Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina.

EPA

STRATEGIC PLAN

Development of the Particulate Matter ($PM_{2.5}$) Quality System for the Chemical Speciation Monitoring Trend Sites

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United States Environmental Protection Agency
Emissions Monitoring and Analysis Division
Monitoring & Quality Assurance Group

FOREWORD

This document contains information regarding program goals and objectives, sampling equipment, guidance recommendations, and other pertinent information concerning the development of the chemical speciation program quality system. This document provides the general outline for the development of this system and any comments are welcome.

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1.0 OVERVIEW

1.1 Introduction

This Strategic Plan outlines the general procedures required for a successful development of the quality system for the $PM_{2.5}$ chemical speciation monitoring program trend sites. Specific tasks and details will be forthcoming and identified in the implementation plan, quality assurance project plan and standard operating procedures. The $PM_{2.5}$ chemical speciation monitoring program is a national program consisting of approximately 54 sites used for long-term trends of selected $PM_{2.5}$ constituents. The quality system will include the managerial practices (quality assurance) as well as the technical procedures (quality control) to ensure the collected data are of acceptable quality as defined by the monitoring quality objectives (MQOs) and data quality objectives (DQOs). This document will outline the general procedures and the stakeholders involved in developing the various phases of the quality system for the trend sites. It is anticipated that the individual States and local air pollution agencies will develop the required documentation for any additional non-trends sites.

1.2 Background

The $PM_{2.5}$ chemical speciation monitoring network is a national air pollution monitoring network developed to provide a basic, long-term record of the characterization of the metals, ions, and carbon constituents of $PM_{2.5}$. About 54 sites will be used for determination of trends. These sites will be part of the National Air Monitoring Stations (NAMS) network and will provide nationally consistent data to serve as a model for other chemical speciation efforts.

On July 18, 1997, the U.S. EPA promulgated a new National Ambient Air Quality Standard (NAAQS) for particulate matter (PM) in Title 40 of the Code of Federal Regulations (CFR) Parts 50, 53, and 58. The new NAAQS applies to the mass concentration of particles with aerodynamic diameters less than 2.5 μm ($PM_{2.5}$). The suite of PM standards is revised to include an annual (long-term) primary $PM_{2.5}$ and a 24-hour (short-term) $PM_{2.5}$ standard. The NAAQS for $PM_{2.5}$ specifies the following:

❑ The three-year average of the annual mean of $PM_{2.5}$ concentrations is not to exceed 15μg/m^3. The average may be based on a single community-oriented monitoring site or the spatial average of community-oriented monitoring sites in a community monitoring zone (CMZ).

❑ The 3-year average of the annual 98th percentiles of twenty-four-hour $PM_{2.5}$ concentrations is not to exceed 65μg/m^3 at any population-oriented monitoring site in a Metropolitan Planning Area (MPA).

The deployment of the national $PM_{2.5}$ monitoring network is a critical component in the implementation of the new NAAQS. Substantial resources are being provided to support the national monitoring network of gravimetric $PM_{2.5}$ sites. Data derived from the national $PM_{2.5}$ monitoring network include both aerosol mass measurements (FRM monitors) and chemically-resolved or speciated data (Speciation monitors). Mass measurements are used principally for identifying areas of attainment or nonattainment. Chemical speciation data serve the needs associated with assessing trends and developing mitigation approaches to reduce ambient aerosol emissions in relation to the State Implementation Plans (SIPs). These needs include emission inventory and air quality model evaluation, source attribution analysis, and tracking the success of emission control programs. Chemical speciation data will not be used for attainment/non-attainment decisions.

1.3 Goals and Components of the Quality System

The overall goal of the national $PM_{2.5}$ monitoring program is to provide ambient data that supports the Nation's air quality program objectives. In prioritized order, the major programmatic objectives for the NAMS $PM_{2.5}$ chemical speciation trends network include:

❑ Annual and seasonal spatial characterizations of aerosols;

❑ Air quality trends analysis and tracking progress of control programs; and

❑ Development of emission control strategies.

The overall goal of the PM2.5 chemical speciation quality system is to provide the stakeholders with a program which allows for a quantification of the measurement uncertainty of the 54 site trends network. This will be done with an established set of quality assurance (QA) and quality control (QC) procedures.

The data collected must be of acceptable quality to meet the program's data quality objectives. These objectives and goals will be met by procedures outlined in the components of the quality system. These components include:

❑ <u>OAQPS Quality Management Plan</u>

♦ A QMP is a formal document that describes the quality system in terms of the organizational structure, functional responsibilities of management and staff, lines of authority, and required interfaces for those planning, implementing, ad assessing all activities conducted.

♦ A review to assure the QMP contains the Speciation program

♦ The OAQPS QMP can be located at www.epa.gov/oar/oaqps/qa/qmp.pdf

❑ <u>An Implementation Plan</u>

♦ An implementation plan is a formal document that describes all components of the specific program is surveys; these include manpower, budget, timelines, individual and group responsibilities, which detail and identify all necessary tasks for program completion.

♦ The PM2.5 program implementation plan will be updated to include all aspects of the chemical speciation quality system

♦ The PM2.5 implementation plan is located at www.epa.gov/ttn/amtic/pmimmp.html

❏ Chemical Speciation Guidance Document

♦ The speciation guidance document is a formal document which incorporates all available information concerning chemical speciation into one concise document. Chapter 8, "Defining the quality system requirements for PM2.5 chemical speciation sampling and analysis", covers the quality system aspects and will be updated.

♦ The guidance document is located at www.epa.gov/ttn/amtic/pmspec.html

❏ Quality Assurance Project Plan.

♦ The QAPP is a formal document describing in comprehensive detail the necessary QA, QC, and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria.

♦ The EPA has developed a work assignment for the development of a field oriented QAPP; this QAPP will eventually be updated to contain all aspects of the quality system encompassing field, lab, and all other procedures into one stand-alone document.

♦ Upon completion, the QAPP for the chemical speciation trends sites will be located on the EPA's AMTIC bulletin board.

❏ Field Standard Operating Procedures

♦ SOPs are written documents that detail the method for an operation, analysis, or action with thoroughly prescribed techniques and steps, and that is officially approved as the method for performing certain routine or repetitive tasks.

♦ The EPA has initiated a field comparison study to document the field SOPs which will then be incorporated into the QAPP.

❏ Laboratory Standard Operating Procedures

♦ See SOP definition above.

♦ The EPA has initiated a contractual mechanism to provide for the development and documentation of laboratory procedures. These lab SOPs will then be incorporated into the QAPP for the chemical speciation trends sites.

1.4 Stakeholders

The interested organizational stakeholders in the development of the quality system for the chemical speciation monitoring network include:

- ❑ The Monitoring & Quality Assurance Group (MQAG) which is part of the Emissions Monitoring and Analysis Division (EMAD) in the EPA's Office of Air Quality Planning and Standards (OAQPS) who will provide personnel to coordinate the activities of the development of the quality system, act as a liaison to the States and local air pollution agencies, and working with the appropriate personnel on the contractual mechanisms.

- ❑ The Office of Research and Development (ORD) who will provide technical consultation services and expertise as needed and requested

- ❑ The Chemical Speciation Expert Panel who will provide technical expertise, background information, and direction. This panel is constructed of nationally recognized experts in the field of chemical speciation.

- ❑ The Chemical Speciation Workgroup who will provide comments and consensus on developed documentation. The workgroup is constructed of interested stakeholders from Regions, States, local air pollution agencies, and others with an interest in the direction of the program. This workgroup also include organizations such as CASAC, STAPPA/ALAPCO, MARAMA, WESTAR, NESCAUM, NAS, and others.

2.0 INSTRUMENTATION

2.1 Contract Development

The EPA developed a national contract which outlined the steps the manufacturers were required to fulfill to be granted a contract award for the speciation monitors. These requirements included:

- ❑ Submission of a proposal in response to the EPA's Request for Proposal; this submission included the design, manufacturing capability, and other details concerning the speciation monitor.

- ❑ The availability of technical staff to answer specific questions referred by the EPA concerning the design, manufacture, or operation of the speciation monitor.

- ❑ Development and subsequent submission of a prototype speciation monitor for review and approval.

After successful completion of these steps, three individual manufacturers were awarded contracts for the speciation monitors. These were:

- ❑ Andersen Instruments (RAAS)

- ❑ Met-One Instruments (SASS)

- ❑ University Research Glassware (MASS)

The EPA 'National PM2.5 Sampler Procurement Contract' includes provisions for the purchase of over 300 speciation monitors, including accessories, for establishing the speciation monitoring network. In some cases, the speciation sampler design is flexible and can include additional filter collection media best-suited for the analysis of specific components. The 40 CFR Part 53 requirements for designation of reference and equivalent methods for PM2.5 do not require designations for speciation monitors. However, it is imperative that all non-reference or equivalent methods incorporate particle inlets and size fractionators with equivalent particle size efficiency curves to the reference method for PM2.5.

Desirable features of a speciation sampler include the following:

- ❑ The inlet cut-point and separation profile must be comparable to the Well Impaction Ninety Six (WINS) fractionators used in the FRM design. A number of laboratory and field tests should be conducted to demonstrate that the fine particle mass collected by the speciation monitor and the FRM are in good agreement (for example, have a slope of 1+/-0.1 and r^2 better than 0.90).

- ❑ The sampler should use proven denuder technology to obtain nitrate and anion/cation measurements. The nitric denuder should be tested for its capacity and efficiency as a function of exposure time and relative humidity. If it is proposed that a denuder will be used for more than one sampling day, it will be important to demonstrate the collection efficiency over time.

- ❑ The sampler should collect samples at a face velocity and sample volume similar to that of the FRM with 46.2 mm diameter filters.

- ❑ The sampler must be reliable, rugged, and employ field-proven monitoring approaches.

There will be four samplers which employ multiple channels and the appropriate filter media for use in implementing the PM2.5 NAMS speciation trends network. The samplers mainly differ by inlet design and approach to collection of particles less than 2.5 microns. More recent designs include the capability to collect semi-volatile organic aerosol particles using diffusion denuders followed by quartz fiber filters and solid sorbent traps. Three candidate sampler designs, the MASS, RAAS, and SASS, are being made available through the EPA's National PM2.5 Sampler Procurement Contract.

2.2 Intercomparison Study

Several different speciation sampler designs could be used in the overall sampling program. Therefore, studies are needed to collect data which show intercomparisons between the samplers relative to the performance of the FRM inlet, chemical species, and corresponding mass measurement. EPA's goal for the intercomparison study is to determine if there are differences between the three PM2.5 speciation samplers available under the EPA national contract, other samplers historically used for PM2.5, and the FRM.

Development of chemical speciation samplers for the national PM2.5 sampler contract was based on performance, rather than design criteria. This allowed innovation in the development of these samplers and resulted in development of three slightly different approaches for meeting the performance criteria. Also as a result of review by the Speciation Expert Panel, the recommendation was made for an intercomparison among the chemical speciation sampler. The intercomparison will also include other historically accepted samplers (e.g. the IMPROVE sampler) and the FRM. The chemical species to be determined during the intercomparison study include only a subset of those specified for the routine NAMS speciation program. The intercomparison studies include:

- ❏ A intercomparison study involving 4 different city locations
- ❏ A study in Atlanta in response to CASAS
- ❏ A 10 site trend site operational evaluation

4.0 DATA QUALITY OBJECTIVES

Data Quality Objectives (DQOs) are a statement of the precise data, the manner in which such data may be combined, and the acceptable uncertainty in those data in order to resolve an environmental problem or condition. This may also include the criteria or specifications needed to design a study that resolves the question or decision addressed by the DQO process. This process is a Total Quality Management (TQM) tool developed by the EPA to facilitate the planning of environmental data collection activities. The DQO process asks planners to focus their planning efforts by specifying the use of the data (the decision), the decision criteria, and their tolerance to accept an incorrect decision based on the data. The products of the DQO process are the DQOs. The process involves 7 specific steps:

- ❏ State the problem
- ❏ Identify the decision
- ❏ Identify the inputs to the decision
- ❏ Define the boundaries of the study
- ❏ Develop a decision rule
- ❏ Specify tolerable limits on decision errors
- ❏ Optimize the design

An important concern in the collection and evaluation of chemical speciation monitoring data is the level of uncertainty in the trends sites data. Uncertainty arises due to temporal and spatial variability in the ambient air, variability in the samplers, and variability in the laboratory analyses. The DQO process was used to structure the $PM_{2.5}$ chemical speciation trends data collection activity. The DQO process provided a systematic procedure for defining the criteria that the PM2.5 speciation data collection design should satisfy, including when to collect samples, where to collect samples, how many samples to collect, and the tolerable level of decision errors.

The MQAG has initiated an effort to ensure that the data collected by the PM2.5 speciation trends network is of a sufficient quantity and quality to support the intended uses of the data. This effort includes development of DQOs for the NAMS trends sites dedicated to measuring national trends in the PM2.5 species and a blueprint of the DQO process for the remaining 250 sites (expected to be available second calendar quarter 1999). An important assumption which will be used within the DQO process is the general similarity of procedures and practices for the chemical speciation monitor to the IMPROVE monitor.

The inputs to the DQO process for the chemical speciation trends sites are:

❏ The detection of trends is the primary objective of the NAMS trends portion of the PM2.5 speciation network

❏ The decision makers wanted to be able to detect a 3-5% annual trend with 3-5 years of data on a site-by-site basis after adjusting for seasonality

❏ The development of the DQOs was done for four analytes, those being sulfate, nitrate, total carbon, and calcium.

Conclusions for the DQO process:

❏ Use of the sampling design that includes 54 trends sites, a sampling frequency of 1 in 3, a filter based sampler, laboratory analyses, and measurement error rates and percentage of non-detects will achieve the decision maker's goal for all species except nitrate.

❏ The design will allow for the detection of annual trends greater than 5% (or less than -5%) within 5 years of collection of data, with a power of 0.8.

❏ For nitrate, annual trends must exceed 6% (or less than -6%) to be detected.

❏ The decision makers further recommend that the DQOs be re-evaluated once data from the trends network becomes available.

This information, along with the DQO documentation, is located at:

❏ http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/dqo3.pdf

To summarize, the DQO for the chemical speciation trends sites:

❏ The detection of annual trends of 5% within 5 years of collection of data with a confidence of 80%.

To reach this DQO, specific monitoring quality objectives (MQOs) must be developed, implemented and achieved. These MQOs are species specific goals involving the individual components of the chemical speciation trend site target analytes. The MQOs are:

- ❑ IONs at 10% coefficient of variation (CV)
- ❑ Carbon at 15% CV
- ❑ Elements at 20% CV

5.0 QUALITY SYSTEM

5.1 Quality Documentation

The quality system is a structured and documented management system describing how and by whom an organization assures quality in its work. The EPA Order 5360.1 requires all environmental programs conducted by the EPA, or on behalf of the EPA, to be supported by a mandatory Quality System (previously referred to as a Quality Assurance Program). The EPA is responsible for developing the quality system for the $PM_{2.5}$ chemical speciation program.

The following quality documentation will be used to develop the quality system for the chemical speciation monitoring program:

- ❑ The QAD R-series: The EPA's Quality Assurance Division has developed specific requirements for quality systems.
- ❑ The QAD G-series: The EPA's Quality Assurance division has also developed specific guidance documentation which further defines the Agency's policy.
- ❑ The EPA executive order 5360.1
- ❑ Quality assurance handbook for air pollution measurement systems. This is a 5-volume set of technical guidance which defines Agency policy. Of importance is section 2.12 of Volume II of the Handbook which outlines the guidance for the PM2.5 mass program.
- ❑ The OAQPS Quality Management Plan
- ❑ The Performance Evaluation Program documentation. This is a national quality assurance program which uses the PM2.5 Portable Audit Sampler to quantify measurement system bias.
- ❑ The Model PM2.5 monitoring QAPP which was developed for national distribution to be used as a guideline for developing individual QAPPs.
- ❑ Operation manuals from the three speciation monitors
- ❑ Operation manual from the IMPROVE monitor
- ❑ Any other documentation available with pertinent information.

5.2 Assumptions

- The chemical speciation program will use the PM2.5 FRM program as a guide only. The same requirements for checking the sampler's flow rate, temperature control, and pressure control have been adopted.

- The chemical speciation program will have an established quality assurance project plan (QAPP) for the trends sites. This QAPP will eventually include all aspects of the program including field SOPs, lab SOPs, and any other quality system components.

- The Date Quality Process (DQO) was used to establish an overall program objective as well as individual species objectives.

- Since the 54 site network was established as a trends detection program, there is no need for the quantification of bias; therefore, the focus of the quality system is on the identification of precision.

5.3 Definitions

- Precision - a measurement of mutual agreement among individual measurements of the same property usually under prescribed similar conditions, expressed generally in terms of the standard deviation;

- Accuracy - the degree of agreement between an observed value and an accepted reference value, accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations;

- Bias - the systematic or persistent distortion of a measurement process which causes errors in one direction.

5.4 Quality Assurance

- Definition: An integrated system of management activities involving planning, implementation, assessment, reporting, and quality improvement to ensure that a process, item, or service is of the type and quality needed an expected by the client.

5.4.1 Precision

<u>Automated methods for PM2.5</u>: A one-point precision check must be performed at least once every two weeks on each automated chemical speciation analyzer used to measure $PM_{2.5}$. The precision check is made by checking the operational flow rate of the analyzer. If a precision flow rate check is made in conjunction with a flow rate adjustment, it must be made prior to such flow rate adjustment.

Randomization of the precision check with respect to time of day, day of week, and routine service and adjustments is encouraged where possible.

Manual methods for PM2.5: Collocate 10% of the chemical speciation monitors with the national trends network. The two collocated samplers must be within 4 meters of each other, and particulate matter samplers must be at least 2 meters apart to preclude airflow interference. Calibration, sampling, and analysis must be the same for both collocated samplers and the same as for all other samplers in the network.

For each pair of collocated samplers, designate one sampler as the primary sampler whose samples will be used to report chemical speciation information for the site, and designate the other as the duplicate sampler. Each duplicate sampler must be operated concurrently with its associated routine sampler. Report the measurements from both samplers at each collocated sampling site.

5.4.2 Accuracy

Automated methods for PM2.5: An independent audit must be performed annually on each automated chemical speciation analyzer used to measure $PM_{2.5}$. The audit is made by checking the operational flow rate of the analyzer with a device. If a precision flow rate check is made in conjunction with a flow rate adjustment, it must be made prior to such flow rate adjustment.

Manual methods for PM2.5: Each calendar quarter, audit the flow rate of each SLAMS $PM_{2.5}$ analyzer. If there are fewer than four $PM_{2.5}$ analyzers within a reporting organization, randomly re-audit one or more analyzers so that at least one analyzer is audited each calendar quarter. Where possible, EPA strongly encourages more frequent auditing, up to an audit frequency of once per quarter for each chemical speciation monitor. The audit is made by measuring the analyzer's normal operating flow rate, using a flow rate transfer standard certified in accordance with section 2.3.3 of 40 CFR Part 58 Appendix A. The flow rate standard used for auditing must not be the same flow rate standard used to calibrate the analyzer. However, both the calibration standard and the audit standard may be referenced to the same primary flow rate or volume standard.

5.5 Quality Control

- ❑ Definition: The overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer; operational techniques and activities that are used to fulfill requirements for quality.

5.5.1 Temperature Control check

- ❑ Monthly check the temperature sensors of the chemical speciation monitor with a certified transfer standard. If the temperature differs more than +/- 2 ºC, perform a multi-point calibration on the sensor.

- ❑ Quarterly check the temperature sensors with an independent temperature standard. If the temperature differs more than +/- 2 ^{o}C, perform a multi-point calibration on the sensor.

- ❑ Should the temperature sensor not maintain its calibrations after the monthly or quarterly checks, maintenance and/or replacement of the sensor may be warranted.

5.5.2 Pressure Control check

- ❑ Monthly check the pressure sensors of the chemical speciation monitor with a certified transfer standard. If the pressure differs more than +/- 10 mm Hg, perform a multi-point calibration on the sensor.

- ❑ Quarterly check the pressure sensors with an independent pressure standard. If the pressure differs more than +/- 10 mm Hg, perform a multi-point calibration on the sensor.

- ❑ Should the pressure sensor not maintain its calibrations after the monthly or quarterly checks, maintenance and/or replacement of the sensor may be warranted.

5.5.3 Flow Rate Control check

- ❑ Monthly check the actual flow rates *of each sampling stream* within the chemical speciation monitor with a certified transfer standard. If the temperature differs more than +/- 4% , perform a multi-point calibration on the sensor.

- ❑ Quarterly check the actual flow rates *of each sampling stream* with an independent flow rate transfer standard. If the flow rate differs more than +/- 4%, perform a multi-point calibration on the sensor.

- ❑ Should the flow rate mechanism not maintain its calibrations after the monthly or quarterly checks, maintenance and/or replacement of the sensor may be warranted.

5.6 Blanks

- ❑ Trip blanks: Utilize a trip blank for every 30 sampling days; there is no standard for trip blanks. These will be used as an investigative tool.

- ❑ Lab blanks: Utilize a lab blank for every 20 filters used; the standard for lab blanks will be 15 micrograms.
- ❑ Field blanks: Utilize a field blank for every 10 sampling days; the standard for field blanks will be 30 micrograms.

5.7 Filter Media

The selection of filter media for the requested sample analyses can vary with the design of the speciation sampler being used by the requesting state or local agency. For the purposes of this solicitation, the table below identifies the filter media to be used for the target analytes of interest for four available speciation samplers. Filter Performance Specifications:

- ❑ Teflon-membrane filters: A one-month storage period in a controlled environment, followed by one week of equilibrium in the weighing environment is needed to reduce the variability to within + or -15μg/filter for re-weights of 47mm filters.

- ❑ Quartz-fiber filters: Quartz fiber filters adsorb organic vapors over time. Blank quartz-fiber filters should be heated for at least three hours at 900 C. A sample of each batch of 100 pre-fired filters is tested for carbon blank levels prior to sampling, and sets of filters with carbon levels exceeding 1μg/cm^2 are re-fired or rejected. All pre-fired filters should be sealed and stored in a freezer prior to preparation for field sampling.

- ❑ Nylon-membrane filters: Nylon-membrane filters absorb nitric acid over time. Blank nylon-membrane filters should be soaked for four hours in 0.015M sodium carbonate and then rinsed in deionized distilled water for 10 minutes, soaked overnight in DDW, rinsed three times in DDW, then dried in a vacuum oven at 60^0 C for 5 to 10 minutes. Extraction efficiency tests have shown that the sodium carbonate IC eluent is needed to remove nitrates from the active sites of the nylon filter. Sets of washed nylon filters with nitrate levels exceeding 1μg/filter should be rejected. Pre-washed nylon filters should be sealed and refrigerated prior to preparation for field sampling.

At least two filters from each lot (typically 100 filters) or a minimum of 2% of the filters purchased from the specified manufacturers should be analyzed for all species to verify that pre-established specifications have been met. Average blank levels are typically less than 0.5μg/filter for ions and less than 0.5μg/cm^2 for carbon. Lots are rejected for chemical analysis when blank levels for individual species exceed 1μg/filter. Each filter should also be individually examined prior to labeling for discoloration, pinholes, creases, separation of ring, chaff or flaking, loose material, or other defects.

Test of sample media should continue through the course of the monitoring support contract. In addition to 2% to 5% of laboratory blanks, approximately 10% of all samples are designated as field blanks, and these follow all handling procedures except for actual sampling. Filter cassettes, sample transport hardware, and sampling modules vary with the particular speciation samplers and these items will be purchased by the State monitoring agencies.

5.8 Laboratory Control

- ❑ On a weekly basis, perform a unknown lab analysis test to verify laboratory analysis procedures

- ❑ On a monthly basis, perform a collocated lab blank test to verify the laboratory analysis procedures

- ❑ On a quarterly basis, perform an audit of the laboratory with an independent analysis mechanism. This audit will be an independent assessment from an entity not involved with the normal laboratory analysis.

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