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Quality Assurance Project Plan

Use of Passive Sampling Devices (PSDs) in a Near-Road Monitoring Environment

Prepared for

Office of Air Quality Planning and Standards (OAQPS)
Air Quality Assessment Division
Ambient Air Monitoring Group
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Prepared by

Sonoma Technology, Inc.
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A. Project Management

A.1 Title and Approvals

Use of Passive Sampling Devices (PSDs) in Near-Road Monitoring Environment

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QAPP Category III
Prepared for

Office of Air Quality Planning and Standards (OAQPS)
Air Quality Assessment Division
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A.5 Distribution List

This Quality Assurance Project Plan (QAPP) will be distributed to all State and local air agencies, contractors, and U.S. Environmental Protection Agency (EPA) staff participating in or supporting the use of passive NO_2 devices as part of the near-road NO_2 monitoring pilot.

Cooperators in this study include

- Ambient Air Section, Air Management Division, Environmental Protection Commission of Hillsborough County, Florida (Tom Taminini, Manager)
- Ambient Air Monitoring Program, Environmental Laboratory, Broward County, Florida (Monica Pognon, Natural Resource Specialist III)
- Maryland Department of the Environment (Jennifer Hains, Research Statistician; Chris Smith, Technical Support Lead)
- Air Quality Division, City of Albuquerque, New Mexico (Ken Lienemann, Air Monitoring Supervisor)
- Idaho Department of Environmental Quality (Bruce Louks, Manager)
- Research Triangle Institute (RTI, Eva Hardison, Manager, Environmental Chemistry Department; Dorothy Pickett)
- EPA Region 6 Houston Laboratory (Johnson Mathew, Senior Scientist/Chemist; Mark Sather, Environmental Scientist; Christy Warren)

A.6 Project Organization

This QAPP for a project using passive sampling devices (PSDs) in a near-road monitoring environment was prepared according to *EPA Requirements for Quality Assurance Projects Plan*, EPA QA/R-5.

The project has three major components: (a) sample collection, (b) chemical analysis, and (c) data validation and analysis. Ms. Hilary Hafner of Sonoma Technology, Inc. (STI) and Mr. Nealson Watkins, the EPA Work Assignment Manager (WAM), will be jointly responsible for all aspects of the project. Samples will be collected using PSDs at a number of sampling locations; typically, from four to ten locations (determined on a case-by-case basis) in each of five selected cities. The PSDs, which are manufactured by Ogawa & Co. USA, Inc. (Ogawa), will be provided by STI for four cities and by a regional laboratory for one city. State and local agencies will deploy the samplers at the sampling sites. The monitoring agencies will train their site operators and provide all of the associated supplies, log sheets, and chain of custody (COC) forms that are associated with the sampling efforts (such as the templates and accompanying PSD standard operating procedures [SOPs] provided by the EPA in this QAPP). STI will be responsible for obtaining completed copies of the field Site Information sheet, the COC form for each sample, and the pertinent laboratory QC information and analytical results for each weekly sampling period for each city. Field documentation forms will be obtained approximately weekly, after samples have been shipped to the lab, and reviewed for completeness. COC forms will also be obtained from the laboratory once analytical procedures are complete so that the sample custody information is entirely available.

Samples collected at the sites as part of the project will be chemically analyzed by either RTI under subcontract to STI or the EPA Region 6 laboratory in Houston, Texas. STI will request that data be made available as soon as possible once analyses are complete so that Level 1 data validation procedures can implemented for the measurements performed on the samples. Level 1 validation will include review of the recorded sampling records and the analytical results. After validation, STI will analyze the data to assess the spatial distribution of ambient nitrogen dioxide (NO_2) and the combination of nitric oxide (NO) and $NO_{2,}$ commonly referred to as oxides of nitrogen (NO_x), near roadways. STI will prepare a final report.

EPA staff are responsible for leading the technical activities of the PSD pilot study. EPA will work with the State monitoring agencies to ensure that monitoring staff are following the SOPs provided in this QAPP. The States will send the PSDs to the analytical laboratory (RTI or the EPA Region 6 laboratory in Houston). STI staff will obtain filter analysis results from the laboratory for evaluation. STI will also keep EPA informed about the data and work with the State agencies as needed. The organizational relationships are shown in **Figure A-1**.

Mr. Nealson Watkins and Dr. Richard Baldauf are the overall leads for the PSD pilot study. Mr. Watkins and Dr. Baldauf will work directly with the State monitoring agency contacts and with STI. Ms. Hilary Hafner will be responsible for assigning STI personnel among work areas and reviewing all technical reports. She also will be responsible for technical management administrative activities, such as developing STI's monthly technical reports and tracking costs. Mr. David Vaughn will provide technical advice for this project and Dr. Paul Roberts will ensure all of STI's products are of the highest quality.

Table A-1 summarizes the roles and responsibilities of the STI project staff selected to conduct the work under this work assignment (WA).

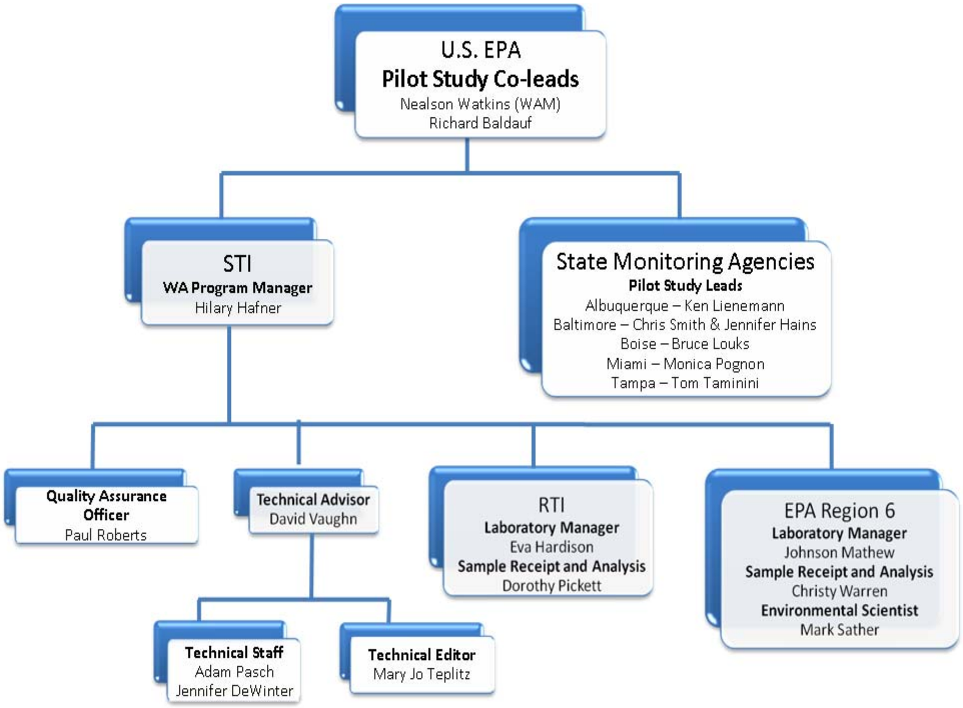

Figure A-1. Organization chart.

Table A-1. Staff selected to provide support to this project.

Staff Member (Affiliation, P-Level)	Project Role	Responsibility	Experience and Qualifications
Hilary Hafner (STI, P4)	STI Project Manager	Overall contract management and supervision	M.S., Chemical Engineering Sr. Vice President, Manager of Air Quality Measurements and Data Analysis Division Experienced air quality data analyst and manager of EPA WAs
David Vaughn (STI, P4)	STI Technical Advisor	Technical support for field-related operations; review of QAPP, SOPs	M.S., Plant Sciences Group Manager, Air Quality and Exposure Measurements Monitoring lead for air quality field studies
Paul Roberts (STI, P4)	STI Quality Assurance Officer	Ensure quality systems are employed	Ph.D., Environmental Engineering Science Executive Vice President; Chief Scientific Officer; Corporate Quality Assurance Officer Experienced in field study design, monitoring methods, and data analysis and interpretation
Adam Pasch (STI, P2)	STI Air Quality Analyst	Analyze and interpret PSD data	Ph.D., Meteorology Meteorologist II Experienced data analyst for a range of air quality and meteorological data sets
Jennifer DeWinter (STI, P2)	STI Air Quality Analyst	Analyze and interpret PSD data	B.S., Earth Science Air Quality Analyst Experienced data analyst for a range of air quality data sets
Mary Jo Teplitz (STI, P3)	STI Technical Editor	Technical editing and graphics support for reports	M.A., Music Literature Technical Editor Experienced editor for a wide range of technical products
Eva Hardison (RTI)	Manager	Overall management of RTI Environmental Chemistry Department	Senior Manager of Environmental Chemistry
Dorothy Pickett (RTI)		Sample receiving and analysis	
Johnson Mathew (EPA Region 6 Houston Lab)	Manager, Sr. Scientist	Laboratory management	
Christy Warren (EPA Region 6 Lab)		Sample receiving and analysis	
Mark Sather (EPA Region 6)	Environmental Scientist	Leading inter-laboratory comparison; assisting with Albuquerque study design and implementation	Air Quality Analysis Section Experienced in designing and implementing PSDs

A.7 Problem Definition/Background

Under the monitoring requirements promulgated as part of the NO_2 National Ambient Air Quality Standards (NAAQS) revisions of 2010, State and local agencies are required to monitor near heavily trafficked roads where peak NO_2 concentrations are expected to occur. Key factors in selecting an appropriate near-road monitoring site to fulfill these requirements are (1) specific roadway characteristics (traffic volume, fleet mix, congestion, roadway design, terrain, and meteorology) and (2) the logistics (safety, access, power, etc.). The EPA is creating a technical assistance document (TAD) to aid states in this endeavor. A key concept discussed in the TAD is the suggested analysis of traffic data by States, specifically traffic volume in the form of annual average daily traffic (AADT), fleet mix, and congestion data, to create a prioritized list of road segments as candidate near-road sites. States would then be in a position to more closely scrutinize candidate road segments based on other key considerations.

State and local agencies also have options by which they may supplement and/or possibly validate their prioritized list of candidate road segments resulting from traffic analysis, including the use of exploratory monitoring and/or modeling. Exploratory monitoring (or sampling) can be accomplished using a variety of methods, which includes using PSDs. PSDs are an attractive resource due to their ease of use and relatively low cost. Using data from PSDs, analysts can directly compare one candidate road section to similar road segments within an urban area. Data gathered by such an effort could then be used to supplement and/or validate any traffic analysis and subsequent candidate road segment evaluations.

Combining knowledge of roadway characteristics and logistical concerns with information gathered through exploratory studies using PSDs will improve state and local agencies' ability to select near roadway monitoring sites with meaningful design values.

The purpose of this work is to assist volunteer State and local air agencies who are collaborating with the National Association of Clean Air Agencies (NACAA) and EPA by providing resources for deploying PSDs sensitive to both NO_2 and NO_x, including PSD hardware, consumables, laboratory analysis, and data analysis, as part of the near-road NO_2 pilot study. Data produced will be used by each state and EPA to (1) verify and validate the near-road site selection process conducted by that state, and (2) provide feedback to the development of the near-road monitoring TAD. Note that the data from individual sites within a Core Based Statistical Area (CBSA) will only be compared to data from other sites within that CBSA.

A.8 Project Description

A select number of volunteer State and/or local agencies will participate in the near-road NO_2 pilot study. These volunteer State and local partners will use PSDs to supplement and evaluate the near-road site selection process, which is initially based upon traffic data analysis. EPA staff will aid in gathering and preparing the preliminary support material to be used by

State and local agencies to identify candidate sites within five target urban areas, specifically defined as CBSAs. The five CBSAs are Albuquerque, New Mexico; Baltimore, Maryland; Boise, Idaho; and Miami and Tampa, Florida; these CBSAs represent a range of near-road monitoring situations typical of conditions throughout the country. EPA aid includes providing traffic and geospatial analysis and a list of possible road segments of interest to the State and local agencies for further evaluation. EPA will then support the agencies in their effort to select up to ten locations in each city for installation of PSDs.

The sampling design is as follows:

- Analyze the PSDs for both NO_2 and NO_x where possible. This action will better ensure the quality of the data. PSDs can be set up to measure both NO_x and NO_2 by using an NO_2 filter in one end of the sample tube and a NO_x filter in the other end. Checking that NO_2 concentrations are less than or equal to NO_x concentrations for the same sampling period provides one quality check of the data. Because of laboratory capacity, CBSAs supported by EPA Region 6 laboratory will not be able to sample for NO_x.
- Place all PSDs at each location in pairs. Having duplicate samples at each sampling location allows for increased precision and should significantly increase the probability of producing valid data for every location for every week (e.g., high data completeness). State and local agencies will conduct weekly passive sampling over a minimum five-week period at each of the sampling locations in the five selected CBSAs.
- Place one of the sampling locations in each city at a routine, continuous NO_2 monitoring site. A PSD sample collocated with a continuous NO_2 monitor provides a measure of accuracy.
- Expose PSDs for one week (i.e., seven days), on a consistent basis throughout the study.
- For quality control (QC), obtain enough field blanks and/or trip blanks to represent approximately 10% of the total sample number. One way to meet this goal is to deploy one to two additional PSDs as blanks per week with NO_2 and NO_x filters.

Selected sites will be used to evaluate possible impacts of sampling at differing heights at a single point and to broadly characterize the impacts of monitor placement at different distances away from the target road segment (known as the pollutant gradient). State and local volunteers are encouraged to conduct sampling at multiple heights and to roughly characterize the gradient, via transect sampling, at one location within their CBSAs.

In support of this study, STI will

1. Provide the PSDs for four CBSAs (Baltimore, Boise, Miami, and Tampa). The PSDs will be on loan from the Children's Health Study of the University of Southern California.
2. Provide laboratory analysis of NO_2 and NO_x exposed in Baltimore, Boise, Miami-Broward, and Tampa CBSA through a contract laboratory (RTI, who will maintain quality assurance [QA] for laboratory operations using their EPA-approved methods).

3. Review the data from all five CBSAs to identify any problematic analytical results.
4. Prepare a report containing statistical summaries and interpretation of results from all five CBSAs.

Albuquerque will use PSD hardware provided by EPA Region 6, with laboratory analysis to be conducted at the EPA Region 6 Laboratory in Houston, Texas. STI will manage the logistics for the State and local partners outside of Region 6 (Baltimore, Boise, Miami-Broward, and Tampa) who require PSD hardware and laboratory analysis. The RTI laboratory will clean the PSDs, load them with prepared filters, ship them to the field, unload the filters upon their return to the laboratory, perform laboratory analyses, report the results, and quality assure the data.

A.8.1 Sample Collection and Field Study Support

The State or local monitoring agency staff will be responsible for following the Near-Road NO_2 Pilot Study PSD SOP regarding installing, handling, and shipping the PSDs. The monitoring agencies will ship the PSDs to RTI or the EPA Region 6 laboratory in Houston for analysis using prepared sample containers supplied by the laboratory. Sampling will be conducted beginning in April, 2011, and run for at least five weeks in each city. Monitoring agencies will select locations based upon traffic data analysis and further candidate road segment reconnaissance. PSDs will be sited in the field according to the *Near-Road NO_2 Monitoring Pilot – Passive Sampling Devices (PSDs) Standard Operating Procedures: Field Operations* manual (**Appendix A** of this QAPP).

Each city is assumed to have 10 sites. (This is a nominal quantity; the actual number of sites in each city will vary depending upon the number of road segments deemed appropriate for sampling.) Each site will have 2 PSDs (duplicate PSDs are for determination of precision and to ensure high data capture) deployed each week for 5 weeks. This yields 10 * 2 * 5 = 100 samples, plus 10% QC samples, for a total of 110 PSDs per city. For the cities of Baltimore, Miami, Tampa, and Boise, each PSD has a NO_2 filter and a NO_x filter, so there will be 110 NO_2 filters and 110 NO_x filters, or a total of 220 filters for analysis from each of those cities (880 filters in total). The Albuquerque sampling will consist of NO_2 only, but duplicate PSDs will still be used, yielding an additional 220 filters. Thus, an overall total of approximately 1,100 filters are expected to be analyzed.

A.8.2 NO_2 Laboratory Analysis of Passive Ogawa Devices

RTI will conduct chemical analyses of the Ogawa PSDs collected from the pilot study sites Baltimore, Maryland; Boise, Idaho; Miami, Florida; and Tampa, Florida. RTI will use two laboratory SOPs to fulfill the analytical requirements for the PSDs used in this study. The determination of nitrite ion concentrations will employ the protocols in a previously developed SOP, *Standard Operating Procedures for National Park Service Filter Preparation, Extraction, and Anion Analysis,* included as **Appendix D**. All other procedures in the lab analysis will follow the Ogawa SOP, *NO, NO_2, NO_x, and SO_2 Sampling Protocol Using the Ogawa Sampler,* which is included in this document as **Appendix B**. RTI will analyze PSDs for NO_2 and NO_x.

Chemical analyses for the Albuquerque, New Mexico, pilot site will be performed by the EPA Region 6 laboratory in Houston, Texas. The EPA Region 6 laboratory will analyze PSDs for NO_2 only, following the protocols detailed in the SOP in **Appendix C**. The laboratory employs a daily multipoint calibration procedure, with a continuing calibration every 10 samples using a single middle point standard, and adheres to an acceptance criteria of 20% (Johnson Matthew, EPA Region 6 lab, personal communication). A continuing calibration outside of 20% requires recalibration of the IC.

A.8.3 Data Validation and Analysis

Once laboratory analyses are completed, STI will construct a database with the NO_2 and NO_x data, plus supporting information (e.g., sample identification information, site coordinates, date range of sample, and important monitoring log notes). STI will check for missing information, prepare summary statistics to understand concentration ranges, assess data completeness, compare sample concentrations to method detection limits (MDLs), compare NO_2 and NO_x concentrations (i.e., collocated NO_2 concentrations should be equal to or less than NO_x concentrations); and compare collocated routine NO_2 and NO_x measurements and PSD results.

Data analyses will include

- Reviewing duplicate samples through scatter plots and computation of precision.
- Reviewing trip and field blanks for differences between the two types and for concentration levels. If concentrations above MDL are observed on any blanks, we will assess the sample concentrations from the matching site/city to determine whether the samples were compromised (e.g., the sample concentrations are beyond three standard deviations of the mean).
- Assessing spatial and temporal patterns in NO_2 and NO_x concentrations within a city.
- Comparing sample concentrations from all sites with road segment selection criteria (e.g., estimated annual average daily traffic), including distance to roadway and sampler height.
- Comparing concentrations along transects.
- Comparing concentrations at the same site from different sampling heights.
- Comparing PSD-derived concentrations to existing routine areawide background NO_2 and NO_x monitoring data.
- Inspecting laboratory QA analysis results for any anomalies.
- Reviewing inter-laboratory comparison results.

Analyses will include summary statistics (minimum, maximum, standard deviation, mean, median, coefficient of variation); concentration distribution histogram; time series; scatter plots (including correlation statistics); and box whisker plots, including confidence intervals. Box plots are especially useful in comparing concentrations among transects, among sampling locations, or between sampling heights. A standard statistical package, such as Systat, will be used.

STI will prepare a report detailing the statistical methods and results.

A.9 Quality Objectives and Criteria

In this study, five sets of week-long NO_2 and NO_x samples will be collected by the States at a city-specific number of sites for each of the five cities. Data quality objectives (DQOs) have been established for completeness, accuracy, and precision based on

- scientific requirements needed to address the major objectives;
- knowledge of the measurement system (i.e., chemistry);
- experience with the sampling methods (i.e., statistical power) and other validation studies, such as the use of replicate or duplicate samples; and
- analyses.

NO_2 and NO_x data will be evaluated for completeness to determine whether sufficient experimental data have been collected. The DQOs for precision, accuracy, and completeness are presented in **Table A-2**, along with the MDL for week-long NO_2 and NO_x samples. Definitions of data quality parameters are provided in **Table A-3**. Samples that do not meet the DQOs shown in Table A-2 will be flagged as suspect; these data may then be subjected to further scrutiny. Suspect data are used in the analyses at the discretion of the analyst and in consideration of analysis goals. For example, in assessing the central tendencies in the data, the analyst may choose to flag suspect data, while in assessing specific pollution events, all valid and flagged data may be included. Data are only flagged by the data analysts if sufficient cause is determined (e.g., a known sampling or analytical error). Concentrations more than three times the standard deviation from the mean will be flagged as suspect and subjected to additional scrutiny. While the main objective of the pilot study does not require comparability of data between CBSAs, an inter-laboratory comparison will be conducted to ensure data comparability.

Table A-2. Data quality objectives.

Parameter (Method: PSD)	MDL (ppb)		Precision (%)	Accuracy (%)	Completeness (%)
	RTI	Region 6			
NO_2 concentration	0.32	1.0	20	15	90
NO_x concentration	0.32	NA	20	15	90

Table A-3. Definitions of data quality parameters.

Parameter	Definition
Method detection limit (MDL)	The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined from analysis of a sample in a given matrix containing the sample. RTI determines the MDL as three times the standard deviation of the lowest concentration laboratory standard.
Precision	A measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions. Precision in this project will be assessed by the collection of duplicate PSD samples at each site.
Accuracy	The degree of agreement of measurements (or an average of measurements) with an accepted reference or true value. Accuracy is a measure of the bias or systematic error in a system. Accuracy in this project will be assessed by using collocated PSD samples and by routinely monitoring continuous NO_2 and NO_x measurements.
Completeness	A measure of the amount of valid data obtained from a measurement system compared to the total number of measurements. Completeness will be assessed by reviewing field and laboratory data logs and field and laboratory logbooks to ensure that all data are validated within established DQOs. Sample loss can occur through lost sample shipments, PSDs that are broken or cracked in shipment, excessive moisture in a sample, or analyte concentration beyond the calibration range. To the extent possible, the field training and field and laboratory SOPs are designed to minimize these potential problems.

A.10 Special Training/Certification

No special training is required for this field study. The chemical analysis in the laboratories and the data analyses will be conducted by highly trained staff with extensive experience in the methods that will be employed for the project.

A.11 Documents and Records

A.11.1 Reporting

The following reports, documents, and databases will be submitted to EPA:

- Validated analytical data
- Results of QA, QC, and performance checks
- Corrective actions for observed and reported discrepancies
- Final report on sampling results and data analysis

All field operations records, raw analytical data, project documents, databases, and hard copies and electronic files relevant to the project will be maintained in the laboratories and with STI until the end of the current project or contract and then will be transferred to EPA according to direction. STI's project manager will work with EPA to ensure everyone involved with the project has the most current versions of the QAPP and SOPs.

Field Operations Records

The site information forms and COC records will be completed by the field sampling personnel. Copies will be maintained by the state or local agency. The original site information form will be forwarded to STI, either by email or by fax. The original COC forms will accompany the samples to the laboratory. The laboratory will complete their portion of the COC form (*received by*, *date*), make a copy for their files, and return the original COC form, along with sample analytical results, to STI. As discussed during weekly coordination conference calls, field operators will document on COC forms any changes to sampling, handling, and shipping procedures.

Laboratory Operations Records

The analytical lab will be responsible for maintaining sample management records (receipt, handling, storage) as well as all information pertinent to analytical results (deviations from SOPs, corrective actions taken). These records shall be transmitted to STI either in electronic format (preferred) or as hard copy. Laboratory records will be delivered to STI as soon as the information is complete, and, based on the weekly sampling schedule within sites, is expected to occur for each site on consistent intervals.

A.11.2 Data Integrity

Staff members who are responsible for recording data must be aware of and adhere to the procedures in this QAPP. Project data will be recorded directly, promptly, and legibly in standardized formats in compliance with SOPs. Laboratory notebook entries will be made in black, permanent ink and will be initialed and dated by the person making the entry. Changes or corrections to data will be indicated with a single line through the original entry. Changes will be initialed, dated, and explained.

As described earlier, standard good data analysis practices will be employed in each aspect of the analyses.

A.11.3 Laboratory Records

QC Sample Preparation

Preparation of QC samples will be documented in laboratory notebooks.

Laboratory Sample Processing

As stated in the RTI SOP in Appendix D, "RTI will provide chain-of-custody documentation with all sample shipments to track and ensure that samples are transferred, stored, and analyzed by authorized and qualified personnel. Sample integrity is maintained during all phases of sample handling and analysis, and an accurate written record will be maintained of sample handling and treatment from the time of its collection, through the laboratory analytical process, to the eventual relinquishing of all data….”

The EPA Region 6 lab in Houston will apply similar protocols for sample handling. At a minimum, the post-collection analysis of samples will be recorded in laboratory notebooks or databases by the person who performs the analysis. The sample identification (ID) number, analyses performed, and a description of any problems noted will be recorded.

B. Data Generation and Acquisition

B.1 Sampling Process Design

State and local air agencies will be collecting NO_2 and NO_x data near heavily trafficked roads within five CBSAs (Albuquerque, Baltimore, Boise, Miami–Broward County, and Tampa) through the use of PSDs. The locations where the PSDs are to be exposed are selected on the basis of traffic data analysis (considering traffic volumes, fleet mix, and congestion patterns) resulting in a prioritized list of road segments where peak NO_2 concentrations may be expected to occur. State and local air agencies then select target road segments from the prioritized list on the basis of additional factors, including roadway design, terrain, meteorology; and logistical considerations, such as access and safety. Those target road segments are surveyed to identify the location or locations adjacent to those segments where PSDs may be deployed. The data collected from the PSDs are to be used to supplement existing traffic data analyses in the identification of locations which are suitable and appropriate for permanent near-road NO_2 monitoring stations. PSD samples will be collected at a number of sites, the number of which are CBSA-specific, during the spring and summer of 2011. The PSDs will be exposed for week-long durations, for at least five weeks, at each sampling location. Duplicate samples will be collected at each sampling location throughout the study. Further, approximately 10% of the samples will be designated as field and/or trip blanks.

Weekly calls will be conducted with the participating state and local agencies to discuss project status. Any changes to this design will be discussed via email or conference call with EPA; EPA will approve or disapprove the change.

B.2 Sampling Methods

The sampling technique is based on the property of molecular diffusion of gases, hence the term passive (also referred to as diffusive) sampling. The gas molecules diffuse into the sampler, where they are collected on an impregnated filter or an absorbent material. This diffusion is accomplished without the need to aspirate the device or otherwise force air across or through the sampling device. Since the passive devices are exposed to the ambient atmosphere for a selected amount of time, a time-integrated (or average) concentration can be determined from the devices. There are no known interferences for NO_2 or NO_x with this method.

B.3 Sample Handling and Custody

Laboratories will provide prepared PSDs to field operators at the onset of sampling operations. All field operations, including site establishment, sample collection, and shipment of exposed PSDs to the laboratory, will be conducted by the State and local monitoring agencies. The agencies will follow the *Near-Road NO_2 Monitoring Pilot – Passive Sampling Devices (PSDs) Standard Operating Procedures: Field Operations* manual (Appendix A of this QAPP), which calls for the use of chain of custody (COC) forms to track the shipping, handling, exposure, and use of each individual PSD used in the study. The SOP provides a COC form, along with a site information form, to use for collecting and maintaining information on the sampling locations themselves, including data on the target road segment and the physical location or locations where PSDs are exposed relative to the target road segment and the terrain. Following the completion of each weekly sampling period, the samples will be shipped to the laboratory for analysis, along with copies of the site information form and COC form for each sampler. It will be the responsibility of the laboratory personnel to maintain laboratory logbooks and records that provide a custody record throughout sample receipt and analysis. Additionally, copies of the site information form and COC form shall be sent to the project manager at STI. The site information form will be returned once siting within each city has been completed. COC forms will be forwarded regularly, upon completion of each weekly sampling period. The project manager will review the site information and COC forms for completeness and consistency, with particular attention to PSD identification numbers and siting information. Information on the forms will be transcribed to a project-specific database.

In addition to the specific entries listed on the field documentation forms, field operators will record any unusual occurrences that may impact the integrity of an individual sample. Examples of this might be “Ogawa sampler fell on the ground,” or “sample retrieval was delayed by 3 hours.”

Filter media will be shipped directly from Ogawa to the Region 6 laboratory or to RTI. If possible, all filter media will be obtained from the same manufacturing batch. Both the RTI laboratory and the EPA Region 6 laboratory will follow the handling and PSD loading procedure as outlined in the EPA Region 6 SOP in Appendix C.

PSD ID formats have been established for each city. Formats for Baltimore, Boise, Tampa, and Miami are standardized, and each PSD will be pre-labeled by RTI during the sampler preparation process. These four cities use an ID with a two-letter prefix identifying the city, as defined in **Table B-1**, followed by a three-digit suffix ranging from 001 through 110 (e.g., BO-012) for the 110 PSDs being shipped to each city. All PSDs originating from RTI will be shipped simultaneously in a single batch, of 110 PSDs each, to the cities of Boise, Baltimore, Tampa, and Miami. Upon receipt, the responsible party at each location will ensure that the PSDs are stored properly. The Region 6 lab will ship all PSDs needed for the Albuquerque sampling, following the same protocol.

When deployed, the COC form for each individual sampler will be populated with the specific site identifier, PSD mounting location identifier, and exposure date and time. The site identifier and PSD mounting location identifier are cross-referenced to the site information form. Mounting details (distance from road, height, etc.) are included on both forms, providing redundancy. Once completed, all field identifier information will be entered into a structured relational database to maintain the integrity of sampling information.

The City of Albuquerque utilizes a separate PSD ID format. Five sites are labeled 1 through 5. Multiple PSD mounts (both horizontal and vertical) are utilized within Site 1 at

Albuquerque, and are denoted by lower case letters immediately following the Site 1 identifying number. The suffixes S1 and S2 are utilized to denote the duplicate samples within a single PSD mount. Site specifics for each site and PSD mount are tracked in the relational database.

Table B-1. Sample ID code values.

City	Prefix	Suffix
Baltimore Boise Miami Tampa	BA BO MI TA	001–110 001–110 001–110 001–110
Albuquerque	1 to 5, with lowercase letters to denote horizontal/vertical gradient	S1, S2

For all cities, the relational database will be populated with all the available field sampling information. The field data will include, when available,

- For each city
  - City name
- For each site within each city
  - Site name
  - Street number
  - Street name
  - ZIP code
  - AADT
  - AADT rank
  - Fleet AADT
  - Fleet rank
  - Heavy duty count
- For each PSD mount within each site
  - PSD mount number
  - Latitude
  - Longitude
  - Distance from road
  - Height
- For each weekly sample within each city, within each site, within each PSD mount
  - Sample ID
  - Exposure date
  - Exposure time
  - Recovery date
  - Recovery time
  - Sample type (sample, field blank, trip blank, lab blank)
  - Wave number (sample week number)

While firm efforts have been made to ensure that sampling procedures and field protocols are complete and correct, real world implementation sometimes reveals that changes in some portion of the protocol may be required to fully meet project objectives, or simply to improve efficiency. Should changes in field or laboratory procedures be required, STI will oversee the preparation, EPA approval, and distribution of written documentation, presented as addendums to the SOPs or this QAPP.

B.4 Analytical Methods

PSDs allow air samples to diffuse through filters that are coated with an absorbing reagent solution, which is applied by the manufacturer. The absorbance value of this reagent is proportional to the pollutant concentration in ambient air.

Field samples, field blanks, trip blanks, and laboratory blanks will be extracted using deionized water and analyzed by ion chromatography as documented in Appendices C (EPA Region 6 laboratory in Houston) and D (RTI International). The Region 6 laboratory will rely solely on their SOP for analytical protocols. For the RTI analyses, the protocols detailed in the Ogawa SOP (Appendix B) will be followed up through the point where the filter pads have been extracted. From that point on, the ion chromatography analytical procedure described in the RTI SOP (Appendix D) will be adhered to.

Analysts will derive concentrations using conversion equations. Consult the lab-specific Appendices C or D for the details of the reagent solutions and the extraction and analysis procedures. Sample storage conditions, conversion equations, and acceptable lifetimes are provided in Appendix B.

B.5 Quality Control

Internal QC checks for sampling and sample analysis activities will be conducted at the frequency shown in **Table B-2**. Internal QC procedures for the analytical laboratory supplying data are required and executed according to the laboratory’s SOPs.

Table B-2. Quality control targets for frequency.

Sample	Target
Field duplicates	100%
Field and trip blanks	10%

B.5.1 Duplicates

QC duplicate samples will be collected at every sampling location each week for the duration of the study. That is, all PSDs will be deployed in pairs. Duplicate samples will provide an estimate of the precision of the measurements and increase potential data completeness. Duplicate samples will be prepared, handled, and analyzed in the same manner as regular samples.

B.5.2 Blanks

Field, trip, and laboratory blanks will be prepared and analyzed throughout the study to ensure sample integrity. Field and trip blanks will comprise 10% of the samples collected for each metric. Blanks will be representative of the media used to collect samples in the field.

Field Blanks

Field blanks will be collected weekly to document sample integrity associated with the shipment, collection, storage, and field mounting of environmental samples. Field blanks will be treated the same as samples, except during deployment of the samples, the field blanks will be placed in the clips and shelters and then immediately removed and stored. When the technicians return to the field to retrieve the samples, the field blanks will be carried to the field, but not exposed. The field blanks will be stored with the samples following deployment to measure potential artifacts introduced during handling during mounting, storage in the field, and shipping for analysis.

Trip Blanks

Trip blanks will be collected weekly to document sample integrity associated with the shipment, collection, and storage of environmental samples. Trip blanks will be treated the same as samples, except they will not be removed from the transport container during sample deployment. The trip blanks will be stored with the samples following deployment to measure potential artifacts introduced during storage in the field and shipping for analysis.

Laboratory Blanks

The laboratories will follow their established SOPs to analyze a suitable number of blanks.

Inter-laboratory Comparison (Laboratory Precision)

Since two laboratories will be used during this study, it is appropriate to conduct inter-laboratory comparisons of known samples. The two labs will exchange extra liquid extracts at the beginning and end of the study, and also conduct one filter exchange mid-way through the study. Each lab will select a site for the comparisons. The results of each laboratory for the same sample material can then be compared to assess relative precision between the two laboratories.

B.6 Instrument and Equipment Testing, Inspection, and Maintenance

Laboratory equipment will be maintained according to individual instrument manuals or the laboratory SOPs. There is no field equipment involved in this project.

B.7 Instrument and Equipment Calibration and Frequency

Each laboratory instrument will be calibrated to ensure accuracy within specified limits as described in the laboratory's SOPs. The calibration of analysis instrumentation used under this project will be the responsibility of the analytical laboratory. An equipment logbook will be available for review, as required. RTI instrumentation is calibrated daily.

B.8 Inspection/Acceptance of Supplies and Consumables

The scientist placing an order will verify that any supplies or consumables received are the items that were ordered. A visual inspection will be performed to ensure that no items were damaged in transport.

It is important to inspect the Ogawa samplers prior to use. Since the sampler bodies and components are reusable, they can become damaged and components may need replacement occasionally. Consumables include the Pre-coated Collection Pads for NO_2 (Ogawa part number PS-134) and NO_x (PS-124). The other sampler components that may need replacement, depending on condition, include diffusion end caps, stainless steel screens, retainer rings, inner base pads, and the cylindrical sampler body. Plastic clips are used to secure the Ogawa sampler, and additional clips are needed to attach the sampler to protective shelters (these components are shown in **Figure B-1)**.

Figure B-1. Plastic clips and protective shelter for the Ogawa passive sampler (photo courtesy Ogawa and Co., USA Inc.).

B.10 Data Management

The data for this project will consist of (1) raw data that have received statistical evaluations consistent with QA/QC operations and (2) data from individual analytical runs sorted and stored in electronic format suitable for review.

Data will be provided by the laboratories to STI in spreadsheet format. The format of the data sets from week to week will be consistent, understandable, and include all relevant information about the individual samples including sample identification, the mass of NO_2 or NO_x

in the sample, and any notes about laboratory handling or analysis that could affect sample integrity. STI will link information received from the laboratory with the COC and field site characterizations (e.g., latitude, longitude, and height) for each sample identification number in a relational database. The database will also contain queries and stored procedures to facilitate retrieval and organization of data for analysis. Data entry from the COC forms to the database will be checked by an analyst separate from the person who performed the initial data entry. Entries to be included in the database are described in Section B.3.

STI data analysts have organized the data sets so that they can be readily understood by all project participants and can be imported into spreadsheets and statistical software.

All data sets will be filed in appropriate directory/subdirectory structures on computers that are backed up on a daily basis. All data files will be archived on DVD at the end of the project.

B.10.1 Data Recording

The analytical laboratories will record sample analysis results in electronic format.

B.10.2 Field, Trip, and Laboratory Blanks and Duplicate Samples

Field, trip, and laboratory blanks will be used to determine potential measurement errors. Duplicate samples will provide data that help assess the sample integrity in storage and shipment and also provide data to assess the accuracy of the field data. Univariate statistics of the equivalent air concentrations of the field and trip blanks will be computed and examined for consistency. The means of these values will be tested, and, if significantly different from 0 at $p = 0.05$, will be subtracted from all sample concentrations. All reported data that have been blank corrected will have a flag indicating that the values were blank corrected.

B.10.3 Data Transformation

Samples collected from Baltimore, Boise, Miami, and Tampa will be analyzed by RTI. RTI uses two separate SOP for the analysis; the lab procedures, calculations, and data transformations for determination of nitrite ion are detailed in RTI SOP, which is included in Appendix D. All other lab protocols (those exclusive of nitrite determination) are included in the Ogawa SOP (included as Appendix B). All calculations made by RTI will be provided to the team, and calculation checks will be performed to ensure accuracy. The EPA Region 6 lab in Houston utilizes the procedures as described in their laboratory SOP, *Monitoring Ground-Level* NO_2 *Using Passive Sampling Devices (PSDs) and Analysis by Ion Chromatography* (**Appendix C**).

C. Assessment and Oversight

C.1 Assessments and Response Actions

All available chain of custody forms, field data sheet data, and laboratory analysis QC measures will be reviewed by STI staff regularly (nominally, on a weekly basis, upon conclusion of weekly sampling efforts, and on subsequent lab analyses) and reported to Ms. Hafner and Mr. Watkins. A summary of these performance measures will be reported to all participants upon conclusion of sampling efforts. No technical system or performance audits are anticipated for this study.

Corrective actions for any activities that are outside of the specified control limits will be presented for approval as they are identified. Problems that involve any changes in scheduling, the sample work plan, or performance of analytical tasks will be handled in a manner agreed on by the STI project manager and the EPA WAM.

C.2 Reports to Management

The progress of the QA program and any QC activities will be reported to the WAM as requested in the STI WA. These narratives will address the following:

- Status of any major QA activities;
- Corrective actions taken during the period;
- Summaries of measures of precision and accuracy for the materials prepared during the period; and
- Significant changes in facilities, personnel, major analytical or support equipment, procedures, data processing, or reporting.

D. Data Validation and Usability

D.1 Data Review, Verification, and Validation

The STI technical personnel assigned to the project will be responsible for data evaluation. Measurements must be accurately acquired, mathematically manipulated, and archived on computer storage devices. Appropriate QA of each step will ensure that transfer errors are eliminated and that data in the database or in plots truly represent the data collected in the field. Data for NO_x and NO_2 will be reported in units of parts per billion by volume.

The following information will be received from the pilot study:

- From each city, NO_2 and NO_x samples will be collected (NO_2 only from Albuquerque)
    - At several road segments
    - At a central city site collocated with a continuous NO_x monitor
    - At two heights on one of the road segments
    - At three transects on one of the road segments
    - In duplicate for each sample
    - With 5% being trip blanks
    - With 5% being field blanks
- From the laboratories will come
    - Laboratory QA analysis results
    - Inter-laboratory comparison results

Review and validation of the NO_2 data will include inspecting site information sheets and chain of custody forms to ensure that information is correct (e.g., site, type of sample, sampling dates, city), generating statistical summaries of data, and comparing individual samples to concentration distribution. Samples that are greater than three times the standard deviation from the mean will be flagged. Data completeness will be determined. A review of the NO_2 versus NO_x results for each sample will be undertaken (NO_2 concentrations should be less than or equal to NO_x concentrations). Samples not meeting this particular rule will be flagged.

The STI technical personnel will also be responsible for reducing analytical data according to the methods developed and for providing both raw and summary data, along with the completed sample calculations, to the STI project manager for validation. Records of all laboratory actions (e.g., system performance checks, blanks) will be provided by the laboratory, as appropriate, along with the raw sample data and notes of problems and corrective action taken.

STI will generate a summary of the data collected and analyzed. These reports, along with the applicable chain of custody documentation, site data sheet information, and any other field data generated will be provided after sampling efforts are concluded on an individual CBSA basis. These analysis reports will be provided electronically by email.

When data are received from the laboratory, they will be reviewed prior to any statistical analyses. Any anomalies identified will be raised with the laboratory for clarification. The statistical analyses (Section A.8.3 in this document) will be performed after the questions are resolved.

D.2 Verification and Validation Methods

Data validation will occur at each level of data collection and reporting. Data will be conditionally validated after collection and after analysis. Conditional validation will be the acknowledgment that field and laboratory staff either did or did not notice problems with sample collection or analysis of a particular sample. Initial knowledge of such problems will depend on field or laboratory operators notifying STI or EPA; such issues are also expected to be noted upon the corresponding chain of custody forms. Conditional validation will help identify problems during collection, storage, shipping, and analysis that could invalidate samples. The STI project manager or a designee will officially validate all data prior to delivery to EPA.

As the first step in the data validation process, individuals collecting samples must ensure that the data reported are complete and that they accurately reflect the validity of the measurement. In some instances (e.g., sampling time outside the specified interval), the field team members may question the validity of the sample, noting the concerns on the data collection sheet and providing this information to the project manager or a designee.

The laboratories will continue the data validation process by first ensuring the samples were transported according to the SOP, including the completion of individual chain of custody forms for each sampler. Also, the analytical data must be complete and must accurately reflect the validity of the analysis in accordance with SOPs. Samples analyzed in accordance with the SOP requirements will be considered valid.

Once STI receives the data from the laboratory, the project manager or a designee will make a visual check to ensure that required data are included, the sample calculations are complete, and the summary data accurately represent the raw data.

Where appropriate, outliers will be tested on the standard deviation of the family of measurements. Appropriate notations will be made in the summary report concerning the flagging of any data as outliers. The project manager or a designee will look at the combined field and laboratory data across samplers, sites, and days, using professional knowledge and routine statistical tools (e.g., unusual single peaks, data more than three times the standard deviation beyond the mean for that measure) to identify potential outlier data. Documentation of validation processes will include a list of all anomalies and the corrective action taken.

The validated data will be assembled and a report will be prepared for EPA. This report will include summary data, summary field notations, notations made during data validation, graphs, and/or basic statistics when observations during data collection warrant further investigation.

D.3 Reconciliation with User Requirements

Measurement precision (such as that between collocated pairs) will be assessed by calculating the relative standard deviation of the results of replicate measurements. The standard deviation is calculated as

$$s = \sqrt{\sum \frac{\left(x_i - \bar{x}\right)^2}{n-1}}$$

where *s* is the standard deviation, x_i is an individual measurement, $\bar{x}$ is the mean of the measurements, and *n* is the number of measurements compared.

Acceptance criteria are based on the relative standard deviation:

$$\mathrm{RSD} = \frac{s}{\bar{x}} * 100\%$$

where RSD is the relative standard deviation, *s* is the standard deviation, and $\bar{x}$ is the mean.

Accuracy will be assessed by measuring the agreement between the accepted value for a QC material versus the determined value:

$$\%R = 100\% * \frac{C_m}{C_a}$$

where *R* is recovery, C_m is the measured concentration of the QC material, and C_a is the accepted value for the QC material.

The performance criteria for solid adsorbent sampling of ambient air stated in EPA's *Compendium Method TO-17* (U.S. Environmental Protection Agency, 1999) are the basis of the following parameters (with the exception of completeness); thus, 85% recovery is the minimum acceptable threshold.

Method detection limits (MDLs) will be calculated by using the following formula:

$$\mathrm{MDL} = t_{(n\text{-}1,\ 1\text{-}\alpha\ =\ 0.99)}S$$

where *t* is the Student's *t* value appropriate to a 99% confidence level and *n* – 1 degrees of freedom and *S* is the standard deviation of replicate analysis.

Analytical precision of duplicate pairs is calculated as the absolute value of the relative difference between two identical samples. The equation used is

$$\text{Analytical Precision} = \left(\frac{|x_1 - x_2|}{x} \right) * 100$$

where x_1 is a measurement value from one of the two samples, x_2 is a measurement value from the second sample, and x is the mean of x_1 and x_2. This is a measure of the precision that is achievable for the entire sampling and analysis procedure. *Compendium Method TO-1*7 specifies analytical precision within 20% for synthetic samples.

Completeness of data will be calculated as follows:

$$\%C = 100 * (V/T)$$

where C is completeness, V is the number of measurements judged valid, and T is the total number of measurements expected.

D.3.1 Data Analysis

Data analyses may include the following actions:

- validating the NO_2 data;
- reviewing the NO_2 versus NO_x results for each sample;
- reviewing duplicate samples (precision) and blanks;
- assessing spatial and temporal patterns in NO_2 and NO_x concentrations within a city and between cities;
- comparing NO_2 and NO_x concentrations to road segment selection criteria, including distance to roadway and sampler height; and
- comparing PSD-derived concentrations to existing, routine, area-wide background NO_2 and NO_x monitoring data.

E. Supporting Documentation

Alion Science and Technology (2009) Quality assurance project plan: land-use regression (LUR) modeling and spatial analysis for Cleveland Multiple Air Pollutant Study (CMAPS). Prepared for National Exposure Research Laboratory, Human Exposure and Atmospheric Sciences Division, Research Triangle Park, NC by Alion Science and Technology, Research Triangle Park, NC, QAPP-LAS-09-02, August.

Mukerjee S., Smith L.A., Norris G.A., Morandi M.T., Gonzales M., Noble C.A., Neas L.M., and Özkaynak A.H. (2004) Field method comparison between passive air samplers and continuous monitors for volatile organic compounds and NO_2 in El Paso, Texas, USA. *J. Air & Waste Manage* **54** (3), 307-319.

U.S. Environmental Protection Agency (1999) Compendium method TO-17: determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, 2nd edition, U. S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Center for Environmental Research Information, Cincinnati, OH. Available on the Internet at http://www.epa.gov/ttnamti1/files/ambient/airtox/tocomp99.pdf.

Appendix A:
Near-Road NO_2 Monitoring Pilot – Passive Sampling Devices (PSDs) Standard Operating Procedures: Field Operations

Note that only procedures for NO_2 and NO_x from this SOP are being used in this study.

Near-Road NO_2 Monitoring Pilot – Passive Sampling Device (PSD) Standard Operating Procedures: Field Operations

Adapted by U.S. EPA – Office of Air and Radiation – Office of Air Quality Planning and Standards

for the Near-road NO_2 Monitoring Pilot (circa 2011)

from the “Monitoring Ground-Level NO_2 Using Passive Sampling Devices

(PSDs) and Analysis by Ion Chromatography” document prepared for

Air Quality Analysis Section

Region 6, South Central

U.S. Environmental Protection Agency

1445 Ross Avenue

Dallas, TX 75202-2733

by

ManTech Environmental Technology, Inc.

Research Triangle Park, NC 27709

Near-Road NO_2 Monitoring Pilot – Passive Sampling Device (PSD) Standard Operating Procedures: Field Operations

Prepared by: Date: ____

Reviewed by: Date: ____

Approved by: Date: ____

Adapted by U.S. EPA – Office of Air and Radiation – Office of Air Quality Planning and Standards
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1.0 Scope and Application

1.1 This SOP is to support State and local air monitoring agencies who, as part of a near-road NO_2 pilot, are evaluating the process by which near-road NO_2 monitoring stations may be identified and/or evaluated through exploratory monitoring using passive sampling devices (PSDs).

1.2 Passive sampling devices (PSDs) (Ogawa Inc., USA, Pompano Beach, FL) are to be deployed for the collection of ground-level NO_2 in ambient air with subsequent ion chromatographic analysis.

1.3 PSDs are intended to be placed as near as practicable to target road segments determined by a process outside the scope of this SOP.

1.4 The detectable range for an NO_2 PSD for a 7-day exposure is 0-3600 ppb (per Ogawa, Inc.).

2.0 Summary of Method

This method describes the application of NO_2 PSDs at candidate near-road NO_2 monitoring sites. PSDs are user-friendly, low-cost sampling devices that require no power to collect NO_2 from ambient air. The Ogawa PSD is a two-sided device that consists of a solid polymeric body (2 cm in diameter and 3 cm long) with a diffusion barrier and two stainless steel screens on each side. NO_2, upon diffusion into the PSD, is collected on a filter coated with triethanolamine (TEA). PSDs are mailed to the site operators on a scheduled basis. At the end of the sampling period, the exposed PSDs and their controls are returned to the laboratory via a commercial courier for analysis. They are extracted with ultra-pure water followed by ion chromatographic analysis of the nitrite ion. The concentrations of NO_2 and NO_x can then be calculated using the Ogawa calculations and the nanograms of nitrite measured.

3.0 Definitions

CBSA	core based statistical area
ID	identification
NO_2	nitrogen dioxide
NO_X	oxides of nitrogen (in this case nitric oxide and nitrogen dioxide)

PSD	passive sampling device
ppb	parts per billion

4.0 Field Deployment of NO_2 PSDs at Candidate Near-Road Sites

The field deployment of the PSDs at candidate near-road NO_2 monitoring sties is being executed by individual State and local air monitoring agencies who volunteered to be part of the near-road NO_2 pilot study. EPA contractor Sonoma Technologies, Inc. (STI), with sub-contractor Research Triangle Institute (RTI), and the EPA Region 6 laboratory in Houston, will provide laboratory support, shipping logistical support, and some field equipment to the volunteer air agencies. The laboratory partners will provide prepared PSDs to each partner State and local agency for deployment, and shall follow laboratory procedures described in their individual SOPs, contained as appendices in the Near-road NO_2 Pilot Study QAPP. Unless a State and local air agency already has PSD mounting equipment (e.g., shelters, clips, etc.), such equipment will be also be supplied by STI or EPA Region 6. State and local agencies may need to procure poles on which PSD shelters may be mounted if needed, which can be obtained at a relatively nominal cost at local hardware stores. Air monitoring agencies are expected to select near-road locations where PSDs will be fielded through a process that focuses on the identification of locating road segments where peak NO_2 concentrations are expected to occur based on traffic volume, fleet mix, congestion patterns, roadway design, terrain, and meteorology. This selection process is outside of the scope of this SOP document and the procedures presented here are made under the assumption that State and local air agencies have already identified a number of candidate road segments where PSDs will be deployed. Upon selecting a site for passive monitoring, air monitoring agencies shall fill out a Site Information Sheet (an example of which is available from the EPA) for each location where PSDs are to be used.

A key objective is that PSD exposures occur over week-long periods in a consistent manner at all candidate near-road segments in a given urban area, specifically defined as Core Based Statistical Areas (CBSAs). Consistency would include exposing the PSDs over the same time period at each candidate road segment, week to week, exchanging PSDs on a set routine throughout the study, and otherwise keeping all manner of PSD exposure constant across all PSD monitoring sites and for each consecutive week of the study. It is recommended that at least 5 consecutive weeks of PSD exposures across all candidate near-road sites be considered for the study.

5.0 PSDs and PSD Shelters

Individual PSDs are prepared in the laboratory before being shipped to field locations for exposure. The PSD assembly is capable of housing two filter media on each end, and each individual filter is associated with five other individual supporting parts. When used for ambient air exposure, pre-exposed PSDs are loaded into clips which affix the PSD to a PSD shelter, which is used to keep the PSD shielded from direct solar radiation, precipitation, and direct exposure to wind. A picture of these components, including an exploded view of a PSD, a PSD in a clip, and two PSDs mounted within a shelter, are shown in Figure 1. The PSD shelters are the one piece of hardware that need to be held or fixed in place the field. Shelters can often be fixed on existing infrastructure such as utility poles, posts, fences, or even road signs. However, if no infrastructure exists at a sampling location, field operators may use poles or posts (metal, PVC, or other suitable material) that can be pounded or otherwise secured to the ground for temporary sampling campaigns. Figures 2 and 3 illustrate PSD shelters mounted on varied infrastructure that have been utilized in past field studies.

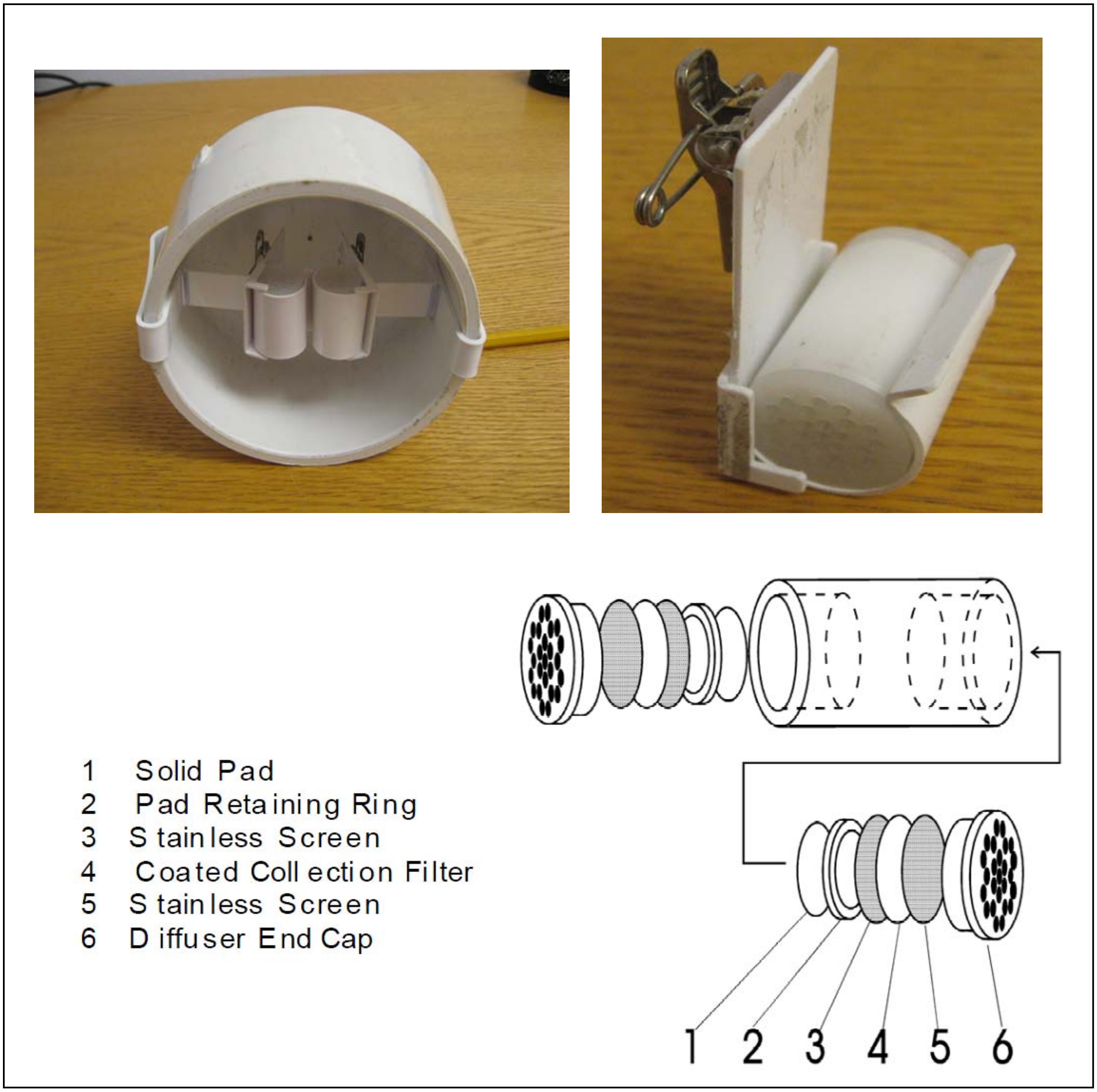

Figure 1. Clockwise from upper left: PSDs in clips which are mounted in a shelter, an individual PSD in a clip, and an exploded diagram of the PSD itself.

Figure 2. PSDs mounted on metal pole.

Figure 3. PSDs mounted on utility pole.

6.0 Installation of PSD Shelters at Near-Road Sites

6.1 Horizontal Spacing

The deployment of PSDs requires very little infrastructure. Typically PSD shelters can be mounted on pre-existing poles or posts that may exist in the near-road environment (e.g., power poles, light poles, and traffic sign posts). PSDs used in the near-road NO_2 pilot are to be deployed as near as practicable to target road segments, where ideally, the target is to be sited within 20 meters[1] (in the horizontal) from the outside edge of the nearest traffic lane of the target road segment. However, deployment of PSD shelters needs to be coordinated across all potential monitoring sites within the same CBSA. It is most desirable to have all PSDs be placed as close to the same distance (in the horizontal) from their respective target road segments as possible. Doing so will allow for an improved ability to compare data from individual road segments to each other without variances in horizontal spacing significantly influencing sampled concentration levels.

6.2 Vertical Spacing

In addition to the horizontal spacing objectives, there are also vertical placement objectives. PSDs used in the near-road NO_2 pilot are to be deployed as close to 2 meters above ground level as

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[1] EPA has selected the target siting criteria for PSD mounts of $\leq$ 20 meters in the horizontal for the near-road NO_2 pilot study based on recommendations from peer-reviewed literature, particularly *Baldauf et al., 2009*.

possible, without being less than 2 meters above ground level. This siting objective is derived from siting criteria for near-road NO_2 monitoring stations, as presented in the Code of Federal Regulations text (40 CFR Part 58, Appendix E). Having all routine PSDs deployed at the same height above ground will allow for an improved ability to compare data from individual road segments to each other without variances in vertical spacing significantly influencing sampled concentration levels.

6.3 Safety Considerations

In the determination of where PSD shelters are to be placed, the safety of air monitoring staff and traffic safety must be considered. It is imperative that the installation of, and subsequent use of, PSDs in the near-road environment do not place air monitoring staff in a highly vulnerable position with regard to the traffic on the nearby target road segments. In particular, PSD shelter location selection should consider the access and egress options of the air monitoring staff who will service the PSDs. It is not recommended that access and egress from a near-road location be accomplished by utilizing the shoulder of the highly trafficked target road segments, unless consultation with a relevant Department of Transportation has provided some level of advice or support. Preferentially, access might be accomplished from nearby service or secondary roads “behind” the PSD shelter location. Further, when options are available, the placement of PSD shelters near the target road segment behind safety features such as guard-rails, or along fencing, may provide additional confidence in maintaining air monitoring staff safety.

7.0 Installing Additional PSD Shelters for Horizontal and Vertical Gradient Monitoring

When possible, it is desirable to select one candidate road segment to conduct monitoring along a horizontal transect, which would be along a line normal to the target road segment with multiple PSDs spaced out at varying distances up to 50 meters[2] away from the road. Conducting such transect monitoring will provide data that can reveal the concentration gradient that exists near the target road segment. It is well documented in peer-reviewed publications that NO_2 concentrations decrease with increasing distance from source roadways. The slope of this gradient can be variable, but the peak NO_2

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[2] The 50-meter distance is the maximum distance that any required near-road NO_2 monitor can be placed from a target road segment per 40 CFR Part 58, Appendix E.

concentrations that might exist along a given road segment are expected to occur most frequently on and very near the road. Conducting transect monitoring provides some insight into the behavior of NO_2 concentrations with increasing distance from the road, and may further highlight the importance of placing any permanent monitoring infrastructure as near as practicable to target road segments.

If transect monitoring is to be conducted, additional PSD shelters should be located at various distances further from the road than the primary PSD shelter location which would ideally be no greater than 20 meters from the outside edge of the target road segment. These additional transect PSD shelters should be placed at the same height above the ground as the primary PSD shelter (target of 2 meters above ground – per Section 6.2 above). An *example* of conducting transect monitoring with 4 individual PSD shelters adjacent to one target road segment might be to place the shelters in a line normal to that target road at distances of 10 meters, 20 meters, 30 meters, and 40 meters, all being 2 meters above the ground.

Further, if horizontal transect monitoring is to be conducted at a particular site, it is also desirable to conduct monitoring at different heights above the ground. If measurements are to be made at multiple heights, the PSD shelter location nearest the target road segment should be the first priority before other locations at increased distances (in the horizontal) are also considered. Although the target height of PSD monitoring in the near-road NO_2 pilot is 2 meters, the siting criteria for required, permanent near-road NO_2 monitoring stations allow for monitor probes to be placed between 2 and 7 meters above the ground. Conducting PSD measurements at two or more heights above the ground would provide data that may give insight into how critical the height above ground can be for a particular candidate monitoring site. If conducting additional PSD exposures in the vertical at one or more horizontal transect locations, it is recommended that the vertical spacing between these individual PSDs be at least 1 to 2 meters apart.

8.0 Receiving and Handling Pre-Exposed PSDs

Field operators will receive shipments of pre-exposed PSDs from the lab on a routine basis, dependent on the sampling schedule and/or laboratory operation routines. Upon receipt, field operators should inspect and document their inventory, without removing the PSDs from the airtight container. It is critical that the PSDs are not removed from their container until in the field at time of insertion into PSD shelters for exposure.

9.0 PSD Exposure Schedule

It is recommended that individual PSD exposures for the near-road pilot be conducted over the course of 1 calendar week. The objective is to capture both morning and afternoon rush hours of a given business week. This means that both rush hours of each business day (Monday through Friday) are ‘captured’ on one PSD. Operators would have a choice on when to exchange PSDs from one week to the next, for example, during the weekend, early Monday morning, or Friday evening. Whatever choice is made, it should be followed at each site for all weeks of the study in a given CBSA.

10.0 Exposing and Recovering PSDs

The PSDs will arrive from the laboratory inside reusable plastic bags which are contained within airtight plastic containers or bottles. In the field, when setting up a routine exposure, field operators will have to first remove the bagged PSD from its airtight container and then remove the PSD from its sealed plastic bag. It is recommended that gloves be employed during the removal and placement of PSDs, however if gloves are not available, field operators should be sure to only handle the PSD by the middle of the barrel and not touch the perforated end caps that cover the filter media. Once the PSD is removed from the plastic bag, the field operator shall place it within a clip, and then mount it within the PSD shelter. When preparing to mount a PSD for exposure, avoid excessive handling of PSD (e.g., walking around with them, breathing on them, etc.) and avoid getting the PSD wet if it is precipitating. When securing the PSD in itsshelter, ensure that the long portion of the PSD is horizontal with the ground. Once the PSD is mounted in the shelter, replace the plastic bag in the airtight plastic container, and then replace the lid, noting that the screw caps on the PSD container must be firmly tightened. Unless already marked, be sure to mark the container of a given PSD with its location ID (using monikers corresponding to Site Information Sheets) and the exposure date and time. This information should also be recorded on corresponding PSD chain of custody forms (an example is available from the EPA).

At the time of recovery of an exposed PSD, field operators must be sure to use the same airtight container that the individual PSD arrived in. When ready to retrieve the exposed PSD, remove the plastic bag from the plastic container, replace the exposed PSD into the plastic bag (pushing out excess air from the bag and sealing the bag), and then place the bagged PSD back into the corresponding (and marked) container. Ensure that the screw cap on the PSD container is firmly tightened.

11.0 Trip Blanks

Trip blanks are a form of quality control. Trip blanks are typically partnered with a routinely exposed PSD, and follow the progression of a routine PSD deployment, but are never removed from their airtight containers. For each PSD serving as a trip blank, its life cycle will mimic a routine PSD (but within its airtight container), consisting of travel to the exposure location, stored in the local field office for the duration of exposure, taken back out to the ambient monitoring site for recovery of its partner PSD that was exposed, and then shipped back to the laboratory in the same shipment. Upon return to the laboratory the trip blank is analyzed like a routine PSD. If the results show some level of contamination, it can be traced, and any problems from the laboratory shipping and handling component of the PSD life cycle can be corrected.

In the near-road NO_2 pilot study, it is recommended that 1-2 (approximately 5%) of the total samples per week be trip blanks, when paired with field blanks (where field blanks would also be approximately 5% of the total samples per week, see Section 12 below). It is advised that that field operators select one or two PSD shelter locations per week for which trip blanks (and field blanks, if used) will be associated with. Further, field operators should select different locations from week to week throughout the study period. However, if an agency only plans to use trip blanks as part of its QA/QC protocols, it is recommended that approximately 10% of the total samples be trip blanks per week.

12.0 Field Blanks

To provide another form of quality control in field operations beyond trip blanks, it is suggested that 1-2 (approximately 5%) of the total samples per week be field blanks (where trip blanks are also approximately 5% of the total samples per week, as discussed in Section 11). Field blanks are similar to trip blanks (as described above in Section 11) in that they mimic the life cycle of a routine PSD. The key difference is that a field blank, after travelling to the field location, is exposed to field handling procedures by brief insertion (only for a few seconds) into the PSD clip, and PSD shelter, followed by immediate removal and replacement in the airtight container. The field blank, like the trip blank, is then stored in the local field office and eventually shipped back to the laboratory for routine analysis with all other PSDs for that week. Any lab results showing some level of contamination can be traced to the source, which in the case of the field blank could be due to handing procedures in the lab or in the field. However, when paired with a trip blank, field blanks and trip blanks together can provide more specific indications on exactly where any contamination may be occurring between both lab and field operations. Specifically, the trip blank may implicate lab problems while the field blank may implicate problems with sample handling in field operations if the trip blank does not indicate laboratory problems. It is advised that field operators pair trip blanks and field blanks to go together to one or two PSD shelter locations each week, selecting different locations from week to week. The recommended objective is to have approximately 10% of the samples that are a combination of trip and field blanks each week.

13.0 Shipping Exposed and QC PSDs to Laboratory

Upon collection of all exposed PSDs for a given week, gather the PSD containers, including any used as field or trip blanks, in preparation for shipment to the analytical laboratory. Complete the information for each PSD on corresponding PSD Chain of Custody forms. The field office should maintain a copy of the Chain of Custody form for field operations records, while the original accompanies the PSDs to the laboratory. Package PSDs (in their containers) with corresponding PSD Chain of Custody forms and affix the appropriate shipping label addressed to the laboratory. It is the option of the field office staff to contact the laboratory in advance of a forthcoming shipment, however, if the laboratory indicates that notification is beneficial, it is recommended that field staff make that accommodation.

14.0 Field Operations Documentation

As has been noted in the above sections, it is recommended that a Site Information Sheet be created and maintained for each location near a road segment or other location where one or more PSD shelters may be utilized in the study. An example Site Information Sheet is available from the EPA. This sheet includes such information as the site name, location, and associated target roadway information. In addition, each Site Information Sheet includes information for each individual PSD shelter at that site, including a number or moniker for each shelter to differentiate them from one another and their individual physical location information within the site itself.

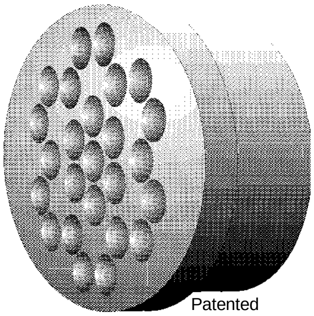
In addition to a Site Information Sheet, field operations need to keep documentation on each individual PSD that is deployed during the study throughout its life cycle. The PSD Chain of Custody form should include information such as the date and time of receipt from the laboratory, whether it is a routine exposure or a trip blank, the location of exposure, exposure and recovery dates and times, and shipping logistical information. An example Chain of Custody form is available from the EPA.

15.0 References

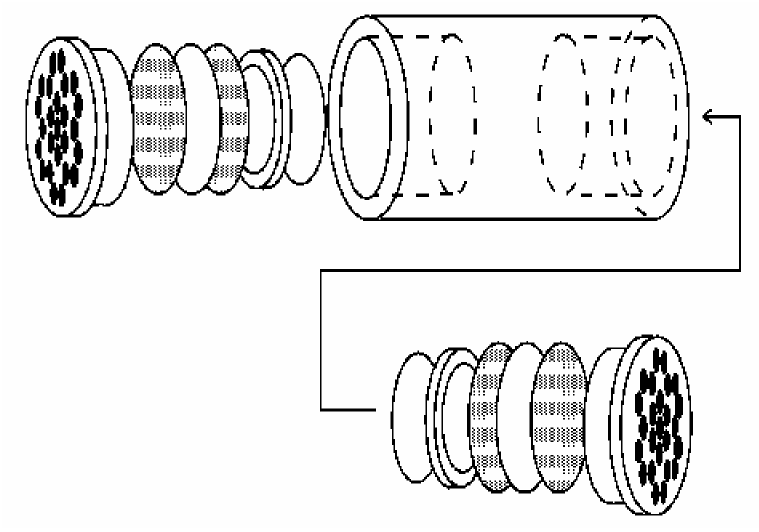
Baldauf, R; Thoma, E; Hays, M; Shores, R; Kinsey, J.; Gullett, B.; Kimbrough, S.; Isakov, V.; Long, T.; Snow, R.; Khylstov, A.; Weinstein, J.; Chen, F.; Seila, R.; Olson, D.; Gilmour, I.; Cho, S.; Watkins, N.; Rowley, P.; Bang. J. (2008). Traffic and Meteorological Impacts on Near-Road Air Quality: Summary of Methods and Trends from the Raleigh Near-Road Study. Air & Waste Manage. Assoc. 58:865-878.

Ogawa & Company, USA, Inc. February 1998. NO, NO_2, NO_X and SO_2 Sampling Protocol Using the Ogawa Sampler, 4th edition.

Appendix B:
NO, NO_2, NO_x, and SO_2
Sampling Protocol
Using the Ogawa Sampler



NO, NO_2, NOx and SO_2 Sampling Protocol Using The Ogawa Sampler*



V6.06

Notice

Version Number

Edition	Month / Year
6.0	June / 2006

* Acknowledgement

System developed by Yokohama City Research Institute of Environmental Science, Yokohama, Japan, Report No. 128, March 1997

Table of Contents

General Information

1. "*Water*", in all cases, shall mean water meeting ASTM Type I specifications. (Equal to Milli-Q by Millipore). Use Reagent grade chemicals for all applications.

2. "*Wash*", in all cases, shall mean cleaning thoroughly with water meeting ASTM Type I specifications.

3. All sampler components should be carefully rinsed and dried before each use. This is an important function, and special care should be taken to do this step carefully.

4. Washing, drying, assembly of sampler, and loading with the proper pre-coated filters should be done in a clean area, free of NOx contamination. It is not necessary to use a glove box.

5. Ideal exposure time is at least 24 hours for monitoring NO, NO2 and NOx. For SO_2 monitoring, the exposure time should be at least several days. This amount of time will develop results from a few PPB to large quantities of PPB's. Shorter exposure times are practical where the expected concentration is known to be high. It is possible to use an exposure time as long as 30 days for low concentrations of NO_2 and SO_2.

6. When the point of research is outdoors, the sampler should be given protection from the sun and rainfall. Ogawa & Co., USA, Inc. has an opaque shelter and mounting bracket designed for this purpose.

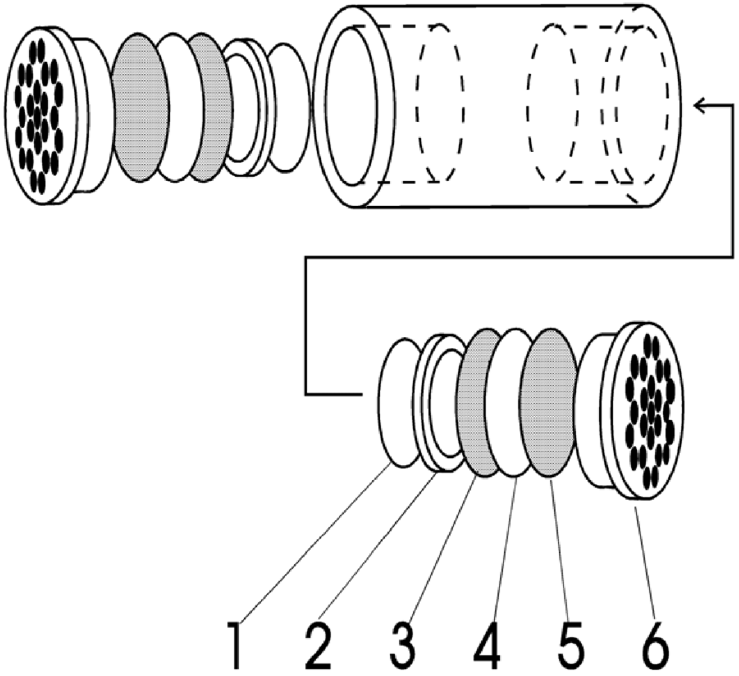
7. Direct exposure of individuals can be easily measured by using the alligator clip to attach the sampler to clothing as close to the face as possible.

8. Concentration conversion coefficients for NO is 60, NO2 is 56 and SO_2 is 39, assuming temperature of 20 ºC, and relative humidity of 70%. Other concentration conversion coefficients, based on different temperatures and humidity, can be obtained from Tables 4 and 6.

9. Satisfactory results have been obtained with concentrations as low as 2 PPB.

Ogawa Sampler Assembly

The sampler is comprised of 2 chambers. In each chamber of the sampler, the assembly stack-up is described below. Start at the innermost position with the pad and progress outwards to the diffuser end cap.



1 Solid Pad
2 Pad Retaining Ring
3 Stainless Screen
4 Coated Collection Filter
5 Stainless Screen
6 Diffuser End Cap

Transport and Storage

After assembly, the loaded sampler is placed into the re-sealable plastic bag, then the bagged sampler is placed into the brown airtight container, provided, and taken to the exposure site. After exposure, the above procedure is again followed to safely seal the used sampler into the brown airtight vial. It is then taken to the laboratory for analysis.

Exposed pads to be analyzed at an off-site laboratory can be safely shipped in the PS-118 8 ml vial. These vials can be rinsed, dried, and reused many times.

The sampler has the following lifetime associated with the various components

	Refrigerated Storage Method	**Frozen Storage Method**
Sealed in original glass vial within the aluminum pouch	90 days	1 year
Resealed in vial, after opening	90 days	
Loaded sampler in bag placed in brown vial with lid	60 days	
Exposed loaded sampler, in bag placed in brown vial with lid*	14-21 days	
*Analysis should be done as soon as possible after exposure.		
Extracted solution in water, in sealed 8 ml vial	90 days	

Table 1: Shelf life associated with Passive Sampler Components

Application of the Sampler in an Outdoor Microenvironment

It is mandatory to protect the loaded sampler from moisture while it is being exposed. To accomplish this task, and still retain proper airflow to the device, it is necessary to use P/N PS-115 Opaque Shelter w/sampler bracket for NO-NO_x, NO_2, and SO_2. O_3 requires P/N PS-106 w/sampler bracket and stainless steel mounting band clamp.

The PS-115 mounting bracket is attached to the site using several small screws or by passing a wire through two holes on each side of the bracket and then around the pole or post.

The sampler easily clips on to the bracket and the cup slides over the bracket to protect the sampler.

The PS-106 sampler bracket, once the sampler is clipped to it, easily slips over the shelter to hold the sampler in the correct position within the shelter.

Analytical Method for NO, NO2 and NOx

While preparing the reagents always use reagent grade chemicals, or highest grade available. For the analysis of NO, NO2, and NOx you will need the following reagents:

Sulfanilamide Solution

The sulfanilamide solution is prepared by dissolving 80 g of reagent grade sulfanilamide in a mixture of 200 ml concentrated phosphoric acid and 700 ml water. This solution is then diluted with water to make a total of 1000 ml.

NEDA Solution

The NEDA solution is prepared by dissolving 0.56 g N-(1-Naphthyl)-ethylenediamine dihydrochloride into 100 ml water. Store in a refrigerator.

Color Producing Reagent

Prepare color-producing reagent immediately before use. Mix the sulfanilamide solution and the NEDA solution in a 10:1 ratio. (10 parts Sulfanilamide solution to 1 part NEDA solution).

Nitrite Standard Stock Solution

Dry Sodium Nitrite, for over 4 hours, at a temperature of 105-110 ºC. Dissolve 1.5 g of this dried Sodium Nitrite in 1-liter water. A 1 ml sample of this solution contains 1000µg of Nitrite.

Nitrite Working Standard Solution

Dilute the Nitrite standard stock solution by 100 times with water. Then, 0, 2, 4,6,8, and 10 ml samples are each diluted with water to make 100 ml solutions. This produces working standard solutions of 0 - 1.0 µg nitrite/ml.

Analytical Operation

Samples

After exposure to the test environment, the stainless screens and cellulose fiber filter are put into a 25 ml glass vial, containing 8ml water, and then shake immediately. Use separate glass vials for NO2 and NOx elements. Vials should be sealed, per accepted laboratory practice.

Over the next 30 minutes, occasional shaking of the vials is recommended.

At the end of the first 30 minute period, vials are cooled to 2-6 ºC, and 2 ml of color producing reagent are added. Shake quickly, after adding the color-producing reagent, and continue to keep vials cool for an additional 30 minutes.

Vials are then allowed to equilibrate at room temperature, for about 20 minutes, and the amount of colored derivative is determined with a spectrophotometer at a wavelength of 545 nm.

Unexposed elements are put through the same procedure to obtain a blank value determination.

Standard Solutions

From the previously prepared nitrite working standard solutions, (those containing 0 - 1.0 µg nitrite/ml), mix 8 ml of each of the nitrite working standards with 2 ml of color reagent, shaking immediately, to prepare a standard curve. Chill standard solution, like samples, before adding color reagent.

Supplement

It is strongly recommended that separate pipettes be used for nitrite standard stock solution from those used for preparing nitrite working standard solutions.

When the exposed NOx element is placed in a vial with 8 ml of water, nitrite ion is produced. When 2 ml of the color-producing reagent is added, and the reaction is allowed to take place at 2-6 ºC, the amount of colored derivative produced is proportional to the amount of original nitrite. If the reaction takes place at warmer temperatures the amount of color derivative produced is not consistent.

It is recommended to use at least 3 blanks for each lot analyzed.

Procedures that help secure accurate analysis results include:

1. Screens and/or filter pads should be added to vials already containing a solution, never into a dry vial.

2. Vials must be shaken immediately after adding color reagent.

3. Cooling must be done according to the protocol.

Flow Injection Method

The flow injection method is a method using analyzing equipment available through various equipment manufacturers

This new method is very useful where the analysis of large numbers of samples is required. It is a very simple and accurate method, minimizing deviations caused by elapsed time, temperature, and other variables. The results, using this method, have high precision.

Calculation of Concentration for NOx, NO_2 and NO

In order to do the calculation you need to do the following steps:

1. Preparing the Standard Curve
2. Calculation of Concentration Data

Preparing the Standard Curve

In this procedure we will establish the Slope of the standard curve. You will need access to a spectrometer or a colorimeter and you will measure the absorbance of 6 standard samples.

1. Refer to Table 2 on the following page. The first two columns refer to values related to the concentration of the standard NO_2 solution. The next three columns refer to values related to the absorbance. The last column refers to the calculation of the Slope of the standard curve. Begin at the top left and proceed by filling in values in the different cells. Those cells which have been "*grayed out*" do not require a numerical value. When you finally enter a value at the bottom right cell you have completed the computation procedure.
2. Make sure that you have access to six standard samples. Make sure that the standard samples are of 0, 0.1, 0.2, 0.4, 0.6 and 0.8 μg/ml NO_2 solutions.
3. The first column requires the concentration of the standard sample (x). Enter the values if they do not exist on the table.
4. The second column requires the calculation of x^2. Enter the values if they do not exist on the table.
5. Compute Σx^2 (sum of all x^2) and enter the value in cell (8).
6. Using your colorimeter or spectrometer to measure the absorbance (y) of each sample. Enter the corresponding values in cell (2) through (7).
7. Cell (2) represents the blank absorbance y_0 (i.e. absorbance when the concentration is 0.0 μg/ml). Using this value calculate ($y - y_0$) and enter the net absorbance A for the various standard samples.
8. The next row represents the product between the concentration and the absorbance. Fill in the values of $x(y - y_o)$.
9. Compute $\Sigma x(y-y_0)$ and enter the sum in cell (9).
10. Compute the Slope by calculating $\frac{\Sigma x(y-y_0)}{\Sigma x^2}$ (cell (9) divided by (8) and enter the value in cell G.

Concentration of Standard NO$_2$ Solution (μg/ml)		Absorbance			Slope
x	x^2	y	y - y_0	x (y - y_0)	$\frac{\Sigma x(y-y_0)}{\Sigma x^2}$
(1)	(1) x (1)		A	(1) x A	(9) / (8)
0	0	(2)			
0.1	0.01	(3)	(3) – (2)		
0.2	0.04	(4)	(4) – (2)		
0.4	0.16	(5)	(5) – (2)		
0.6	0.36	(6)	(6) – (2)		
0.8	0.64	(7)	(7) – (2)		
	Σx^2			$\Sigma x(y-y_0)$	(9) / (8)
(8)	1.21			(9)	G

Table 2: Preparing the Standard Curve for NO, NO2 and NOx

CALCULATION OF CONCENTRATION DATA

After the Slope for the standard curve has been prepared, you will calculate the concentration. You will need access to a spectrometer or a colorimeter and you will measure the absorbance of the sample that you have collected. Here are the steps:

1. Refer to Table 3 on the following page. Each calculation has to be repeated several times depending upon the samples which you have.

2. Enter the location (descriptive term) for each site.

3. Enter the exposure time associated with each site. Enter values in row (3).

NOx Calculation

4. Using your spectrometer or colorimeter measure the absorbance for the sample associated with each site. Enter the values in row (4).

5. Measure the absorbance associated with a blank sample (0 μg/ml). Enter the values in row (1).

6. Calculate the absorbance for each sample. Enter the values in row (5) by taking the difference between rows (4) and (1).

7. Calculate the solution concentration in row 4. This is done by taking the absorbance in row (5) and dividing it by G – the Slope of the standard curve. Note, G was computed previously using Table 2 .

8. Calculate the collected weight in ng and enter the value in row (7). This value is obtained by taking a product of the solution concentration (6) and the abstract amount (usually 8 ml) and a factor of 1000 (for converting from PPM to PPB).

NO_2 Calculation

9. Using your spectrometer or colorimeter measure the absorbance for the sample associated with each site. Enter the values in row (9).

10. Measure the absorbance associated with a blank sample (0 μg/ml). Enter the values in row (2).

11. Calculate the absorbance for each sample. Enter the values in row (10) by taking the difference between rows (9) and (2).

12. Calculate the solution concentration in row (11). This is done by taking the absorbance in row (10) and dividing it by G – the Slope of the standard curve. Note, G was computed previously using Table 2.

13. Calculate the collected weight in ng and enter the value in row (12). This value is obtained by taking a product of the solution concentration (11) and the abstract amount (usually 8 ml) and a factor of 1000 (for converting from PPM to PPB).

14. Next calculate the concentration in row (13). This value is obtained by multiplying the concentration conversion coefficient α_{NO2} by the collected weight (12) and dividing by the exposure time (3). At 20ºC and 70% relative humidity $\alpha_{NO2} = 56$. For other values of temperature and relative humidity please refer to the following section for calculation of α_{NO2} .

NO Calculation

15. Calculate the collected weight in ng and enter the value in row (14). This value is obtained by taking a difference of the NOx weight (7) and the NO2 weight (12).

16. Next calculate the concentration in row (13). This value is obtained by multiplying the concentration conversion coefficient α_{NO} by the collected weight (12) and dividing by the exposure time (3). At 20ºC and 70% relative humidity $\alpha_{NO} = 60$. For other values of temperature and relative humidity please refer to the following section for calculation of α_{NO} .

NOx Calculation

17. Calculate the concentration of NOx in row (8) by adding the concentration of NO2 (13) and NO (15).

Compound	Blank Absorbance			Average	Slope of the Standard Curve	Temperature ºC	Relative Humidity (%)	Concentration Conversion Coefficient	
	B1	B2	B3					αNO_2	αNO
NOx				(1)=	G =	(20ºC)	(70%)	α_{NO2} = (56)	α_{NO} = (60)
NO_2				(2)=				α_{NO2} =	α_{NO} =

- α_{NO2} = 56 and α_{NO} = 60 when Temperature = 20ºC and Relative Humidity = 70%. For other combinations of temperature and relative humidity please refer to the discussion provided in following section.

	Specification		Samples			
	Sample Number		1	2	3	4
	Sample Location					
	Sampling Time (min) (3)	=(3)				
NOx	Sample Absorbance (4)	=(4)				
	Absorbance (5)	= (4) – (1)				
	Solution Concentration (µg/ml) (6)	= (5) / G				
	Collected Weight (ng) (7)	= (6) x 8 x 1000				
	Concentration (PPB) (8)	= (13) + (15)				
NO_2	Sample Absorbance (9)	= (9)				
	Absorbance (10)	= (9) – (2)				
	Solution Concentration (µg/ml) (11)	= (10) / G				
	Collected Weight (ng) (12)	= (11) x 8 x 1000				
	Concentration (PPB) (13)	= α_{NO2} x (12) / (3)				
NO	Collected Weight (ng) (14)	= (7) – (12)				
	Concentration (PPB) (15)	= α_{NO} x (14) / (3)				

Table 3: Calculation of Concentration Data For NOx , NO2 and NO

Calculation of Concentration Conversion Coefficients for NO and NO_2

Typical values of α_{NO} and α_{NO2} are provided in Table 4.

For a combination of temperature and relative humidity which does not exist in Table 4 you can calculate α_{NO} and α_{NO2} using the following formulas:

$[T] =$ Ambient temperature in degree Centigrade
$[RH] =$ Relative humidity in %

$P_N = 17.535$ (water vapor pressure in mm Hg at 20 degC)

$P_T =$ Vapor pressure of water at the ambient temperature $[T]$
(see Table 5 for typical values)

$$[P] = \left\{ \frac{2P_N}{P_T + P_N} \right\}^{2/3}$$

(see Table 5 for typical values)

$$\alpha_{NO} = \frac{10000}{(-0.78x[P]x[RH]) + 220}$$

$$\alpha_{NO_2} = \frac{10000}{(0.677x[P]x[RH]) + (2.009x[T]) + 89.8}$$

Example Calculation for α_{NO} and α_{NO2}

Let us calculate α_{NO} and α_{NO2} at 9 °C and 60% Relative Humidity.

Looking at Table 4 we have $\alpha_{NO} = 61$ and $\alpha_{NO2} = 64$.

Let us now use the formulas provided earlier:

$$
\begin{aligned}
&[T] = 9 \\
&[RH] = 60 \\
&P_N = 17.535 \\
&P_T = 8.609 \text{ (see Table 5)} \\
&[P] = \left\{ \frac{2P_N}{P_T + P_N} \right\}^{2/3} \\
&\quad = \left\{ \frac{2 x 17.535}{8.609 + 17.535} \right\}^{2/3} \\
&\quad = 1.216 \text{ (see Table 5)} \\
&\alpha_{NO} = \frac{10000}{(-0.78 x [P] x [RH]) + 220} \\
&\quad = \frac{10000}{(-0.78 x 1.216 x 60) + 220} \\
&\quad = 61.32 \\
&\alpha_{NO_2} = \frac{10000}{(0.677 x [P] x [RH]) + (2.009 x [T]) + 89.8} \\
&\quad = \frac{10000}{(0.677 x 1.216 x 60) + (2.009 x 9) + 89.8} \\
&\quad = 63.58
\end{aligned}
$$

Temperature (ºC)	**Relative Humidity(%)**	α_{NO2}	α_{NO}
-10	50	84	61
-9	50	83	61
-8	50	81	61
-7	50	80	61
-6	50	79	61
-5	50	78	61
-4	50	77	61
-3	50	76	60
-2	50	75	60
-1	50	74	60
0	50	74	60
1	60	68	64
2	60	68	63
3	60	67	63
4	60	66	63
5	60	66	63
6	60	65	62
7	60	65	62
8	60	64	62
9	60	64	61
10	60	63	61
11	60	63	61
12	60	62	60
13	60	62	60
14	60	61	60
15	70	58	63
16	70	58	62
17	70	57	62
18	70	57	61
19	70	57	61
20	70	56	60

Table 4: α_{NO} and α_{NO2} as a function of temperature and relative humidity

… Table continued on next page

Temperature (ºC)	**Relative Humidity(%)**	α_{NO2}	α_{NO}
21	70	56	60
22	70	56	60
23	70	55	59
24	70	55	59
25	80	53	61
26	80	52	61
27	80	52	60
28	80	52	60
29	80	52	59
30	80	52	59
31	80	52	58
32	80	51	58
33	80	51	57
34	80	51	57
35	80	50	57
36	80	50	56
37	80	50	56
38	80	50	56
39	80	49	55
40	80	49	55

Table 4: α_{NO} and α_{NO2} as a function of temperature and relative humidity

Temperature [T] degC	Water Vapor Pressure [P_T] mmHg	Vapor Pressure Coefficient [P] dimensionless
-10	2.149	1.4697
-9	2.326	1.4609
-8	2.514	1.4518
-7	2.715	1.4421
-6	2.931	1.4320
-5	3.163	1.4213
-4	3.410	1.4101
-3	3.673	1.3984
-2	3.956	1.3861
-1	4.258	1.3732
0	4.579	1.3599
1	4.926	1.3459
2	5.294	1.3314
3	5.685	1.3164
4	6.101	1.3009
5	6.543	1.2849
6	7.013	1.2685
7	7.513	1.2515
8	8.045	1.2341
9	8.609	1.2163
10	9.209	1.1980
11	9.844	1.1794
12	10.518	1.1605
13	11.231	1.1412
14	11.987	1.1217
15	12.788	1.1018

Table 5: Water Vapor Coefficients as a function of Temperature

…Table continued on next page

Temperature **[T]** **degC**	**Water Vapor Pressure** **[P_T]** **mmHg**	**Vapor Pressure Coefficient** **[P]** **dimensionless**
16	13.634	1.0818
17	14.530	1.0615
18	15.477	1.0411
19	16.477	1.0206
20	17.535	1.0000
21	18.650	0.9794
22	19.827	0.9587
23	21.068	0.9380
24	22.377	0.9174
25	23.756	0.8969
26	25.209	0.8764
27	26.739	0.8561
28	28.349	0.8360
29	30.043	0.8160
30	31.824	0.7962
31	33.695	0.7767
32	35.663	0.7575
33	37.729	0.7385
34	39.898	0.7198
35	42.175	0.7013
36	44.563	0.6832
37	47.067	0.6655
38	49.692	0.6480
39	52.442	0.6309
40	55.324	0.6142

Table 5: Water Vapor Coefficients as a function of Temperature

Analytical Method for SO_2

Sample (One exposed filter pad only)

After exposure to the test environment, the stainless screens and cellulose fiber filter are put into a 25 ml glass vial, containing 8ml water, and then shake immediately. Vials should be stoppered, per accepted laboratory practice.

Over the next 30 minutes, occasional shaking of the vials is recommended.

Add 0.2 ml of Hydrogen Peroxide solution (1.75% solution), and shake slowly for 10 minutes.

Vials are then allowed to equilibrate at room temperature, for about 20 minutes, then sent for IC analysis

Unexposed elements are put through the same procedure to obtain a blank value determination.

Analysis by Ion Chromatograph

Analyzer	Dionex Ion Chromatograph 4000i
Columns	AS4A Separation Columns
Flow Rate	1.7 ml/min
Detector Range	30 µs, 10 µs, 1 µs
Eluant	1.8 mM Na_2CO_3 + 1.7 mM $NaHCO_3$
Regenerant	0.25 N H_2SO_4
Sample Loop	100 µl

Calculation of Concentration for SO2

$$SO_2 \text{ concentration (ppb)} = \alpha_{SO_2} \times \frac{WSO_2}{t}$$

where :

WSO_2 is the sulfate quantity (in ng) collected on the SO_2 elements, determined using the standard curve.

α_{SO2} is the ppb concentration conversion coefficients (ppb - min/ng). At 20 °C the value of $\alpha_{SO2} = 39$.

t is sample collection time in minutes

If you have sample conditions other than 20 °C please refer to Table 6 which provides α_{SO2} at various commonly encountered values.

Temperature T ºC	Diffusion Coefficient D_T cm^2/sec	Ratio of Diffusion Coefficients D_{20}/D_T dimensionless	Conversion Coefficient α_{SO2} PPB-min/ng
-10	0.1068	1.22	47.5
-9	0.1076	1.21	47.2
-8	0.1083	1.20	46.9
-7	0.1091	1.19	46.5
-6	0.1098	1.19	46.2
-5	0.1106	1.18	45.9
-4	0.1113	1.17	45.6
-3	0.1121	1.16	45.3
-2	0.1129	1.15	45.0
-1	0.1136	1.15	44.7
0	0.1144	1.14	44.4
1	0.1151	1.13	44.1
2	0.1159	1.12	43.8
3	0.1167	1.12	43.5
4	0.1175	1.11	43.2
5	0.1182	1.10	43.0
6	0.1190	1.09	42.7
7	0.1198	1.09	42.4
8	0.1206	1.08	42.1
9	0.1214	1.07	41.8
10	0.1222	1.07	41.5
11	0.1230	1.06	41.3
12	0.1237	1.05	41.0
13	0.1245	1.05	40.8
14	0.1253	1.04	40.5

Table 6: Conversion Coefficient αSO2 for SO2 as a function of Temperature

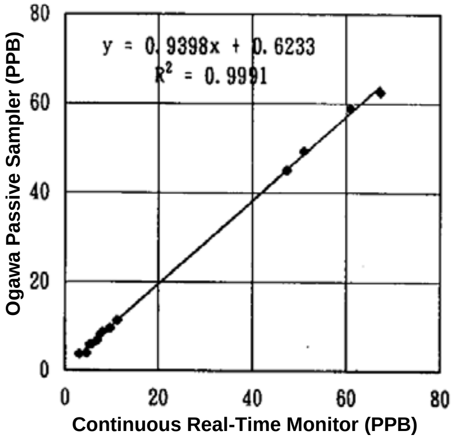
…Table continued on next page

Temperature T ºC	Diffusion Coefficient D_T cm^2/sec	Ratio of Diffusion Coefficients D_{20}/D_T dimensionless	Conversion Coefficient α_{SO2} PPB-min/ng
15	0.1261	1.03	40.3
16	0.1269	1.03	40.0
17	0.1277	1.02	39.8
18	0.1286	1.01	39.5
19	0.1294	1.01	39.2
20	0.1302	1.00	39.0
21	0.1310	0.99	38.8
22	0.1318	0.99	38.5
23	0.1326	0.98	38.3
24	0.1334	0.98	38.1
25	0.1343	0.97	37.8
26	0.1351	0.96	37.6
27	0.1359	0.96	37.4
28	0.1367	0.95	37.1
29	0.1376	0.95	36.9
30	0.1384	0.94	36.7
31	0.1392	0.94	36.5
32	0.1401	0.93	36.2
33	0.1409	0.92	36.0
34	0.1418	0.92	35.8
35	0.1426	0.91	35.6
36	0.1435	0.91	35.4
37	0.1443	0.90	35.2
38	0.1452	0.90	35.0
39	0.1460	0.89	34.8
40	0.1469	0.89	34.6

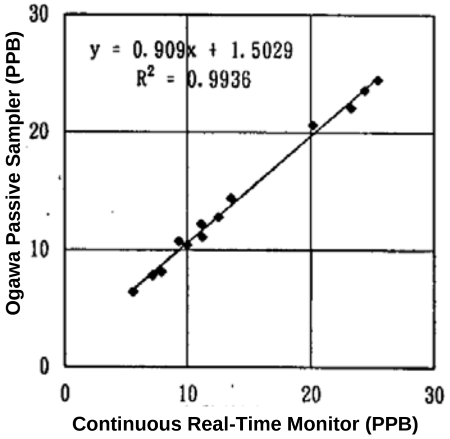
Table 6: Conversion Coefficient αSO2 for SO2 as a function of Temperature

Comparison of Integrated Sampling and Real-Time Monitors

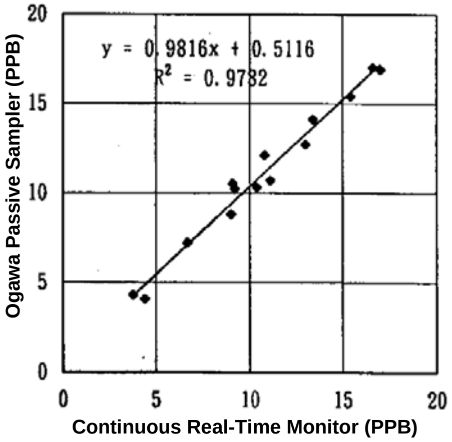
NO



NO2



SO2



Reference:

Yokohama City Research Institute of Environmental Science, Yokohama, Japan, Report No. 128, March 1997

Blank Test Values

Below is the obtained absorbance for 3 unexposed filters coated for NO_2 and NO_x.

NO2 Absorbance	NOx Absorbance
0.009	0.155
0.009	0.142
0.008	0.149
0.009	0.149
Average 0.009	Average 0.149

The higher blank test for NOx compared to that of NO2 is due to PTIO also reacting when color producing is being done. This makes the produced material absorbing wavelength stay near the determining wave length. But, as the NOx collection element holds a fixed quantity of 1.5mg PTIO, the blank value will be stable if the analytical operation is done in a short time. Blank values can also be made lower by taking away PTIO blue color, by extracting with ethyl ether.

Example Calculations

Exposure was made in the ambient air at roadside for 1432 minutes, from 10:32 hrs. August 4th to 10:24 hrs. August 5th. The samplers determined NOx at 0.343 and NO2 at 0.094. The collected NOx quantity is determined as follows:

$$WNOx = \frac{SABNOx - BABNOx}{S} \times V$$

Where: WNOx is in ug of nitrite.
SABNOx is absorbance of NOx sample.
BABNOx is absorbance of NOx blank.
S= Slope (for this calculation assume it is 0.8415)
V= volume of extract in ml.

$$= \frac{0.343-0.149}{.8415} (8) = 1.844 \text{ ug nitrite} = 1844 \text{ ng nitrite.}$$

Collected NO2 Quantity Is Converted to NO2 Quantity as follows:

$$WNO2 = \frac{SABNO2 - BABNO2}{S} \times V$$

Where: WNO2 is in ug of nitrite.
SABNO2 is absorbance of NO2 sample.
BABNO2 is absorbance of NO2 blank.
S= Slope (for this calculation assume it is 0.8415)
V= Volume of extract in ml.

$$= \frac{0.094-.009}{.8415} (8) = 0.808 \text{ ug nitrite} = 808 \text{ ng nitrite}$$

From the WNOx and WNO2 values, using equation (5) we can calculate the PPB of NO in the air sample:

$$\begin{aligned} NO\ (PPB) &= \alpha_{NO} (WNOx-WNO2) / t \\ &= 60\ (1844-808) / 1432 \\ &= 43\ PPB \end{aligned}$$

Using equation (6) we can calculate the PPB of NO2:

$$\begin{aligned} NO2(PPB) &= \alpha_{NO2} (WNO2) / t \\ &= 56\ (808) / 1432 \\ &= 32\ PPB \end{aligned}$$

Since the NOx concentration is the sum of the NOx and NO2:

$$NOx\ (PPB) = 43 + 32 = 75\ PPB$$

Appendix C:
Monitoring Ground-Level NO_2 Using Passive Sampling Devices (PSDs) and Analysis by Ion Chromatography
(EPA SOP-EHD-04-06)

SOP-EHD-04-06 September 2004

Monitoring Ground-Level NO_2 Using Passive Sampling Devices (PSDs) and Analysis by Ion Chromatography

Prepared for

Air Quality Analysis Section
Region 6, South Central
U.S. Environmental Protection Agency
1445 Ross Avenue
Dallas, TX 75202-2733

Prepared by

ManTech Environmental Technology, Inc.
Research Triangle Park, NC 27709

Monitoring Ground-Level NO_2 Using Passive Sampling Devices (PSDs) and Analysis by Ion Chromatography

Prepared by: ______________________ Date: ______________

Reviewed by: ______________________ Date: ______________

Approved by: ______________________ Date: ______________

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Contents

1.0 Scope and Application

1.1 Passive sampling devices (PSDs) (Ogawa Inc., USA, Pompano Beach, FL) are deployed for the collection of ground-level NO_2 in ambient air with subsequent ion chromatographic analysis.

1.2 The detection limit is 1 ppb NO_2 for a 2-week collection period using a Dionex (Sunnyvale, CA) ion chromatograph (IC).

1.3 The detection range is 1–10 ppb NO_2 for a 2-week collection period. If concentrations greater than 10 ppb NO_2 are found, the extract is diluted and reanalyzed.

1.4 When there are no data for temperature and humidity, we assume temperature is 20 °C and humidity is 70%. The concentration conversion coefficient for NO_2 is 56.

2.0 Summary of Method

This method describes regional networking of NO_2 PSD sites. PSDs are user-friendly, low-cost sampling devices that require no power to collect NO_2 from ambient air. The Ogawa PSD is a two-sided device that consists of a solid polymeric body (2 cm in diameter and 3 cm long) with a diffusion barrier and two stainless steel screens on each side. NO_2, upon diffusion into the PSD, is collected on a filter coated with triethanolamine (TEA).

PSDs are mailed to the site operators on a scheduled basis. At the end of the sampling period, the exposed PSDs and their controls are returned to the laboratory via FedEx for analyses. They are extracted with ultra-pure water followed by ion chromatographic analysis of the nitrite ion. The concentration of NO_2 can then be calculated using the Ogawa calculations and the nanograms of nitrite measured.

3.0 Definitions

µL	microliter
µg	microgram
cm	centimeter
g	gram
ID	identification
i.d.	inner diameter
IC	ion chromatograph
in.	inch
L	liter
lb	pound
min	minute
mL	milliliter
mM	millimole
ng	nanogram
ppb	parts per billion
ppm	parts per million
PSD	passive sampling device
psi	pounds per square inch
TEA	triethanolamine

4.0 Field Deployment of NO_2 PSDs

The field deployment of the PSDs is being handled by Region 6 and will not be discussed here. ManTech will ship the pole assemblies to Region 6 for deployment before the study.

5.0 Laboratory Handling of PSDs

The following subsections describe the loading of unexposed PSD collection pads, their removal following field exposure, and their subsequent extraction for IC analysis. It is not necessary to clean new PSDs prior to loading of collection pads. However, used PSDs must be cleaned. (See the cleaning procedure in section 11.0.)

5.1 Loading PSDs

1. Prior to a field study with PSDs, make labels with sample identification (ID) numbers in triplicate for the entire project (see Figure 1).
2. Lay out four new PSDs in their containers on a laboratory counter top covered with clean, white counter paper (Versi-Dry) (see Figure 2).
3. Remove each PSD from its container. Place two of the three identical labels on the container and the third on the PSD holder. Do this for all four PSD containers for each site each week.
4. Disassemble the four PSDs by removing the diffusion barrier and stainless steel screens from each side. (If the PSDs are not new and have been cleaned, disassembly is not needed because they have already been disassembled for analysis and cleaning.)
5. Remove an aluminum foil package containing a vial of 40 TEA-coated collection pads from the refrigerator. Take the vial out of the aluminum foil package and use a flat spatula to remove eight individual collection pads from the vial and place them on a Teflon grid (see Figure 3).

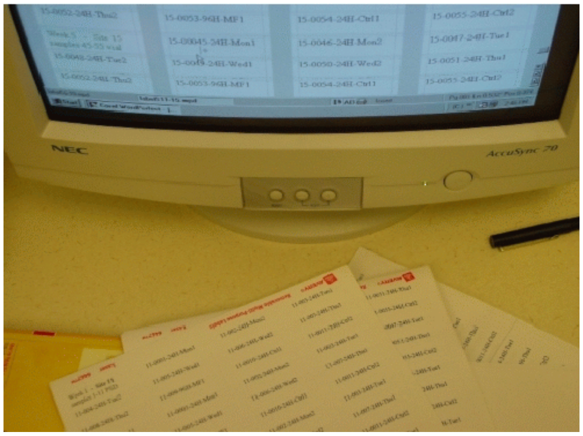

Figure 1. Labels made in triplicate.

Figure 2. PSD layout for loading.

6. To reassemble the PSD, use tweezers to pick up a stainless steel screen and place it in one side of the PSD body, followed by a TEA-coated collection pad from the Teflon grid, a second stainless steel screen, and then the diffusion barrier. Follow the same procedure for the other side of the PSD. Place the reassembled PSD in its holder and then back into the PSD container. ***Tighten the lid firmly on the container.***
7. Place the four containers with loaded PSDs into the proper holes in the foam insert and place the insert in the FedEx mailing box along with the log sheet and preaddressed, prepaid return FedEx air bill and pouch. Seal the box, add the computer-generated FedEx air bill to a plastic pouch, and attach the pouch to the box. Do this for all FedEx site boxes that will be mailed that week (see Figure 4).

Figures 3. PSD loading: (a) pad grid tray, (b) tools, (c) loading process, (d) sandwich configuration, and (e) loading station.

Figure 4. Loaded PSD mailer readied for shipment.

5.2 Unloading PSDs for Analysis

1. When the FedEx boxes containing the exposed PSDs arrive from the monitoring sites, remove the PSD containers from one site box at a time and lay them out on the bench top. Also remove the log sheet from the box and check for weather conditions and any comments the site operator may have had.
2. Disassemble each PSD by taking the end diffusion caps off and removing the screens and collection pads from both sides of the PSD. Handle the two collection pads with stainless steel tweezers.
3. Place two collection pads from each PSD in individual 30-mL polypropylene bottles with 8 mL of ultra-pure water for extraction. Remove the label on the container that each PSD comes out of and place it on the 30-mL extraction bottle for sample identification.

5.3 Extraction of Collection Pads

1. Place the four 30-mL polypropylene bottles containing the exposed NO_2 collection pads and 8 mL of ultra-pure water in a rack that fits an ultrasonic extraction bath (see Figure 5).
2. Place water in the bath at the level of the 8 mL of ultra-pure water in the 30-mL containers holding the collection pads.
3. Place the rack with the PSD extraction bottles in the ultrasonic bath for 15 min.
4. Pour approximately 2 mL of each extract into IC autosampler vials for IC analysis, and write the ID number on the autosampler vials. Pour the remainder of each extract into 6-mL vials, and identify them by taking the ID labels off the 30-mL polypropylene bottles and putting them on the 6-mL vial. Then cap the vials with a compression lid. Place these leftover extracts in a refrigerator as a group in case any of the analyses need to be repeated.

a

b

c

Figure 5. Preparation for analysis: (a) pad removal, (b) sonication, and (c) transfer to autosampler tubes.

6.0 IC Analysis of NO_2 PSDs

A Model 500 Dionex IC equipped with an AS-14 anion analytical column with 1.2 mL/min eluent flow, a 50-µL sample loop, an anion self-regenerating suppressor (ASRS-1), and a 1.0 mM $NaHCO_3$/3.5 mM Na_2CO_3 eluent is used to analyze the water extracts of the TEA-coated collection pads from the NO_2 PSDs. Half of each extract is used for IC analysis of the nitrite ion and the other half is stored in the refrigerator for reanalysis later if necessary.

1. While extraction is ongoing for the collection pads from the first site, set up the schedule on the IC for the analysis of the extracts from that site as follows:
    a. Go to the main menu and click Schedule, File, Open, Anion Schedule, Open.
    b. Type the standard in the first block and then type in each label ID from the PSDs that are being extracted; for example, if the extraction is being done for site 1, week 1, type the standard followed by the four PSD extracts and then another standard.
    c. Click File, Save, File, Print. This prints the IC analysis schedule for the PSD extracts from site 1, week 1.

    The ultrasonic extraction of site 1, week 1, collection pads is generally finished by the time the IC operator has completed setting up the IC schedule to analyze them.
2. Place a cassette vial containing an anion standard in the first slot of the autosampler (AS-40) cassette identified with a black dot. Pour 2 mL of each extract into AS-40 cassette vials and label each cassette vial with a marking pen to match the computer printout of the sampling schedule you just prepared. Place the vials with the extracts from site 1, week 1, in the next cassette slots followed by another standard.
3. Load the schedule by clicking the load schedule icon, which is second from the left in the top set of icons. A block comes up that indicates the number of loops for schedule 1. Click OK.
4. Click Run and the samples will run automatically.
5. Analyze immediately a few of the audit NO_2 PSDs, which were collected on-site prior to the study, and then at regular intervals during the study.
6. Calculate the NO_2 concentration in ambient air. Following is an example calculation:

    Concentration conversion coefficient = 56.

    Sampling time = 20160 min.

    NO_2 PSD was exposed in EPA parking lot for 2 weeks.

    NO_2 diffused into the PSD and converted the TEA coating on the PSD disc to nitrite. The nitrite ion was extracted from the disc with 8 mL of ultra-pure water. The amount of nitrite found by IC analysis was 0.2368 µg/mL.

    The NO_2 concentration is calculated as follows:

    NO_2 concentration (ppb) = 56(WNO2)/t,

    where WNO2 is the nitrite quantities (in nanograms) collected on the NO_2 pads and t is the sampling time in minutes.

    WNO2 = 0.2368 µg/mL x 8 mL = 1.8944 µg = 1894.4 ng.

    NO_2 concentration (ppb) = 56(1894.4 ng)/20160 min = 5.26 ppb.

7.0 Apparatus and Instrumentation

Ogawa NO_2 PSDs and rain shelters

Analytical balance capable of accurately weighing 0.01 g ± 0.0001 g

Auto pipettes with disposable tips

Repeating pipettes, 100-µL dispensing volume

Ultrasonic bath

PSD sampling pole, 40-in. conduit pipe with a 2¾-in. i.d. connected with a thumbscrew union

Dionex Model 500 IC

Foam inserts with holes that hold the PSDs for shipment to and from monitoring sites each week

Tweezers and spatula for handling collection pads

8.0 Consumable Materials and Reagents

30-mL screw-cap polypropylene vials for extraction of NO_2 collection pads

4-mL compression-cap polypropylene vials for storage of unused PSD extract solution in refrigerator for later use if necessary

Ogawa TEA-coated collection pads for NO_2

White removable ID labels, ½-in. x 1¾-in. Avery laser labels, no. 6467

Helium to actuate valves on IC

3-in. x 12-in. x 18-in. mailing boxes to ship PSDs to and from monitoring sites, air bills (no. 0210), and air bill pouches—all free from FedEx

42-in. x 12-in. x 6-in. boxes to mail PSD sampling poles and shelters

3-lb hammer and wood block (hammer and block of wood are kept by the operators)

Extra tape to seal boxes for return of sampling pole and shelters at end of study

Kimwipes

Sodium sulfate, Baker analyzed reagent, lot 35578, J.T. Baker Co., Phillipsburg, NJ

Sodium nitrate, certified A.C.S., Fisher Scientific Company, Raleigh, NC

Sodium nitrite, certified A.C.S., Fisher Scientific Company, Raleigh, NC

9.0 Chromatographic Standards

It is good practice to run standards at the beginning, middle, and end of each day to ensure constant instrument response because external standard quantitation is used. It is critical that standard solutions be prepared correctly.

1. Prepare 1 L each of the following 1000-ppm standards for calibration curves:
    - 1000 ppm NO_2 = 1.5000 g of $NaNO_2$
    - 1000 ppm NO_3 = 1.3708 g of $NaNO_3$
    - 1000 ppm SO_4 = 1.8152 g of K_2SO_4
2. Oven dry reagent at 105 °C for a half hour and cool prior to weighing.

3. Use the following anion standards: 1.0 ppm NO_2, 2.0 ppm NO_3, 2.0 ppm SO_4.
4. Run a standard before and after each set of PSD extracts to determine that the IC is functioning properly. If standards are not repeating within 5%, then it may be necessary to check retention times and/or recalibrate.
5. Do the following to check retention times:
    a. Go to the main menu by clicking the last icon on the right.
    b. Click Method, File, Open.
    c. Highlight the anion and click Open.
    d. Highlight Ed40 and click on the second icon from the right in the data-processing block.
    e. Type in the actual retention times from the computer printout.
    f. Click File, Save, and then Save on the pull-down menu.
    g. Click File and Exit.
    h. Click Run and then the red icon again to reload the method.
    i. Highlight the anion and click Open, OK, Run, Start ,OK.
6. Do the following to recalibrate:
    a. Go to the main menu by clicking the last icon on the right.
    b. Click Optimize, File, Open Data File. (Use the computer printout to find the data file name, e.g., 010703_N001.)
    c. Highlight the file name and click OK (chromatogram comes up).
    d. Go to Operations, then click Calibrate and OK.
    e. Click on Accept for peaks that you want.
    f. Click File, Save Data File, OK. When asked if it exists, say yes.
    g. Click File, Save Method File, OK, Yes, File, Exit.
    h. Click Run, then load the method by clicking the red icon.
    i. Highlight the anion and click Open, OK, Start.
    j. Type in the anion standard and click OK.

10.0 Cautions

10.1 Positioning the PSD in the rain cover is critical. The long portion of the PSD must be horizontal with the ground when attaching the PSD to the rain cover clip.

10.2 The screw caps on the PSD brown containers must be firmly tightened for shipment both to and from the monitoring site.

10.3 Each site should have a spare PSD clip holder in case one breaks during the study.

10.4 When operating the IC, remember to check the eluent levels daily; helium pressure should not be allowed to drop below 400 psi on the main tank pressure gauge. Also, make sure there is sufficient paper in the computer printer for the IC.

11.0 Cleaning Procedure for Used PSDs

After the collection pads have been removed for extraction and analysis, place the PSD body, four stainless steel screens, and two diffusion barriers from each PSD in a 400-mL beaker of distilled water for 15 min for ultrasonic cleaning. Follow with three rinses with clean, distilled water. When draining the water rinses, make sure no parts are poured down the drain. Lay out the parts on Kimwipes to dry overnight. Parts from 50 PSDs can be cleaned at one time. (See Figures 6 and 7.)

Figure 6. Cleaning of PSD components.

Figure 7. Clean and dried PSD components ready for reassembly.

12.0 References

Ogawa & Company, USA, Inc. February 1998. NO, NO_2, NO_X and SO_2 Sampling Protocol Using the Ogawa Sampler, 4th edition.

Sather, M.E., et al. 2001. Passive Ozone Network of Dallas: A Modeling Opportunity with Community Involvement, 2. *Environ. Sci. Technol.* 35:4426–4435.

Varns, J.L., Mulik, J.D., and Betz, E.A. 1998. EPA/600-V-98/001 Video: Site Training for the POND (Passive Ozone Network in Dallas), a peer-reviewed video created for generic instruction of lay operations in a passive ozone monitoring network; distributed to a 30-site network in and surrounding Dallas, TX, 12 min.

Varns, J.L., et al. 2001. Passive Ozone Network of Dallas: A Modeling Opportunity with Community Involvement, 1. *Environ. Sci. Technol.* 35:845–855.

Appendix D: Standard Operating Procedures for National Park Service Filter Preparation, Extraction, and Anion Analysis

Standard Operating Procedures for National Park Service Filter Preparation, Extraction, and Anion Analysis

Environmental Chemistry Department
Environmental and Industrial Sciences Division
RTI International∗
Research Triangle Park, NC

∗ RTI International is a trade name of Research Triangle Institute.

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Standard Operating Procedures
for National Park Service Filter Preparation, Extraction, and Anion Analysis

1.0 Procedural Section

1.1 Purpose and Applicability

This document outlines procedures for the filter preparation and extraction, as well as the subsequent determination of anions in filter extracts. Analytical procedures outlined are specific to the Dionex ion chromatographs in RTI International's (RTI's) Environmental Chemistry Department of the Environmental and Industrial Sciences Division.

1.2 Summary of Method

Nylon filters for the collection of anions do not require pretreatment. Quartz fiber filters are impregnated with potassium carbonate (K_2CO_3)/2% glycerol solution for collection of gaseous sulfur dioxide (SO_2). Exposed filter samples are extracted by a method appropriate for the analyte(s) of interest. Nylon filters are extracted with deionized water. Extraction with deionized water makes it possible to analyze for both anions and cations. Carbonate-impregnated quartz fiber filters are extracted with a 0.1% peroxide solution that oxidizes the SO_2 to sulfate ion.

Sample extracts are passed through a column of ion chromatographic resin consisting of polymer beads coated with quaternary ammonium active sites. During passage through the column, anion separation occurs due to the different affinities of the anions for the active resin sites. Following separation, the anions pass through a suppressor column, which exchanges all cations for hydrogen ions (H^+). An eluent that yields a low-conducting acid is used. Species are detected and quantified as their acids (e.g., hydrochloric acid [HCl]) by a conductivity meter.

1.3 Health and Safety Warnings

The National Park Service (NPS) ion analysis operations do not involve unusual risks from electrical equipment or chemical exposures. Standard RTI laboratory health and safety procedures will be followed.

1.4 Cautions

Laboratory personnel should always wear clean clothes and wash hands thoroughly before performing filter handling and analysis procedures. The use of gloves is required and will minimize the potential for laboratory contamination.

1.5 Interferences

Large amounts of anions eluting close to the ions of interest will result in an interference. No interferences have been observed in nylon filter samples analyzed to date. If interferences are observed, several steps to increase separation can be taken, such as reducing eluent strength and/or flow rate or replacing the guard and/or separator column.

Analysis of the extracts of K_2CO_3/glycerol-impregnated filters, which are used for SO_2 collection, requires careful quantitation of the sulfate peak. The sulfate peaks of undiluted extracts are broad and asymmetrical compared to the sulfate peaks of the standards, resulting in low concentrations when peak height or area is used for quantitation. A five-fold dilution of the extract reduces the K_2CO_3/glycerol matrix interference sufficiently to produce a sulfate peak that is symmetrical and quantifiable. This method is used for all extracts of K_2CO_3/glycerol-impregnated filters, with careful monitoring of recoveries through the use of spiked extracts.

1.6 Personnel Qualifications

Personnel employed to perform ion analysis operations will have at least an associate's degree in a laboratory science and will be trained by a supervisor before being allowed to process client samples for the Interagency Monitoring of Protected Visual Environments (IMPROVE) program.

1.7 Apparatus and Materials

1.7.1 Carbonate-Impregnated Filter Preparation

- Quartz fiber filters (Pallflex No. 2500 AT-UP, 25 mm, or equivalent)
- Analytical balance, capable of weighing to 0.0001 g
- Volumetric flask, 1000-mL
- Crystallizing dish (flat bottom and straight sides), 150 mm x 75 mm
- Tweezers
- Glass rod drying racks
- Vacuum drying oven.

1.7.2 Filter Extraction and Analysis (Nylon and Carbonate-Impregnated)

- Disposable polypropylene centrifuge tubes with screw caps, 50-mL
- Calibrated Rainin electronic pipette (10-mL capacity) and adjustable Eppendorf pipette (10–100 µL).
- Tweezers or forceps
- Ultrasonic bath fitted with epoxy-coated test-tube rack to hold centrifuge tubes
- Ion chromatograph complete with workstation (see **Table 1**)
- Pressurized eluent and regenerant reservoirs
- Volumetric flasks (an assortment of sizes)
- Autosampler vials with filter caps
- Coldroom at ≤ 4ºC
- Refrigerators.

Table 1. Configurations of Ion Chromatographs Used for Anion Analysis

Instrument ID	A1	A2	A3	A4	A5	A6	A7	A8	A9
Dionex Model	DX-500	DX-500	DX-500	DX-600	DX-600	ICS-2000	ICS-3000	ICS-3000	ICS-3000
Chromatography module	LC20	LC20	LC20	LC30	LC30	None	ICS–DC	ICS–DC	ICS–DC
Pump	GP50	IP25	IP20	IP25	IS25	IS2000	ICS–DP	ICS–DP	ICS–DP
Conductivity detector	CD20 DS3 cell	CD20 DS3 cell	CD20 DS1A cell	CD20 DS3 cell	CD25 DS3 cell	Built-in DS6	ICS–3000 Conductivity cell	ICS – 3000 Conductivity cell	ICS -3000 Conductivity cell
Autosampler	AS40	AS40	AS40	AS40	AS40	AS40	AS40	AS40	AS40
Software	Windows 2000 Dionex PeakNet 5.2	Windows 2000 Dionex PeakNet 5.2	Windows 2000 Dionex PeakNet 5.2	Windows 2000 Dionex PeakNet 5.2	Windows XP Dionex Chromeleon	Windows XP Dionex Chromeleon	Windows XP Professional Chromeleon	Windows XP Professional Chromeleon	Windows XP Professional Chromeleon
Guard column	AG12A	AG12A	AG12A	AG12A	AG12A	AG12A	AG12A	AG12A	AG12A
Separator column	AS12A	AS12A	AS12A	AS12A	AS12A	AS12A	AS12A	AS12A	AS12A
Suppressor column	AMMSIII	AMMSIII	AMMSIII	AMMSIII	ASRS 300	ASRS 300	ASRS 300	ASRS 300	ASRS 300
Other	—	—	—	—	—	Built-in eluent generator (Not used)	ICS–EG eluent generator	—	—

1.8 Reagents

1.8.1 Chemicals

Note: All chemicals must be American Chemical Society (ACS) reagent-grade or better.

- Potassium carbonate (K_2CO_3)
- Glycerol
- 30% hydrogen peroxide (H_2O_2)
- Sodium bicarbonate ($NaHCO_3$)
- Sodium carbonate (Na_2CO_3)
- 5.0N H_2SO_4
- Sodium nitrite ($NaNO_2$)
- Sodium nitrate ($NaNO_3$)
- Potassium sulfate (K_2SO_4)
- Sodium chloride (NaCl)
- Commercially-prepared, National Institute of Standards and Technology (NIST)–traceable quality assurance (QA) standards(purchased from CPI (www.cpichem.com), GFS Chemicals (www.gfschemicals.com), or equivalent

1.8.2 Solutions

Note: Use ACS reagent-grade chemicals and 18.2 MΩ-cm deionized water for the preparation of all solutions.

1.8.2.1 Carbonate-Impregnated Filter Preparation

- K_2CO_3/2% glycerol impregnating solution: Transfer 100 g reagent-grade K_2CO_3 and 20 g glycerol to a 1-L volumetric flask. Dilute to the mark with deionized water.

1.8.2.2 Carbonate-Impregnated Filter Extraction

- 0.1% H_2O_2 extracting solution: Dilute 6.68 mL 30% reagent-grade H_2O_2 to 2000 mL using deionized water. Prepare fresh each extraction day.

1.8.2.3 Anion Analysis

- Concentrated anion eluent (100X), 30 mM $NaHCO_3$ /270 mM Na_2CO_3: Dissolve 2.5209 g $NaHCO_3$ and 28.6178 g Na_2CO_3 in 1 L of deionized water. (Note: Do NOT dry the salts that are used to prepare the eluent.)
- Working anion eluent, 0.3 mM $NaHCO_3$ /2.7mM Na_2CO_3: Dilute 200 mL of concentrated eluent to 20 L with deionized water.
- Regenerant, 0.025 N H_2SO_4: Dilute 100 mL 5.0 N H_2SO_4 to 20 L with deionized water. (Note: This reagent is not used for an ion chromatography system equipped

with a self-regenerating suppressor).

1.9 Calibration Standards

Dry the salts used for the preparation of calibration standards at 105 EC for 2 hours and allow to cool to room temperature in a desiccator before use.

1. Mixed Anion Stock Solution, 1000 mg/L NO_2^-, NO_3^-, and SO_4^{2-}, and 200 mg/L $C1^-$: Dissolve 1.4998 g $NaNO_2$, 1.3708 g $NaNO_3$, 1.8142 g K_2SO_4, and 0.3297 g NaCl in 1 L of deionized water.
2. Standard Anion Solution A (100 mg/L NO_2^-, NO_3^-, SO_4^{2-}, and 20 mg/L $C1^-$): Dilute 10 mL of mixed-stock solution to 100 mL with deionized water.
3. Standard Anion Solution B (10 mg/L NO_2^-, NO_3^-, and SO_4^{2-}, and 2 mg/L $C1^-$): Dilute 10 mL of Standard Solution A to 100 mL with deionized water.
4. Anion Calibration Standards: Using Standard Solutions A and B, prepare calibration standards with deionized water in 100-mL volumetric flasks as shown in **Table 2**. Prepare fresh calibration standards weekly.

Table 2. Preparation of Anion Calibration Standards

Starting Solution	Calibration Standard	Cl^-, mg/L	NO_2^-, NO_3^-, SO_4^{2-} (mg/L)	mL of Starting Solution/100 mL
Standard Solution A	1	5.0	25.0	25.0
	2	2.0	10.0	10.0*
	3	0.6	3.0	3.0
Standard Solution B	4	0.2	1.0	10.0*
	6	0.1	0.5	5.0
	7	0.04	0.2	2.0
Calibration Standard 4	8	0.02	0.1	10.0*
	9	0.01	0.05	5.0*

*For these solutions, use two times the stated mL of standard solution in a 200-mL flask.

1.10 Quality Control Solutions

Dry the salts used for the preparation of calibration standards at 105 EC for 2 hours and allow to cool in a desiccator prior to use. Quality control (QC) solutions must be prepared independent of the calibration solutions.

1. Chloride Stock Solution, 1000 mg/L $C1^-$: Dissolve 0.8243 g NaCl in 500 mL of deionized water.
2. Nitrite Stock Solution, 1000 mg/L NO_2^-: Dissolve 0.7499 g $NaNO_2$ in 500 mL of deionized water.
3. Nitrate Stock Solution, 1000 mg/L NO_3^-: Dissolve 0.6854 g $NaNO_3$ in 500 mL of deionized water.
4. Sulfate Stock Solution, 1,000 mg/L SO_4^{2-}: Dissolve 0.9071 g K_2SO_4, in 500 mL of

deionized water.

5. QC–Intermediate Solution, 10 mg/L C1$^-$, 20 mg/L NO_2^-, 30 mg/L NO_3^-, and 60 mg/L SO_4^{2-}: Pipette 1 mL of 1000 mg/L C1$^-$, 2 mL of 1,000 mg/L NO_2^-, 3 mL of 1000 mg/L NO_3^-, and 6 mL of 1000 mg/L of SO_4^{2-} into a 100-mL volumetric flask. Dilute to the mark with deionized water.
6. QC Samples: Using the QC–Intermediate Solution, prepare calibration standards with deionized water in 100-mL volumetric flasks as shown in **Table 3**. Prepare fresh calibration standards weekly.

Table 3. Preparation of Anion Quality Control Samples

QC Sample ID	mL QC–Intermediate Solution	Final Volume, mL (Volumetric Flask Size)	Cl^- Conc (mg/L)	NO_2^- Conc (mg/L)	NO_3^- Conc (mg/L)	SO_4^{2-} Conc (mg/L)
QC-LOW	2.0	100	0.2	0.4	0.6	1.2
QC-MED	5.0	100	0.5	1.0	1.5	3.0
QC-HIGH	10.0	50	2.0	4.0	6.0	12.0

1.11 Quality Assurance Solutions

Use commercially prepared, NIST–traceable solutions to prepare an intermediate quality assurance solution known concentrations of C1$^-$, NO_2^-, NO_3^-, and SO_4^{2-}. Solutions can be purchased from CPI (www.cpichem.com), GFS Chemicals (www.gfschemicals.com), or equivalent.

1. QA–Intermediate Solution, 10 mg/L C1$^-$, 20 mg/L NO_2^-, 30 mg/L NO_3^-, and 60 mg/L SO_4^{2-}: Pipette 1 mL of 1000 mg/L C1$^-$, 2 mL of 1,000 mg/L NO_2^-, 3 mL of 1,000 mg/L NO_3^-, and 6 mL of 1000 mg/L SO_4^{2-} into a 100-mL volumetric flask. Dilute to the mark with deionized water.
2. Using the QA–Intermediate Solution, prepare calibration standards with deionized water in 100-mL volumetric flasks as shown in **Table 4**. Prepare fresh QA samples as needed.

Table 4. Preparation of Anion Quality Assurance Samples

QA Sample ID	mL QA–Intermediate Solution	Final Volume, mL (Volumetric Flask Size)	Cl^- Conc (mg/L)	NO_2^- Conc (mg/L)	NO_3^- Conc (mg/L)	SO_4^{2-} Conc (mg/L)
QA-CPI_LOW	2.0	100	0.2	0.4	0.6	1.2
QA-CPI_MED-HI	10.0	100	1.0	2.0	3.0	6.0

1.12 Carbonate-Impregnated Filter Preparation

Use the following procedures to prepare filters for collection of SO_2. The chemist will wear cleanroom gloves and handle the filter with forceps or tweezers.

1. Purchase quartz fiber filters (Pallflex No. 2500 AT-UP, 25 mm, or equivalent for 24-hour sampling).
2. Inspect all filters for imperfections. Analyze at least one blank filter from every 100 for sulfate to verify the manufacturer's pre-established specifications. Return rejected filters to the manufacturer for credit.
3. Pour approximately 250 mL of filter-impregnating solution (Section 1.8.2.1) into a 150-mm x 75-mm crystallizing dish (with a flat bottom and straight sides).
4. Saturate a batch of 50, 25-mm quartz filters in the filter-impregnating solution. Allow the filters to remain in the filter-impregnating solution for 5 minutes. Using forceps or tweezers, remove the filters one at a time from the impregnating solution and drain for a few seconds. Place the filters on a clean, glass rod drying rack and dry the filters in an SO_2–free oven under vacuum at 60 EC for 30 minutes, or until dry. Note: Overdrying will cause the filters to become brittle. Place the filters in a clean, resealable polyethylene bag, then store the bag in a freezer.
5. Extract and analyze 1% of the newly made filters for SO_4^{2-} background. Reject the batch if the mean sulfate loading is greater than ≥ 0.35 µg/filter).

1.13 Sample Collection

Sample collection is not applicable to this standard operating procedure because samples are acquired by the Particulate Monitoring Coordinator Contractor (PMCC).

1.14 Sample Handling

RTI will provide chain-of-custody documentation with all sample shipments to track and ensure that samples are transferred, stored, and analyzed by authorized and qualified personnel. Sample integrity is maintained during all phases of sample handling and analysis, and an accurate written record will be maintained of sample handling and treatment from the time of its collection, through the laboratory analytical process, to the eventual relinquishing of all data to the PMCC.

1.15 Filter Extraction Procedure

1.15.1 Nylon Filters

Note: Nylon filters to be analyzed for the NPS IMPROVE network are extracted with deionized water. Extraction with deionized water makes it possible to analyze for both anions and cations, if requested.

To extract the filters, the analyst will perform the following:

1. Remove filters to be extracted from the freezer and allow them to equilibrate to room temperature.

2. Using gloved hands and tweezers, place each filter in a polypropylene centrifuge tube that has been labeled with the sample ID printed on a durable (water-resistant) label.
3. Label a 50-mL extraction tube as “Reagent Blank SO_2”.
4. Add exactly 20 mL of 0.1% H_2O_2 using a calibrated Rainin electronic pipette.

5. Screw the cap tightly on each tube.
6. Ensure that the filter is completely submerged in the extraction solution.
7. Place the batch of centrifuge tubes in an epoxy-coated wire test tube rack, expose them to ultrasonic energy in a bath for 30 minutes, and then allow them to sit at room temperature overnight. Refrigerate at least one additional night prior to analysis.

CAUTION: Monitor the bath temperature during sonication. The temperature should not exceed 27 EC. Add ice initially to lower the temperature, and add ice as necessary during the sonication to maintain an acceptable temperature.

8. Record the date of extraction on the RTI Sample Log Form.
9. Store the extracts in a refrigerator until analysis.

1.15.2 Carbonate-Impregnated Quartz Filters for SO_2

To extract the filters, the analyst will perform the following:

1. Remove filters to be extracted from the freezer and allow them to equilibrate to room temperature.
2. Using gloved hands and tweezers, place each filter in a polyproylene centrifuge tube that has been labeled with the sample ID printed on a durable (water-resistant) label.
3. Label a 50-mL extraction tube as “Reagent Blank SO_2.”
4. Using a calibrated automatic pipette, add exactly 20.0 mL of 0.1% H_2O_2 using a calibrated Rainin electronic pipette (see Section 1.8.2.2).
5. Screw the cap tightly on the centrifuge tube.
6. Ensure that the filter is completely submerged in the extraction solution.
7. Place the batch of centrifuge tubes in an epoxy-coated wire test tube rack, expose them to ultrasonic energy in a bath for 30 minutes, and then allow them to sit at room temperature overnight. Refrigerate at least one additional night prior to analysis.

CAUTION: Monitor the bath temperature during sonication. The temperature should not exceed 27 EC. Add ice initially to lower the temperature, and add ice as necessary during the sonication to maintain an acceptable temperature.

8. Record the date of extraction on the RTI Sample Filter Processing Form.

9. Store the extracts in a refrigerator until analysis.

1.16 Ion Chromatography Procedure

1. Fill the eluent reservoirs with the eluent and the regenerant reservoirs with regenerant and pressurize the reservoirs.
2. Start the eluent flow at 1.5 mL/min, and if using a self-regenerating suppressor, activate it. Allow the baseline to stabilize.
3. Inject two deionized water blanks to flush the system and to ensure that the system is operating properly.
4. Using the calibration schedule, perform the daily multipoint calibration over the range 0.01 to 5.0 ppm Cl^- and 0.05 to 25.0 ppm NO_2^-, NO_3^- and SO_4^{2-}, followed by QA/QC samples listed below.

    - A QC sample containing concentrations of Cl^-, NO_2^-, NO_3^- and SO_4^{2-} typical of those found in the mid-range of actual filter extract concentrations (QC-MED).

    - A QC sample containing concentrations of Cl^-, NO_2^-, NO_3^- and SO_4^{2-} typical of those found at the lower end of actual filter extract concentrations (QC-LOW).

    - A commercially prepared, NIST–traceable QA sample containing known concentrations of Cl^-, NO_2^-, NO_3^- and SO_4^{2-} (QA-CPI_LOW).

    If the observed value for any ion differs by more than 10% from the known value, identify and correct the problem before analyzing samples.
5. Remove filter extracts from the refrigerator and allow them to equilibrate to room temperature (Note: This should be performed while the system is stabilizing and the calibration is being conducted.)
6. Load the filter extracts into the autosampler vials according to the schedule prepared for that day. Typically, 75 field samples are analyzed per day. The daily schedule includes, at a minimum, three duplicate samples, two spiked samples, and five QA/QC samples.
7. Begin the analysis run, checking throughout the run to ensure that the system is operating properly.
8. Examine the autosampler vials at the end of the run. If any vial indicates that the extract was not completely sampled (i.e., if extract remains in the vial), note it on the sample queue and add a fresh aliquot of that sample to the set of samples to be analyzed the following day.

9. Examine the data at the end of the run. If the concentration of any ion exceeds the upper end of the calibration curve, dilute the sample appropriately and analyze that day or include with the samples to be analyzed the following day.

1.17 Calculations and Data Reduction

Peak areas are entered into the computer where calculations are performed using a quadratic fit to the calibration data. The quadratic fit yields the following, as shown in Equation 1:

$$y_i = ax_i^2 + bx_i + c \qquad \text{(Eq. 1)}$$

where

y = Calculated cation concentration (µg/L)
x = Instrument response

Initially, the calibration curve from 0.01 to 2.0 ppm is used for the calculation of the extract chloride concentrations, and the calibration curves from 0.05 to 10.0 ppm are used for nitrite, nitrate, and sulfate concentrations. All chloride concentrations that exceed 2 ppm are recalculated with the 5 ppm standard added to the calibration curve, and all nitrite, nitrate, and/or sulfate concentrations that exceed 10 ppm are recalculated with the 25.0 ppm standard added to the calibration curve. If a recalculated chloride exceeds 5 ppm or a recalculated nitrite, nitrate, or sulfate concentration exceeds 25 ppm, the extract is diluted appropriately (usually five-fold) to bring the ion concentration into the calibration range and re-analyzed.

2.0 Quality Assurance and Quality Control

Compare the regression parameters (a, b, c, and correlation coefficient) for the standard curves with those obtained in the past. If they exceed the control limits, stop the analysis and identify the problem.

Analyze QA/QC samples (see Sections 1.10 and 1.11) at the beginning of every analytical run. Compare the results with those obtained during previous QA/QC tests. If the observed concentration of any ion differs from the known value by greater than 10%, stop the analysis until the problem is identified and corrected. Analyze a duplicate sample, a QA/QC sample, or a spiked sample after at least every 10 to 15 field samples.