PAMS program currently recommends the sampling and analysis of 55 VOCs and three carbonyl compounds: formaldehyde, acetaldehyde, and acetone. The measurement of acetone is now optional (see PAMSGRAM, Volume 16). For the measurement of carbonyl species, States are required to obtain 3-hour and 24-hour integrated samples, at collection frequencies specified for each type of enhanced ozone monitoring site.

The measurement method for carbonyls in PAMS is based on U.S. EPA Compendium Method TO-11A, which incorporates the use of sorbent cartridges coated with 2,4-dinitrophenylhydrazine (DNPH) for sample collection.[2] The analyses are performed with high performance liquid chromatography (HPLC). The two sorbents described in the compendium method are silica gel and octadecylsilane bonded silica substrate (C18). For consistency, silica gel is recommended for use in the PAMS program. For the PAMS program,
carbonyl methodology is further explained in the Technical Assistance Document (TAD), which more thoroughly discusses specific topics including monitoring instrumentation, ozone scrubbers, and cartridge blanks.[3] The guidance provided here supercedes that given in the TAD where applicable.

Currently, numerous State, federal, and private laboratories are conducting carbonyl sampling and analytical activities as part of the PAMS program. However, there are concerns about the existing carbonyl database and data quality in general. As a result of these concerns, a series of conference calls were conducted with several such groups, representing a wide range of procedures used during the sampling and analysis efforts.[4]

The mechanical integrity of field sampling devices and the lack of field audit and sampling protocols are key issues for PAMS carbonyl measurements. One concern is the failure of aging

carbonyl sampling equipment as a result of leaks, which are often extremely difficult to detect and may go unnoticed until data quality or other quality assurance/quality control (QA/QC) results indicate a problem. Collocated sampling with duplicate equipment is one QA/QC approach to evaluate sampling abnormalities, but State agencies often do not have the necessary extra equipment. Current performance audits for the carbonyl sampling in the PAMS program employ a DNPH-silica gel cartridge spiked with selected carbonyl derivatives. National Institute of Standards and Technology (NIST) gas-phase carbonyl standards are not currently available for method calibration and bias determinations. Consequently, until these standards are available, the integrity of carbonyl sampling equipment cannot be completely tested.

Suitable QA/QC procedures are particularly important in light of discrepancies observed among nominally identical carbonyl sampling and analytical systems operating at some of the PAMS sites. The present PAMS carbonyl sampling methodology could benefit from the development of procedures to enhance sampling precision and accuracy. Greater standardization of sampling and analysis techniques should result in better data comparability from different sites, more consistent assessment of data quality, and better estimation of seasonal and long-term trends in air quality. Detailed procedural guidance for existing PAMS equipment is critical to addressing the measurement issues.

The purpose of this document is to provide guidance for use by Agencies in order to obtain **more consistency** in conducting carbonyl monitoring in the PAMS program. This document identifies critical requirements for the collection and analysis of formaldehyde, acetaldehyde, and acetone, and addresses the necessary QA/QC procedures to assure good quality data for the PAMS program. It focuses on five subject areas: sampling system, sampling cartridges, analytical system, blanks and data reporting. This document is not intended to replace TO-11A and the PAMS TAD, but is intended to outline, clarify and emphasize important and critical aspects of the cartridge carbonyl methodology essential in obtaining good quality data. The following specific guidance is given to help improve the quality of the PAMS carbonyl data collected:

- Commercially available DNPH-cartridges and sampling equipment are to be used.
- Cartridge field blank subtractions are not be required.
- Flow rates for the 3-hr and 24-hr sampling are specified.
- Cartridge shipping procedures are clearly defined.
- Analytical information provided to EPA will be posted on the PAMS website (see Section III.A.2).
- A routine ozone scrubber change-out schedule is specified.

The following sections provide the rationale and further details for implementation of these PAMS carbonyl monitoring recommendations.

I. Sampling System

This section focuses on the physical requirements, the calibration, and the operation of the carbonyl sampling system. At a minimum, the following components should be included in the PAMS carbonyl sampler. These items are also described in Section 5.2 of the PAMS Technical Assistance Document.[3]

A. Carbonyl Sampling System

- Carbonyl samplers should be constructed so that all material coming in contact with the sampled air is glass, stainless steel, and/or Teflon™.
- A heated inlet line to the sampler is strongly recommended to prevent condensation of water and/or organic compounds. The material of construction for the inlet line should be stainless steel, or Teflon™. The elevated temperature of the inlet should be at -50 ± 15EC.
- A denuder or cartridge type ozone scrubber is required to remove ambient ozone from the sample stream. If a copper coil denuder is used, then it should be wrapped with a cord heater and controlled to an elevated temperature (-50 ± 15EC) to prevent condensation of water and/or organic compounds in the sampling line.

- Inlet check valves, solenoid valves, or a multi-port rotary valve are recommended to direct sample to, and to isolate, the individual sampling cartridges. Diffusive sampling may occur if such valves are not present and operational.

- A multiport cartridge assembly is recommended to support multi-event sampling and allow for easy insertion and removal of DNPH sampling cartridges.

- The outlet side of the sample cartridge assemblies also must be equipped with check valves (or equivalent) to isolate individual sampling cartridges.

- A mass flow controller or mass flow meter/control valve must be used to maintain constant flow rate over the specified sampling period.

- An oil-less vacuum pump, capable of achieving a pressure drop of -25 inches Hg, is necessary to draw sample through the sampling cartridge during collection.

- An event control and data acquisition device is required to allow unattended operation of the collection system and to record sampling event information such as start and stop times, collection flow rates, etc.

Although the above list consists of generally available standard components of air sampling equipment, proper assembly requires tedious and time-consuming testing and evaluation. It is strongly recommended that future users consider commercially available instruments that have been tested and evaluated to meet carbonyl sampling requirements.

A separate commercial sampler also should be used for the 24-hour time integrated samples, unless a single commercial unit is equipped to perform both types of sampling. At a minimum, the 24-hr sampler should contain the same components as the 3-hr sampler except that the multi-port cartridge assembly is not needed. Commercial samplers that can be automatically leak checked are highly preferred.

Current commercial vendors of carbonyl sampling systems include:

- ATEC Atmospheric Technology, P.O. Box 8062, Calabasas, CA 91372-8062, (310) 457-2671

- Atmospheric Analysis and Consulting (AAC) Inc., 4572 Telephone Road, Suite 920, Ventura, CA 93003, (805) 650-1642

- Millipore/Waters Chromatography, P.O. Box 9162, Marlborough, MA 01752-9748, (800) 252-4752
- Scientific Instrumentation Specialists, P.O. Box 8941, Moscow, ID, (209) 882-3860
- SKC Inc., 334 Valley View Road, Eighty Four, PA 15330-9614, (800) 752-8472
- Supelco, Supelco Park, Bellefonte, PA 16823-0048, (800) 247-6628
- XonTech, Inc., 6862 Hayvenhurst Avenue, Van Nuys, CA 91406, (818) 787-7380

The mention of vendor names does not constitute endorsement or recommendation by the U.S. EPA. Each user should evaluate the system to make educated purchases and determine if it meets the individual's needs.

B. Requirements for an Ozone Scrubber

The EPA has previously determined through laboratory tests that ozone present in ambient air interferes with the measurement of carbonyl compounds when using Method TO-11A. As stated in the Technical Assistance Document,[3] ozone can interfere with carbonyl analyses in three ways:

- The ozone reacts with the DNPH on the cartridge, making the DNPH unavailable for derivatizing carbonyl compounds
- The ozone degrades the carbonyl derivatives formed on the cartridge during sampling
- If the analytical separation is insufficient, the DNPH degradation products can coelute with the target carbonyl derivatives.

The extent of interference depends upon the ambient concentration of both ozone and the carbonyl compounds, and on the duration of sampling. Carbonyl compound losses can be as high as 50 percent on days when the ambient ozone concentration reaches 120 ppbv.[3] As a result it is mandatory that an ozone scrubber be used for carbonyl sampling in the PAMS program and that it be properly maintained.

Two types of scrubbers have been developed ! the ozone denuder and the ozone cartridge scrubber. Both scrubbers use potassium iodide (KI) as the scrubbing agent, and their designs

effectively allow for the removal of ozone at sampling flow rates up to 1 liter/minute. Details on the equipment and preparation of these scrubbers are provided in the TAD, TO-11A, and PAMSGRam, Volume 12 [5] documentation. Below is a brief description and recommended change-out time of each device.

The ozone denuder is a copper tube coated internally with a saturated solution of KI. The tube is coiled and housed in a temperature-controlled chamber that is maintained at elevated temperature (~50 ± 15EC). The elevated temperature prevents condensation of water vapor and organic compounds in the coil during sampling. The ozone denuder as described in the TAD has a usable lifetime of up to 100,000 ppb-hours. This lifetime period was determined during laboratory tests using controlled relative humidity (RH) conditions. Denuder performance may be affected by the variable pollutant and RH conditions in the ambient atmosphere. On a conservative basis, however, the scrubber should be effective for up to 30 days of continuous ambient air sampling. To assure consistent performance, replacement of the ozone denuder is recommended after the equivalent of 30 days of use, e.g., six months of sampling on every sixth day. The scrubber is reusable, and the re-coating procedure is described in the TAD.

The second type of ozone removal device described in the TAD is the cartridge scrubber. This device is commercially available (e.g., Supelco, Waters) and is filled with approximately 1 gram of ACS reagent grade KI (the cartridge is identical in size and shape to the precoated DNPH silica cartridges). The scrubber cartridge is positioned at the sample inlet, just ahead of the DNPH-coated cartridge. During high humidity/temperature conditions, it is recommended that the cartridge scrubber be maintained at elevated temperature (~50 ± 15EC) to prevent condensation of water vapor and organic compounds. According to the TAD, the theoretical removal capacity for ozone is 200 mg, based upon the assumption of 100 percent consumption of KI. As a result, change-out of the cartridge scrubber every three weeks is recommended.

C. Sample Probe Line and Connection to Primary Manifold

The primary sampling manifold must meet the criteria for the PAMS network. These criteria can be found in Section 5.2.3 of the Technical Assistance Document.[3] The carbonyl sampler should be connected to the primary manifold using a 1/4 inch O.D. heated line that is made of stainless steel or

Teflon™. The ozone scrubber and carbonyl sample cartridge should be placed as close as possible to the primary manifold. The carbonyl sampling line should be connected to the primary manifold at a location that is downstream of the connection line used for VOC sampling (in order to minimize the possibility of acetonitrile solvent back-diffusing into the VOC sampling line).

D. Calibration and Operation of Carbonyl Sampling System

Procedures for the calibration and operation of the carbonyl sampling system include implementation of field check procedures, operation at specified flow rates, flow checks, and employment of calibration gases to challenge the sampler. Table 1 provides a checklist to assess the performance of the sampling system.

Table 1. Sampler Quality Control Criteria Checklist

Parameter	Frequency	Limits	Corrective Action
Flow Check	Each Sampling Event, Pre- and Post-Checks	3 hr, 1.0 liter/minute (± 20%) 24 hr, 0.13 liter/minute (± 20%)	Repair/Exchange Unit
Mass Flow Controller (or mass flow meter)	Start, Midpoint, End of Season	100 ± 10% (Reference Meter)	Repair/Recalibrate Unit
Leak Check	Before Each Sampling Event	No Air Flow	Recheck for Leaks, Modify as Necessary
Sampler Blank	Pre- and Post-Seasons	<0.15 µg Formaldehyde/ Cartridge	Clean or Replace Sampler
Collocated Samples	10% of Field Samples	± 20 %	Mark Samples as Suspect
Backup Cartridges[(a)]	10% of Field Samples	# 10% of Total on Backup Cartridge	Use Backup Cartridges for All Samples
Trip Blanks	Square Root of the Number of Field Samples	<0.15 µg Formaldehyde/ Cartridge	Evaluate Sampling and Analysis Procedures, Purchase New Batch
Field Blanks	Square Root of the Number of Field Samples	<0.15 µg Formaldehyde/ Cartridge	Evaluate Sampling and Analysis Procedures, Purchase New Batch
Sampler Challenge (With Gas Mixtures)	Pre- and Post-Seasons	70 to 130% Recovery	Clean or Replace Sampler

(a) Not needed if recommended flow rates are used; see Section I.D.2.

1. Implementation of field check procedures

The TAD mentions several key activities that should be performed to assure proper operation of the carbonyl sampler; however, re-emphasis and further details are provided here. First, a leak check should be performed before each sampling event. The sampler should be on for at least 10 minutes prior to the leak test. The inlet line should then be sealed and the mass flow controller (or mass flow meter) readout from the sampler should drop to zero (within a few minutes). If leaks are detected, recheck, tighten, and/or modify the system. Once the absence of leaks has been confirmed, the inlet line is opened, and sampler flow should be checked with a NIST-traceable flow meter to assure that the target flow rate is achieved (1.0 liter/minute for 3-hr sample, 0.13 liter/minute for 24-hr sample).

Second, the mass flow controller for each sampler should be checked at the start, at the midpoint, and at the end of each ozone season. For acceptability, the calibration reading should be within 100 ± 10 percent of the reading from a NIST-certified flow meter. Deviations from this range should be noted and the mass flow controller should be recalibrated or exchanged. Third, a sampling system blank check should be performed as a pre- and post-season validation of the performance of the sampler. This check is performed by obtaining a 3-hr cartridge sample while supplying aldehyde-free air to the sampler inlet. It is recommended that aldehyde-free air be generated by placing a DNPH cartridge at the inlet to the sampler. The sampler itself is then operated at 1.0 liter/minute flow rate over its normal 3-hr sampling period. The amount of aldehydes found in the resulting sample must originate from within the sampling system and can be compared to ambient levels. The current requirement is that the system blank check loading should be less than the Method TO-11A acceptance criteria (<0.15 µg formaldehyde/cartridge). If not, the data need to be qualified and the sampler should be cleaned/exchanged. The user should contact the vendor for specific cleaning instructions.

As part of the normal QC activities for field sampling, it is recommended that the following samples also be collected: collocated samples, backup cartridges, trip

blanks, and field blanks. However, if the flow rates of 1.0 liter/minute for the 3-hr sampling and 0.13 liter/minute for the 24-hr sampling are used, then backup cartridges are not necessary. Each of these blank types should be collected on a frequency as shown in Table 1. Table 1 summarizes the critical QC activities and is intended to replace Table 5-3 in the TAD for these nine parameters.

2. Operation at specified flow rates

For carbonyl measurements in the PAMs program, the target collection volume through a DNPH cartridge is ~180 liters of air. Thus, for the 3-hr sample, the required flow rate is 1.0 liter/minute (± 20 percent). For the 24-hr sample, the required flow rate is 0.13 liter/minute (± 20 percent). As indicated in Table 1, if these flow rates are used, then backup cartridges are not required.

3. Employment of calibration gases

Commercially available calibration cylinders have been prepared that contain stable ppb levels of aldehydes. It is recommended that these calibration gas cylinders be purchased from a specialty gas vendor and used to challenge the field sampling units. Percent recovered should be within 100 ± 30 percent of the delivered quantity of carbonyl (based on the stated cylinder value). If the recovery values are outside this range, appropriate troubleshooting procedures should be initiated. For additional comparability, the cylinders should be exchanged across PAMS sites.

II. Cartridges

This section is intended to re-emphasize important TAD and TO-11A information addressing the acquisition, handling, shipping, and storage of DNPH-coated cartridges.

A. Preparation/Acquisition of Cartridges

Cartridges should be acquired in bulk quantities from commercial vendors. Preparation of cartridges by individual laboratories is tedious, labor intensive, requiring clean room conditions, and is

not recommended. Noncommercial preparation is likely to result in more lot- to-lot variability than is found in commercially prepared cartridges. This approach is counter-productive to improving consistency in the PAMS program. Information on the cartridges such as vendor, quantity received, date of receipt, lot number, and expiration date should be recorded in a laboratory note book.

Major commercial suppliers of DNPH-coated cartridges include:

- Supelco, Supelco Park, Bennefonte, PA 16823-0048, (800) 247-6628
- Millipore/Waters Chromatography, P.O. Box 9162, Marlborough, MA 01752-9748, (800) 252-4752
- Atmospheric Analysis and Consulting (AAC) Inc., 4572 Telephone Road, Suite 920, Ventura, CA 93003, (805) 650-1642
- SKC Inc., 334 Valley View Road, Eighty Four, PA 15330-9614, (800) 752-8472.

The mention of vendor names does not constitute endorsement or recommendation by the U.S. EPA. Each user should evaluate the cartridges to determine if they meet the program's needs.

The receiving laboratory should certify acceptability of the cartridge lot by following the blank analysis procedure specified in the Technical Assistance Document.[3] For a minimum of three cartridge lot blanks analyzed, the average blank value plus three times the standard deviation of the blank values (i.e., $\bar{0}$ + 3s) must meet the criteria for acceptance set out in Method TO-11A, which are

formaldehyde	<0.15 µg/cartridge
acetaldehyde	<0.10 µg/cartridge
acetone *	<0.10 µg/cartridge

*** Note: analysis for acetone is now optional for PAMS.**

The certification blank value and lot number must be recorded in the laboratory record book and the cartridge lot rejected and returned to the vendor if any acceptance value is not met.

B. Handling Cartridges

Biological processes produce carbonyl species from the skin and breath. Therefore, gloves should be worn when handling cartridges. Polyethylene gloves (or equivalent) are recommended during

field usage of the cartridges. Nitrile gloves are recommended to protect the hands of the laboratory chemist during the extraction of the cartridge with acetonitrile.

The field operator and laboratory chemist should minimize the time that unsealed cartridges are exposed to the environment. Diffusive sampling does occur when the cartridge caps are removed and can be significant depending upon background concentrations of the carbonyl species. DNPH is also light sensitive, and the cartridges should be protected from direct light by retaining them in the sealed foil pouch provided by the manufacturer or by covering with aluminum foil or similar material. Finally, to further reduce the possibility of contamination, avoid writing directly on the cartridges or placing adhesives onto the cartridges.

C. Shipping and Storing Cartridges

At a minimum, the shipment and storage of cartridges for the PAMS program should follow the guidelines indicated below:

- All cartridges should be stored in a dedicated refrigerator (4EC) until use ! adhere to vendor's expiration dates for use of cartridges.
- All cartridges should contain sealing caps (or plugs). Make sure caps are in place ! discard any cartridge found with a missing cap.
- All commercial cartridges should be transported inside their original shipping containers (as shown in Figure 5 of the TO-11A document). Some commercial containers include sealed foil pouches and glass culture tubes for individual cartridges; others include polypropylene holders equipped with foam inserts for holding multiple tubes.
- If the original shipping container is unavailable, friction-top metal cans should be used. The cans should be partially filled with a layer of activated charcoal.
- The shipping container should be padded with either polyethylene-air bubble padding or clean laboratory tissue paper. Polyurethane foam or inked paper should never be used as padding material.
- Cold packs are not required for cartridge shipment. Bulk shipment at room temperature with second-day delivery is acceptable.
- Cartridges should be stored in a dedicated refrigerator (4EC) upon arrival at the laboratory or field site.

III. Analytical System

This section focuses on the equipment requirements and the calibration and operation of the DNPH-cartridge extraction and HPLC analysis systems.

The analytical system should include an adequate cartridge extraction apparatus as well as a high performance liquid chromatographic system.

1. Cartridge extraction

   The highest purity acetonitrile should be used to extract the sampled cartridges. Some commercial manufacturers sell a carbonyl-free acetonitrile which is preferred. The solvent lot should be analyzed upon receipt to determine the initial purity level, and then periodically re-analyzed over the life of the bottle to track the aldehyde buildup over time.

   All glassware should be cleaned by rinsing with acetonitrile, then dried by heating to 60EC in a vacuum oven. The use of a nitrogen-purged glove box (bag) further reduces the risk of contamination.

   The sampled cartridge should be fore-flushed with acetonitrile to extract the derivatized carbonyls. The alternative back-flush elution approach is not recommended because it sometimes adds particulate materials also collected on the cartridge to the acetonitrile extract solution. During analysis, the particles can cause premature sample valve failure and can increase the column back pressure. Because the acetonitrile holdup volume is ~ 0.3 ml, an extraction volume of 5 ml is recommended.

2. HPLC analysis system

   Section 11.3.1 of the TO-11A document specifies the HPLC operating parameters and an isocratic elution program is adequate for sample analysis when formaldehyde is the only carbonyl of interest. For more complex carbonyl samples, Section 14.3.1 of the TO-11A document describes an HPLC gradient elution program that will resolve acetaldehyde, acetone, propionaldehyde, and the higher molecular weight carbonyls. More recently, several commercial vendors have demonstrated similar separation

capabilities using their own specific brand of column and operating conditions. For documentation and PAMS network consistency purposes, all PAMS measurement groups are encouraged to provide the following information to Nash Gerald at rice.joann@epa.gov:

- Name of Organization
- HPLC (type/manufacturer)
- Detector (type/manufacturer and wavelength)
- Data Handling System (type/manufacturer)
- Analytical Column (type/manufacturer)
- Guard Column (type/manufacturer)
- Column Operating Temperature
- Mobile Phase - Gradient Conditions (isocratic conditions)
- Solvents (manufacturer and lot number)
- Column Flow Rate/Column Head Pressure
- HPLC Run Time/Representative Calibration Run
- Sample Injection Volume
- Calibration Results ! MDL, Range, R^2, etc.

This information will be tabulated and posted on the PAMS homepage at www.epa.gov/oar/oaqps/pams.

Although acetone is no longer a required target compound, it is recommended that calibration data continue to be examined for the separation of the three C-3 carbonyl species that may be present in the chromatogram (acrolein*, acetone, and propionaldehyde). The resolution of these three peaks should be tracked over time to evaluate column performance (for the lowest calibration mixture, each valley between the three successive peaks should be less than 50 percent of the highest peak). Further decreases in resolution and/or excessive column pressure buildup indicate the need for column replacement or refurbishing.

*** Note: Method TO-11A no longer considered applicable to acrolein.[6]**

A. Calibration of Analytical System and Implementation of QA/QC Procedures

To ensure consistency across the PAMS network, the following calibration procedures are recommended. The frequency, acceptance criteria, and corrective actions associated with these procedures are shown in Table 2. Many of the table items are updated parameters from Table 5-3 of the TAD.

Table 2. Analysis System Quality Control Criteria Checklist

Parameter	Frequency	Limits	Corrective Action
Multipoint Calibration	Every 6 Months	$R^2 > 0.99$	Recalibrate
Check Standard	Daily	± 10%	Recalibrate
Method Detection Limit	Annually	<0.1 ppb or 0.22 Fg for a 180-liter Sample	Check/Service Instrument
Replicate Injections	Daily	± 10%	Check/Service Instrument
NPAP Audit Samples	One to Three Times Per Year	-23% to +22%	Recalibrate
Resolution of C-3 Carbonyl Species[(a)]	Daily	Valley Between Peaks #50% of Highest Peak	Change Column Program/ Change Column
Matrix Spike	Each Lot	± 30%	Check Against New Matrix Spike
Laboratory/Extraction Blank	Each Extraction Batch	#Lot Certification Blank	Check Laboratory Processes

(a) Recommended for labs that continue to monitor the C-3 carbonyl species.

1. Calibration standards

Calibration standards should be purchased from commercial vendors. Material can be purchased as solid DNPH-carbonyl derivatives or as dilute liquid mixtures. The liquid mixtures are generally supplied in a range from 1 to 50 µg/ml as the carbonyl compound. Further dilutions should be made with volumetric glassware.

2. Multipoint calibration

A working standard range from 10 ng/ml up to 2000 ng/ml should be targeted. A multipoint calibration is recommended every six months, and a minimum of five calibration points (including zero) should be used. Analyses at each point should be in triplicate. A linear least-squares fit of the data should be conducted and an R^2 value of 0.99 or better should be attained. The slope of the calibration curve for each component provides a response factor (RF).

3. Calibration check standard

A separate, independent calibration standard near the expected levels of the target carbonyl concentrations should be used for daily calibration checks of the analytical system. The day-to-day variation of the components should be within ±10 percent of the initial calibration value. If greater variability is observed, a fresh check standard should be prepared. If results with the fresh standard deviate from the original calibration curve slope by more than 15 percent, then a new multipoint curve should be constructed. A plot of daily values on a Quality Control Chart should be made and used by the analyst to check on long-term performance of the analytical system.

4. Method Detection Limits (MDLs)

The MDL determination should be done on an annual basis using the procedures specified in the Code of Federal Regulations (40 CFR Part 136B).[7] In brief, a low level standard is prepared at a concentration that is approximately two to five times the estimated MDL. The standard is injected seven times. The average concentration is

calculated from the original calibration curve. The standard deviation and the appropriate student t-value are used to calculate the MDL as described in the CFR.

C. Operation/Performance of Analytical System and Implementation of QA/QC Procedures

1. Daily precision checks

   Precision checks should be done on a daily basis and should include analyses of both standard and sample. The precision (as relative standard deviation) should be within 10 percent, based on three replicate injections.

2. Chromatogram checks

   Daily inspections should be made to check if retention times are drifting. A control chart should be used to determine if trends are occurring.

3. NPAP - spiked cartridges/performance audit samples

   The National Performance Assessment Program (NPAP) is an ongoing program to check analytical accuracy of participating laboratories. Cartridges spiked with know amounts of liquid carbonyls (underivatized) are prepared and distributed to analytical laboratories. All PAMS participants should perform analyses on the NPAP audit samples. It is recommended that laboratories participate at least once per year.

2. Matrix spike

   A matrix spike test is recommended per cartridge lot. This procedure involves spiking cartridges (at least three) with non-derivatized carbonyls, and provides an evaluation of both the derivatization and the extraction processes. The underivatized carbonyls should be obtained from commercial vendors. A target acceptance criterion is 70 to 130 percent recovery. If this criterion is not met, then the analyst should recheck the matrix standard mixture against a new mixture.

5. Laboratory/extraction blank

Laboratory/extraction blanks should be analyzed for each batch of cartridges that are extracted. The results from these analyzed samples will indicate the combined cartridge, solvent, and glassware contamination level for each carbonyl compound. This QC activity will guide the analyst in verifying that laboratory operations are being conducted appropriately.

6. Internal Standard (IS)

An internal standard, such as the cyclohexanone-DNPH derivative, is recommended as another means of tracking instrument performance. The IS is not used for calibration purposes but rather to track detector response and certify the injection of each sample vial. The cyclohexanone derivative can be added to the acetonitrile prior to cartridge extraction.

7. Acetonitrile purity

Acetonitrile used for extractions should be evaluated upon receipt and periodically during use as described in Section III.A.1 of this document. A carbonyl free grade of acetonitrile should be used.

IV. Blanks

To ensure the quality of the data and to obtain more consistent results, the collection of sample blanks is necessary. As indicated in the TAD, there are four types of blanks: lot certification blanks, field blanks, trip blanks, and sampling system blanks. In this section, the purpose of each type of blank is described, the number of blanks necessary is discussed, and finally, procedures to be used in reporting the blank data are provided.

C. Types of Blanks

- **Lot Certification Blanks** ! Certification blanks consist of a minimum of three laboratory blank cartridges that are eluted with acetonitrile and analyzed to verify acceptability of a specified cartridge lot number from a commercial vendor. Certification blank analysis is required for each cartridge lot number.

- **Field Blanks** ! Field blanks are blank cartridges that are sent to the field, connected to the sampling system, and treated identically to the samples except that no air is drawn through the cartridge. Field blanks are used to assess the background carbonyl level for cartridges used during the ambient sample collection process.

- **Trip Blanks** ! Trip blanks are cartridges of the same lot number that are sent to the field, stored, and returned to the laboratory with the sampled cartridges. Trip blank cartridges are not connected to the sampling system. Trip blanks are optional and are intended to be used to resolve contamination problems determined from the field blanks. Trip blanks can be used to determine whether the contamination occurred during the sampling process or during the shipping and storage process.

- **Sampling System Blanks** ! Pre- and post-season validation of the performance of the sampling system is necessary. These system blanks are used to assess the contamination level of the sampler itself, as described in Section I.D.1 of this document.

B. Certification Blank

The blank value associated with the cartridge acceptance criteria is discussed here. The criteria for certification are taken from TO-11A and are very conservative; most results will be well within these values. For the certification blanks to be acceptable, the following criteria must be met:

- Formaldehyde: <0.15 µg per cartridge*
- Acetaldehyde: <0.10 µg per cartridge
- Acetone: <0.30 µg per cartridge.

* The equivalent formaldehyde concentration for a 180-liter sample volume is 0.679 ppbv.

If the analysis of the three unsampled DNPH cartridges provide blank values with a mean plus three standard deviations (0 + 3s) that is less than the above criteria, then the sample lot is acceptable. If the value is above the criteria, then additional blanks must be processed. The sample lot cannot be used

unless the above criteria have been met. Field blank values should be consistently less than 2 times the mean value of the certification blanks (i.e., < 20).

A sampling system blank also should be determined for each sampler prior to and after the ozone season. To collect a sampling system blank, the system is challenged with carbonyl- free air. Carbonyl-free air can be generated by passing the incoming air through acidic DNPH solution in a bubbling device, or through DNPH-coated cartridges. Alternatively, air containing a predetermined level of carbonyls can be used. The same sampling procedure used for actual samples should be used for the system blank (e.g., flow rate, time - see Section I.D.2).

C. Frequency of Obtaining Blank Data

As discussed earlier, a minimum of three laboratory blanks from each lot of DNPH cartridges are required for certification of that lot. Also, as stated in the TAD, it is recommended that a number of cartridges equal to the square root of the total number of samples be analyzed as field blanks. Table 3 gives a few examples of the minimum number of blanks per field samples. Table 4 provides a guideline for tracking the certified and field blanks over time. Critical information for the table includes the vendor; date of receipt of cartridge; lot number; expiration, extraction, and analysis dates; and lot certified and field blank values.

Table 3. Minimum Number of Blanks Per Field Samples

Number of Field Samples	Lab Blanks for Certification of Sample Lot	Field Blanks Required (square root of sample size)
50	3	7
100	3	10
200	3	14

V. Data Reporting

The collection and analysis of field blanks should be distributed over the entire period that the cartridge lot is used for ambient air sampling. The data from Table 4 should be used to evaluate

background carbonyl buildup over time. A trend plot also can be used to track background values versus time. The trend plot should show the certified blank mean value and the ± 3s level for that particular lot. Field blank values are then plotted in the trend plot as they become available (see Figure 1).

The PAMS Technical Assistance Document (Section 5.3.2) requires subtraction of the lot average field blank value from all samples. However, this approach can sometimes obscure the relative magnitude of the blanks and sample results. As a result, for data reduction and reporting purposes**, field blank subtraction for PAMS should not normally be done**. The following approach is recommended:

1. If the field blank values are all within the 0 ± 3s range, then blank subtraction is not necessary. Field blank results must be reported with the appropriate data set.

2. If the field blank mass loadings exceed the 0 ± 3s range but are still less than the certification criteria (e.g., formaldehyde <0.15 µg per cartridge), then blank subtraction is again not necessary. However, it is recommended that a new sample lot of cartridges be integrated into the program immediately. Field blank results must be reported with the appropriate data set.

3. If the field blank mass loadings exceed the certification criteria (e.g. formaldehyde >0.15 µg per cartridge), then blank subtraction should be done and the sample lot of cartridges should be phased out as quickly as possible. Field blank data must be reported with the appropriate data set.

VI. Concluding Remarks

The purpose of this document is to provide more consistency in conducting carbonyl monitoring in the PAMS program. This document focuses on improving consistency in five subject areas: sampling system, sampling cartridges, analytical system, blanks and data reporting. This is considered a working

document and PAMS participants are encouraged to provide comments and suggest improvements. Please send any comments to : rice.joann@epa.gov.

Table 4. Proposed Checklist Table for Tracking Cartridges

Vendor	Date of Receipt	Lot Number	Expiration Date	Extraction Date	Analysis Date	Lot Certified Blank Value	Field Blank Value

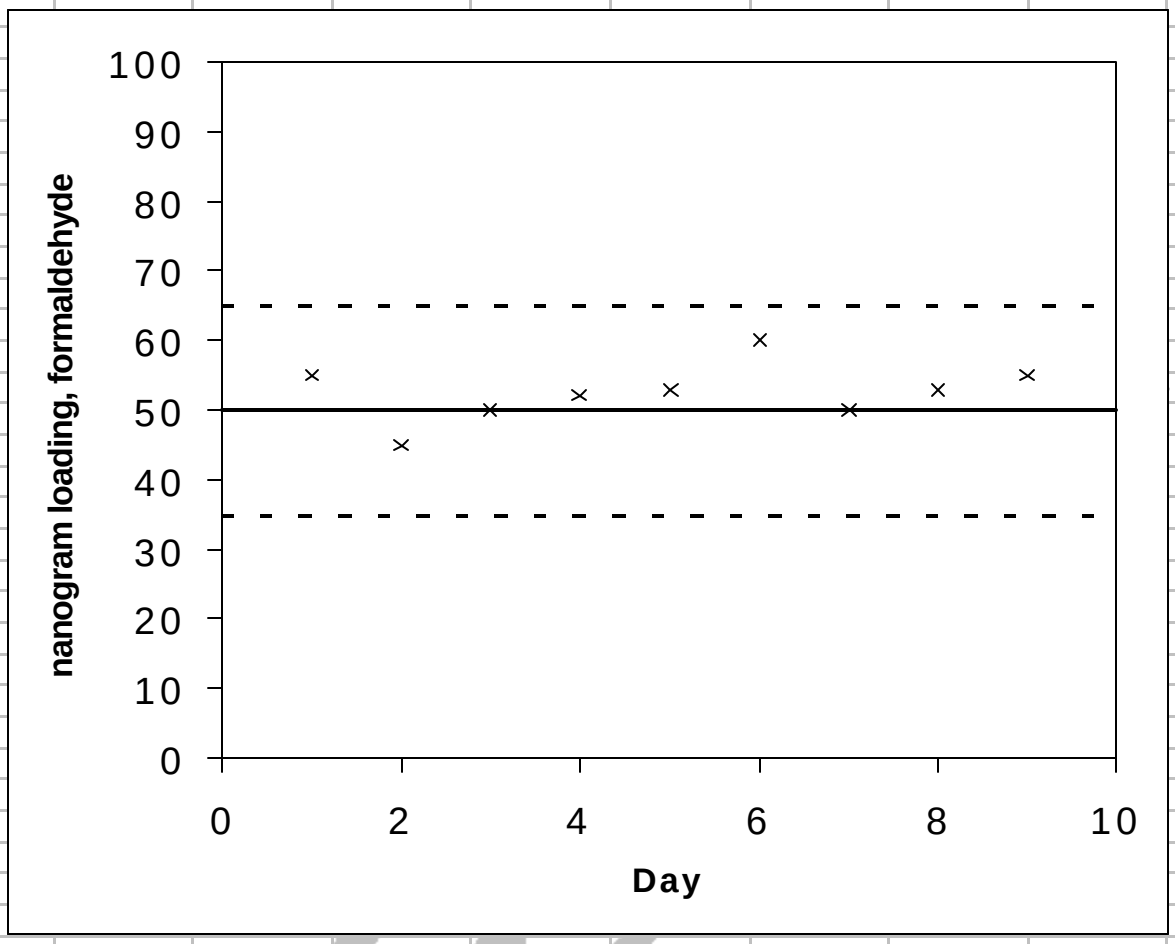

Figure 1. Control Chart for Plotting Cartridge Field Blank Values Versus Time (Certified blank mean is shown as the solid line with dashed lines as the +/- 3 standard deviation values)

References

1. Code of Federal Regulations. Title 40, Part 58. Ambient Air Quality Surveillance, Final Rule Federal Register, Vol. 58, No. 28, February 12, 1993.

2. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air–TO-11A, U.S. Environmental Protection Agency, EPA/625R-96/010b, Research Triangle Park, NC, January 1997.

3. Technical Assistance Document for Sampling and Analysis of Ozone Precursors, U.S. Environmental Protection Agency, EPA/600-R-98/161, Research Triangle Park, NC, September 1998.

4. Assessment of Carbonyl Measurements at Photochemical Assessment Monitoring Stations (PAMS) – Conference Calls, Battelle Report to U.S. EPA, Contract 68-D-98-030, Work Assignment 2-03, January, 1999.

5. The Use of KI-coated Copper Ozone Denuders for Carbonyl Measurements at PAMS. EPA PAMSGRam, Volume #12, October 13, 1998.

6. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air - Second Edition, ADDENDUM, April 15, 1999.

7. U.S. Environmental Protection Agency. Code of Federal Regulations. Title 40, Chapter 1, Part 136, Appendix B. Office of the Federal Register, July 1, 1987.

Appendix E

"Methodology for Determining Carbonyl Compounds in Ambient Air", Section 5 from the PAMS Technical Assistance Document for the Sampling and Analysis of Ozone Precursors, EPA/600-R-98/161

See: http://www.epa.gov/ttn/amtic/files/ambient/pams/newtad.pdf

Appendix F

Inorganic Compendium Method IO-3.5, "Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma/Mass Spectrometry, ICP/MS"

See: http://www.epa.gov/ttn/amtic/files/ambient/inorganic/mthd-3-5.pdf

Appendix G

Inorganic Compendium Method IO-3.1, "Selection, Preparation and Extraction of Filter Material"

See: http://www.epa.gov/ttn/amtic/files/ambient/inorganic/mthd-3-1.pdf

Appendix H

40 CFR Appendix B to Part 136 - "Definition and Procedure for the Determination of the Method Detection Limit", Revision 1.11

TABLE 6.—ACID EXTRACTABLE COMPOUND CHARACTERISTIC M/Z'S

Compound	Labeled analog	Primary m/z[1]
p-Cresol	d_7	108/116
Benzoic acid	d_5	105/110

[1]Numbers in charge ratio
[2]Not established

TABLE 7.—ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS

EGD No.	Compound	Acceptance criteria: Initial precision and accuracy section 9.2 (µg/L) s (µg/L)	X	Labeled compound recovery sec. 8.3 and 14.2 P (percent)	Calibration verification sec. 12.5 (µg/L)	Ongoing accuracy sec. 12.7 R (µg/L)
755	Acetophenone	34	44–97		69–113	76–162
656	Acetophenone-d_3	51	53–754	45–102	89–115	92–287
757	Aniline	32	30–71		61–119	33–154
647	Aniline-d_7	71	19–276	55–154	65–113	72–344
760	Benzaldehyde	ns	66–76		79–122	ns-ns
680	Benzaldehyde-d_6	26	66–93	19–ns	66–94	ns-343
576	2,3-Dichloroaniline	13	40–60		65–119	27–144
771	o-Cresol	40	31–226		65–115	56–136
671	o-Cresol-d_7	23	50–140	35–158	85–113	91–142
1744	p-Cresol	18	54–140		69–119	37–308
1344	p-Cresol-d_7	22	11–675	57–283	85–115	46–415
1329	Pyridine	30	10–121		63–117	18–238
1220	Pyridine-d_5	ns	7–382	15–238	89–115	4–671
905	1-Methylphenanthrene	16	39–241		76–122	76–304

s=Standard deviation of four recovery measurements.
X=Average recovery for four recovery measurements.
EGD=Effluent Guidelines Division.
ns=no specification; limit is outside the range that can be measured reliably.

[49 FR 43261, Oct. 26, 1984; 50 FR 692, 695, Jan. 4, 1985, as amended at 51 FR 23703, June 30, 1986; 62 FR 43405, Sept. 15, 1997; 65 FR 3044, Jan. 19, 2000]

APPENDIX B TO PART 136—DEFINITION AND PROCEDURE FOR THE DETERMINATION OF THE METHOD DETECTION LIMIT—REVISION 1.11

Definition

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

(c) That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

(d) Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interference concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1) Obtain another sample with a lower level of analyte in the same matrix if possible.

(2) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the required reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimation of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data.

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} X_i^2 - \frac{\left(\sum_{i=1}^{n} X\right)^2}{n}\right] \qquad S = \left(S^2\right)^{\frac{1}{2}}$$

where:

X_i $i=1$ to n, are the analytical results in the final method reporting units obtained from the n sample aliquots and Σ refers to the sum of the X values from $i=1$ to n.

6. (a) Compute the MDL as follows:

$$MDL = t_{(n-1,1-\alpha=0.99)} \times (S) \quad (5)$$

where:

MDL = the method detection limit

$t_{(n-1,1-\alpha=0.99)}$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.

S = standard deviation of the replicate analyses.

(9) The 95% confidence interval estimates for the MDL derived in 8a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (χ^2/df).

LCL = 0.64 MDL

UCL = 2.20 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at this calculated MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the other into the denominator S^2_B. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: If $S^2_A/S^2_B \leq 3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S_A^2 + 6S_B^2}{12}\right]^{\frac{1}{2}}$$

if $S^2_A/S^2_B > 3.05$, respike at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in 7b to compute the final MDL according to the following equation:

$$MDL = 2.681 (S_{pooled})$$

where 2.681 is equal to $t_{(n-1,1-\alpha=0.99)}$.

(c) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from percentiles of the chi squared over degrees of freedom distribution.

LCL = 0.72 MDL

UCL = 1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 24 aliquots.

TABLES OF STUDENTS' T VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1,\alpha=0.99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
90	89	2.368

Reporting

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was performed. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or exceeds 10

times the MDL of the analyte in reagent water, do not report a value for the MDL.

[49 FR 43430, Oct. 26, 1984; 50 FR 694, 696, Jan. 4, 1985, as amended at 51 FR 23703, June 30, 1986]

APPENDIX C TO PART 136—INDUCTIVELY COUPLED PLASMA—ATOMIC EMISSION SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSIS OF WATER AND WASTES METHOD 200.7

1. Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, and domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See Section 5.)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. (See Section 5.)

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instruction provided by the manufacturer of the particular instrument.

2. Summary of Method

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 5.1 (and tests for their presence as described in 5.2) should also be recognized and appropriate corrections made.

3. Definitions

3.1 *Dissolved*—Those elements which will pass through a 0.45 μm membrane filter.

3.2 *Suspended*—Those elements which are retained by a 0.45 μm membrane filter.

3.3 *Total*—The concentration determined on an unfiltered sample following vigorous digestion (Section 9.3) or the sum of the dissolved plus suspended concentrations. (Section 3.1 plus 3.2).

3.4 *Total recoverable*—The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (Section 9.4).

3.5 *Instrumental detection limit*—The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.6 *Sensitivity*—The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration.

3.7 *Instrument check standard*—A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See 7.6.1)

3.8 *Interference check sample*—A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors. (See 7.6.2.)

3.9 *Quality control sample*—A solution obtained from an outside source having known, concentration values to be used to verify the calibration standards. (See 7.6.3)

3.10 *Calibration standards*—A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). (See 7.4)

TECHNICAL REPORT DATA

(Please read Instructions on reverse before completing)

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

This summary of guidelines provides agreed-upon measurement procedures needed to provide consistent data for the FY2000 National Air Toxics Pilot Monitoring Program, initiated by EPA through the S103 Grant Process. Although the details of the procedures herein are not entirely consistent with the Compendium of Methods, items called out are specific to the data quality goals of the Pilot Monitoring Program.

This document is not policy and does not contain legally binding requirements, nor is it regulation. While it presents recommendations and suggestions regarding techniques for the measurement of toxic air pollutants for the Program discussed above, it may not be appropriate for other situations. This document is intended for use by those already familiar with the analysis of field samples for volatile organic compounds (VOC's), carbonyl compounds and metals.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
VOC Particulates carbonyls toxic monitoring metals Replicates, duplicates, field blanks MDL filters TSP	Air Pollution control Air Pollution monitoring	

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