Federal Reference Methods for NO_y and p-SO_4 for the New Combined NO_x and SO_x Secondary NAAQS

Research Plan

January 20, 2011

Project Period: July 2010 to July 2012

United States Environmental Protection Agency
Office of Research and Development
National Exposure Research Laboratory
Human Exposure and Atmospheric Sciences Division

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I. Acronyms

AIM -	Ambient Ion Monitor
APS -	Aerodynamic Particle Sizer
CASTNET -	Clean Air Status and Trends Network
FEM -	Federal Equivalent Method
FP -	Filter Pack
FRM -	Federal Reference Method
GPT -	Gas Phase Titration
$H_2O_{(g)}$ -	Water Vapor
HEASD -	Human Exposure and Atmospheric Sciences Division
HNO_2 -	Nitrous Acid
HNO_3 -	Nitric Acid
IPN -	Isopropyl Nitrate
NAAQS -	National Ambient Air Quality Standard
NCORE -	Multi-pollutant Network
NERL -	National Exposure Research Laboratory
NH_3 -	Ammonia
NO -	Nitric Oxide
NO_2 -	Nitrogen Dioxide
NO_x -	Oxides of Nitrogen ($NO_x = NO + NO_2$)
NO_y -	Total Reactive Nitrogen
NO_z-	Reacted Oxides of Nitrogen ($NO_z = NO_y - NO_x$)
NPN -	N-Propyl Nitrate
O_3 -	Ozone
OAP -	Office of Atmospheric Programs
OAQPS -	Office of Air Quality Planning and Standards
OAR -	Office of Air and Radiation
ORD -	office of research and Development
PAN -	Peroxyacetyl Nitrate
p-NH_4 -	Particulate Ammonium
p-NO_3 -	Particulate Nitrate
p-SO_4 -	Particulate Sulfate
QAPP -	Quality Assurance Project Plan
SO_2 -	Sulfur Dioxide
SOP -	Standard Operating Procedures
SO_x -	Oxides of Sulfur
t-NO_3 -	Total Nitrate (t-$NO_3 = HNO_3$ + p-NO_3)
UVF -	Ultraviolet Fluorescence
VOAG -	Vibrating Orifice Aerosol Generator

II. Abstract Summary Information

Title: Federal Reference Methods for NO_y and p-SO_4 for the New Combined NO_x and SO_x Secondary NAAQS

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Project Period: July 2010-July 2012

Project Summary: EPA has been considering an indicator with a combination of measurements (SO_2, p-SO_4, and NO_y) that form the NAAQS measured component of a new combined NO_x and SO_x secondary standard. Federal reference and/or equivalent methods (FRM/FEM) are currently available only for SO_2. However, p-SO_4 is measured at over 500 sites nationally, most often through the use of a filter pack sampler followed by off-line ion chromatographic analysis. Based on an initial survey of available information, methods of this type are reliable and provide consistent data. The determination of NO_y is attempted in near real time using optical monitors employing an externally locate catalytic converter to convert all NO_y species to NO, prior to possible line losses, which can then be detected using O_3-chemiluminescence. This NO_y methodology is now being deployed in EPA's national NCORE network. However, a large degree of uncertainty exists as to the quality of the NO_y data, the ability to measure total NO_y, and the applicability of this method for routine regulatory use.

This research will result in the development and evaluation of sampling and analytical methods required to support the promulgation of the proposed NO_x and SO_x secondary NAAQS. It is anticipated that these newly developed/evaluated methods will be promulgated as the federal reference methods for the combined standard. For SO_2, no work is needed as a designated FRM already exists for the primary standard. For p-SO_4, the CASTNET filter pack (FP) method will be adopted and modified as needed to make it suitable for use as an FRM. The catalytic conversion/chemiluminescence based method for NO_y, will require significant research to assess its adequacy for use as an FRM. Key unresolved science questions associated with this method need to be identified and studies performed to address these questions. After the available data and information on NO_y measurement methods is compiled, HEASD will be able to describe the accuracy, precision, and reliability of the NO_y method. Measurement uncertainties associated with existing NO_y methods fall mainly in these important areas: total NO_y capture (i.e., particulate NO_3); converter performance (efficiency with respect to individual NO_y species, consistency (i.e., changes in efficiency over time); inlet placement (i.e., vertical distribution of NO_y in ambient air); potential interferences; and instrument calibration, and challenge (zero, span, precision) procedures.

Following procurement and evaluation of commercially available NO_y monitors, HEASD will conduct field and laboratory based studies to address the above mentioned measurement uncertainties and to evaluate the method for use as a FRM. It is anticipated that test results and developed procedures will provide guidance to regional, state and local monitoring agencies in deployment and operation of the proposed NO_x and SO_x secondary FRM monitoring network. In addition, these approved measurement methods will serve as important tools for monitoring agencies towards development of effective implementation plans aimed at deposition of acidic species into aquatic systems.

III. Project Implementation Plan

A. Objectives

1. Adopt FRM specifications for SO_2 based upon current FRM for primary SO_2 NAAQS.
2. Propose and finalize FRM specifications for p-SO_4 based upon adoption of CASTNET FP method for p-SO_4.
3. Evaluate the catalytic conversion/chemiluminescence based method as a potential FRM for NO_y.
   a. Quantify overall uncertainties associated with the NO_y method
   b. Identify and quantify interferences and measurement challenges associated with the NO_y measurement method.
   c. Investigate vertical NO_y distribution in a representative air shed to establish inlet placement criteria.
   d. Develop calibration and challenge procedures for NO_y method
   e. Evaluate commercially available chemiluminescence based NO_y monitors for use as FRMs
4. Propose and finalize FRM specifications for NO_y.

B. Technical Approach

Adopt FRM specifications for SO_2. The existing FRM for the primary SO_2 NAAQS is based upon ultra-violet fluorescence (UVF)[1]. FRM analyzers using this UVF technique can provide the needed detection limits, precision, and accuracy and thus fulfill all purposes of an FRM. As a result, no work will be done on the current SO_2 FRM and it will be adopted as the FRM for the SO_2 indicator of the proposed secondary standard.

Additionally, some interest has been expressed by OAR/OAQPS in pursuing the CASTNET FP method for SO_2[2, 3] as an additional FRM or possible FEM due to the expected prohibitive cost associated with equipping a site with UVF FRM monitors. As a result, HEASD will use the substantive, readily available data and information available for the FP SO_2 method. HEASD will provide a technical summary of the data and develop the basis/rationale for making it an FRM/FEM. HEASD will prepare docket materials, proposal preambles, response to comments, and the FRM in regulatory text format.

Propose and finalize FRM specifications for p-SO_4. HEASD would use the readily available and documented data, procedures and information available for the CASTNET p-SO_4 FP method[2, 3]. HEASD will provide a technical summary of the data and supporting information and develop the basis/rationale for adopting it as an FRM. HEASD will prepare docket materials, proposal preambles, response to comments, and the FRM in regulatory text format. This approach for a p-SO_4 FRM when combined with the above two approaches for a SO_2 FRM will provide scientifically defendable methods where SO_x deposition is involved.

Evaluate the catalytic conversion/chemiluminescence based method as a potential FRM for NO_y. Current NO_y instruments based upon catalytic conversion and chemiluminescence detection methodology are available commercially but have not been assessed thoroughly enough to develop as an FRM. As a result, HEASD has identified measurement uncertainties and key unresolved science questions associated with this method. These uncertainties and associated questions are:

(1) Total NO_y capture – It iis well established that the proposed method is capable of the near quantitative capture of certain key gaseous components of NO_y such as NO and NO_2. However, there are questions about this methods capability in capturing the two components of NO_y most relevant to nitrogen deposition, nitric acid (HNO_3) and particulate nitrate (p-NO_3).

(2) Converter efficiency – The catalytic converter most often employed in instrumentation of this type is a heated molybdenum converter wherein the more highly oxidized oxides of nitrogen (NO_2, HNO_3, HNO_2, p-NO_3, PAN) are converted to NO which can then be detected via O_3-chemiluminescence. It is well established for the species NO_2, that the converter efficiency is $\geq$98% thus the basis for use of this method as the FRM for the NO_2 primary NAAQS. However, what is not known is how efficient the molybdenum converter is in converting other oxides of nitrogen to NO for detection. This particular aspect will be important as these proposed FRMs will be deployed in air sheds with differing NO_y compositions. In addition, uncertainties also exist associated with the stability of the converter over extended periods of time with respect to total NO_y and the individual components.

(3) Inlet placement – It is standard practice in the determination of total NO_y to locate the molybdenum converter externally, very near to the point of sampling to reduce sample transfer line losses of species such as p-NO_3 and HNO_3. Most often the converter and inlet probe are placed at a height of 10 m to eliminate any bias associated with vertical concentration gradients of HNO_3 and p-NO_3. However, additional research needs to be performed to identify and quantify potential vertical gradients in total NO_y. This research will result in the inlet siting criteria for the proposed FRM.

(4) Interferences – potential interfering species in the catalytic conversion/chemiluminescence determination of NO_y include certain hydrocarbons, $H_2O_{(g)}$ and NH_3. However, the extent to which, and under what circumstances these species interfere is not known and must be identified and quantified.

(5) Calibration/challenge procedures – Although not an uncertainty, detailed method calibration and operating procedures must be developed and demonstrated as part of the FRM process. This includes procedures to test the performance of the FRM (i.e., zero, span, precision checks). It is anticipated that calibration procedures will be similar to those used in the NO_2 primary NAAQS FRM with slight modification to account for the elevated converter height. However, performance challenge criteria will have to be identified that best represent the mixture of NO_y species that are expected to be present in the various air sheds across the U.S.

To address the above mentioned science questions, uncertainties and measurement challenges, the following approach will be taken:

(1) Quantify overall uncertainties associated with the NO_y method – Overall uncertainty will be quantified by collocated pair sampling to determine precision, bias and comparability between identical instruments under laboratory and ambient conditions. The laboratory based studies will

allow these figures of merit to be determined for individual NO_y species and various NO_y mixes under controlled laboratory conditions using simulated NO_y species while the ambient studies will result in an assessment of precision, bias, and comparability under conditions that the FRMs would experience upon routine deployment. All ambient air studies will be conducted at the AIRS sampling site on EPAs RTP, NC campus as it is anticipated that this site is representative of the proposed sites in the NO_x and SO_x combined secondary standard network. There are currently three commercially available NO_y instruments (Teledyne API, Thermo Environmental, and American Ecotech) that will be evaluated for use as FRMs. Table 1 gives an inventory of the instrumentation/equipment to be used during the laboratory based and ambient studies.

Table 1. Inventory of instrumentation/equipment for laboratory and ambient studies.

Instrument	Species Analyzed	Parameters Investigated
Thermo 42i-Y NO_y Monitor	NO, NO_y, NO_2+NO_z	precision, bias, Total NO_y, speciated NO_y, NO_y capture, converter efficiency/stability, vertical NO_y flux
American Ecotech 9843 NO_y Monitor	NO, NO_y, NO_2+NO_z	precision, bias, Total NO_y, speciated NO_y, NO_y capture, converter efficiency/stability, vertical NO_y flux
Teledyne API T200U NO_y Monitor	NO, NO_y, NO_2+NO_z	precision, bias, Total NO_y, speciated NO_y, NO_y capture, converter efficiency/stability, vertical NO_y flux
Teledyne API 200EU Photolytic NO_2 Monitor	NO, NO_2, NO_x	speciated NO_y
URG 9000D Ambient Ion Monitor	p-NO_3, p-NH_4, HNO_3, HNO_2, NH_3	speciated NO_y, interfering species
GC-based PAN	PAN	speciated NO_y
TSI VOAG	p-NO_3, p-NH_4	speciated NO_y, NO_y capture, converter efficiency, interfering species
Perm Tube Oven	HNO_3, NH_3	speciated NO_y, NO_y capture, converter efficiency, interfering species
Dynamic Dilution Gas Manifold	gas phase species	speciated NO_y, NO_y capture, converter efficiency, interfering species

(2) Identify and quantify interferences and measurement challenges associated with the NO_y measurement method – Potential measurement challenges and interferences will be identified, quantified and documented through rigorous laboratory based and ambient method evaluations. In the laboratory based studies these include using state of the science equipment and facilities to challenge the NO_y instrumentation with simulated individual NO_y species and mixtures of species to gain an understanding of NO_y capture (inlet and sampling losses), molybdenum converter efficiency and stability with respect to individual NO_y species and total NO_y, and measurement interferences of other atmospherically relevant species in the NO_y determination. A TSI Vibrating Orifice Aerosol Generator (VOAG) will be used to generate test aerosols of known particle size, composition, and concentration to introduce to the candidate method as shown in Figure 1. A TSI Aerodynamic Particle Sizer (APS) will be used to monitor the

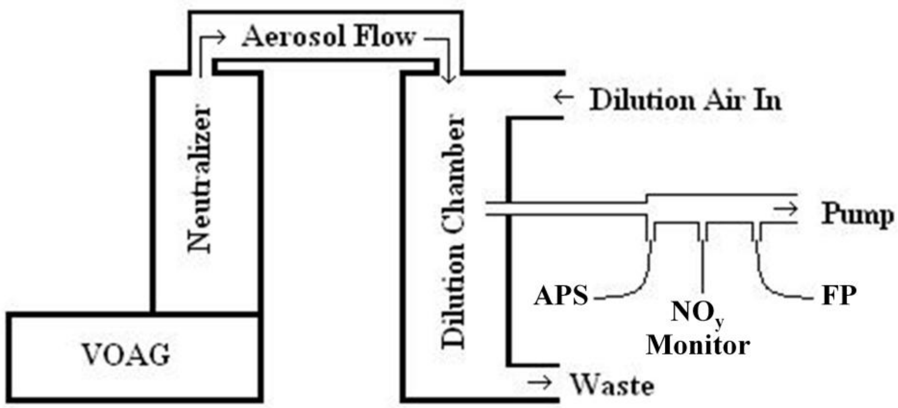

Figure 1. Schematic representation of the aerosol generation system to be used during the ambient studies.

aerodynamic diameter of the generated particles and a filter pack sample will be used as a reference. The filter pack sample will be collected and analyzed according to EPAs Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, IO-2[4] and IO-3[5]. A dynamic dilution system will be used to provide gas phase species to the candidate method as shown in Figure 2. The source gas will be obtained either through compressed gas cylinders (NO, NO_2) or thorough the use of permeation tubes (HNO_3, HNO_2, NH_3). An annular denuder sample collected and analyzed according to EPAs Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, IO-4[6] will be used as a reference. The aerosol and gas generation systems will allow HEASD to produce individual NO_y components and potential interfering species under extremely controlled conditions. Ambient studies will confirm laboratory findings under conditions that the potential FRMs will experience upon deployment. During the ambient based studies, NO_y will be speciated into its individual components and summed for comparison with results obtained with the method for total NO_y. This comparison will allow for the assessment of the capability of the method in determining NO_y as an FRM and identify any sampling shortcomings. Currently, HEASD has the capability for the high time resolution determination of the majority of the NO_y components including the most atmospherically and deposition relevant p-NO_3 and HNO_3 and the most abundant component, NO_2 (Table 1).

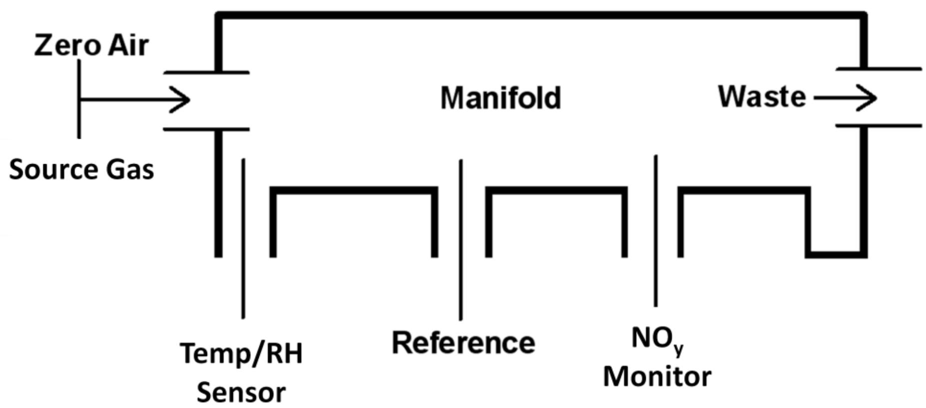

Figure 2. Schematic representation of the dynamic dilution gas generations system to be used during the laboratory based studies

(3) Investigate vertical NO_y distribution in a representative air shed to establish inlet placement criteria – The vertical distribution of NO_y concentrations will be investigated using collocated sampling with comparable instruments where inlet probes and converter boxes are located at differing heights along a 10m telescoping or lean down tower. As stated previously, the results of this investigation will provide data for inlet siting criteria of the proposed FRM.

(4) Develop calibration and challenge procedures for NO_y method – Currently, the FRM for the primary NO_2 NAAQS is based on internally located molybdenum conversion and chemiluminescence detection technology[7]. Per the FRM, detailed calibration and challenge procedures are given. Since the proposed NO_y method is based upon similar technology, HEASD will investigate and develop calibration procedures based upon those for the NO_2 FRM. However, the more complex composition of NO_y will result in the need for investigation and development of new procedures for challenging the NO_y FRMs calibration. This includes identification and testing of existing gases (i.e., NO_2 by GPT, IPN, and NPN) to establish representative test gases to assess the molybdenum converter efficiency.

(5) Evaluate commercially available chemiluminescence based NO_y monitors for use as FRMs – The commercially available instrumentation will be evaluated primarily in an ambient setting over a period of at least 1 year to assess the applicability of each monitor as an FRM. During the evaluations, the monitors will be calibrated, operated and challenged as if they were FRMs according to a detailed SOP that will be developed during the evaluation process.

<u>Propose and finalize FRM specifications for NO_y</u>. After compilation of the generated data and information on the NO_y measurement method, HEASD will be able to describe the accuracy, precision, and reliability of the NO_y instruments and their applicability as FRM. Therefore,

HEASD will provide a technical summary of the data and supporting information and develop the basis/rationale for adopting it as an FRM. HEASD will prepare docket materials, proposal preambles, response to comments, and the FRM in regulatory text format.

Based upon results from literature searches and available data and information, it was the original intent of HEASD researchers to pursue a FRM based upon the most deposition relevant species of total nitrate (t-NO_3, p-NO_3 + HNO_3) as the indicator. As a result HEASD may consider, as resources allow, the CASTNET FP method for t-NO_3[2, 3] as an additional FRM or possible FEM with the surrogate indicator of t-NO_3 due to the expected prohibitive cost associated with equipping a site with NO_y monitors. HEASD may use the substantive, readily available data and information available for the FP t-NO_3 method and provide a technical summary of the data and develop the basis/rationale for making it a surrogate FRM/FEM. HEASD would prepare docket materials, proposal preambles, response to comments, and the FRM in regulatory text format.

C. Project Schedule and Planned Products

Propose and finalize FRM specifications for SO_2.

This effort began in July 2010. HEASD is recommending that the current UVF FRM for the primary SO_2 NAAQS be designated as the FRM for the SO_2 secondary standard. Therefore, HEASD will provide this recommendation by the initial rule making date in July 2011. HEASD will provide response to comments and a final recommendation by the final rule making date in March 2012.

Alternatively, HEASD is currently collecting available data and information for the FP SO_2 method. HEASD will provide a technical summary of the data and develop the basis/rationale for making it an FRM/FEM by April 2011. HEASD will prepare docket materials, proposal preambles and provide the FRM in regulatory text format by the initial rulemaking date of July 2011. HEASD will provide response to comments and the final FRM in regulatory text format by the March 2012 final rule making date. Results from this effort will serve as the basis of the SO_2 FRM.

Propose and finalize FRM specifications for p-SO_4.

This effort began in July 2010. HEASD is currently collecting available data and information for the FP p-SO_4 method. HEASD will provide a technical summary of the data and develop the basis/rationale for making it an FRM/FEM by April 2011. HEASD will prepare docket materials, proposal preambles and provide the FRM in regulatory text format by the initial rulemaking date of July 2011. HEASD will provide response to comments and the final FRM for p-SO_4 in regulatory text format by the March 2012 final rule making date. Results from this effort will serve as the basis of the p-SO_4 FRM.

Evaluate the catalytic conversion/chemiluminescence based method as a FRM for NO_y.

Field and laboratory evaluation of the NO_y method relative accuracy, precision, and correlation began in May 2010 and will continue through May 2012. Following data analysis, data validation, and data interpretation, a summary report of the results will be completed by July 2012. Results from this research effort will be published in a peer-reviewed journal article(s).

Propose and finalize FRM specifications for NO_y.
Concurrent to the NO_y FRM development and evaluation research, HEASD will provide a technical summary of the available data and develop the basis/rationale for making it an FRM by May 2011. HEASD will prepare docket materials, proposal preambles and provide a description of the proposed NO_y FRM in regulatory text format by the initial rulemaking date of July 2011. Method evaluations will continue during the period between initial and final rule making (July 2011-March 2012). HEASD will provide response to comments and the final FRM for NO_y in regulatory text format by the March 2012 final rule making. Results from this effort will serve as the basis for the NO_y FRM.

Alternatively, HEASD is collecting available data and information for the FP t-NO_3 method. HEASD will provide a technical summary of the data and develop the basis/rationale for making it an alternative FRM by April 2011. HEASD will prepare docket materials, proposal preambles and provide the FRM in regulatory text format by the initial rulemaking date of July 2011. HEASD will provide response to comments and the final FRM in regulatory text format by the March 2012 final rule making date. Results from this effort will serve as the basis of the t-NO_3 FRM.

D. Expected Results and Benefits

The U.S. EPA plans a 2012 promulgation of a new combined NO_x and SO_x secondary NAAQS, which will require sampling and analysis methods that are capable of measuring these metrics with known quality and thus ensure accurate compliance determinations. Developing, proposing and finalizing the FRMs for p-SO_4 and NO_y will be a critical component of the final ruling. These approved measurement methods will serve as important tools for monitoring agencies towards development of effective implementation plans aimed at deposition of acidic species into aquatic systems.

Following promulgation of the new secondary NAAQS for NO_x and SO_x, states will be required to develop state implementation plans which will outline measures designed to achieve compliance with the new NAAQS. In order to effectively develop these plans, States must first have an understanding of the factors influencing deposition of nitrogen and sulfur containing species within specific airsheds. Included in these factors is the capability to accurately determine the concentrations of these species in the ambient air. Thus, HEASDs evaluation of these potential FRMs and development of sampling criteria will establish the tools needed for in SO_2, p-SO_4 and NO_y determination. In addition, this information will be valuable to future multiple air pollutant exposure studies and provide key data for source apportionment modeling and deterministic model evaluations. The NO_y method research will also provide valuable methodology and data to assess the role of NO_y species in key atmospheric chemistry processes.

E. Collaboration

HEASD will collaborate with key personnel from OAR/OAQPS during the research and development work as well as the regulatory writing tasks associated with this project. HEASD responses to the public comments, as they relate to finalizing the proposed FRM regulations, will be reviewed by OAR. Laboratory and field evaluation of the NO_y monitors will involve collaboration with their respective manufacturers and potentially State/local air agencies.

HEASD will collaborate with OAP (managers for CASTNET) on adoption and modification of the CASTNET FP method for SO_2, p-SO_4 and t-NO_3 as FRMs.

IV. Quality Assurance and Communication Strategy

A. Quality assurance (QA)

The detailed quality assurance project plan (QAPP) "Identification, Evaluation, and Intercomparison of Methods for Oxides of Nitrogen and Sulfur" (QAPP-KDO-10-01) will address QA consistent with EPA's Quality Manual for Environmental Programs (found at http://www.epa.gov/quality/qs-docs/5360.pdf). The proposed research and subsequent data analysis in this project have a strong foundation in quality assurance in that they come from an existing organization/system with rigorous QA requirements and have been used extensively by the HEASD team. The derived data from the proposed research will be evaluated and review extensively by HEASD researchers in their corresponding areas of expertise

B. Communication Strategy

The project will use a variety of communication methods. There will be regular meetings to discuss progress and periodic meetings with a larger group to provide updates and ensure the team is meeting expectations. Materials will be produced to inform all stakeholders of the project. Scientific outputs will be produce in the form of reports, manuscripts, symposium/conference presentations to inform the scientific community and general public of the project technical outcomes.

V. Appendices

A. References

1. Reference Measurement Principle and Calibration Procedure for the Measurement of Sulfur Dioxide in the Atmosphere (Ultraviolet Fluorescence Method), 40 CFR Part 50 Appendix A-1.
2. Clean Air Status and Trends Network, Quality Assurance Project Plan, Revision 6.0, Appendix 1: CASTNET Field Standard Operating Procedures, November 2009. http://epa.gov/castnet/javaweb/docs/qapp_v6_App_01_Field_SOP.pdf
3. Clean Air Status and Trends Network, Quality Assurance Project Plan, Revision 6.0, Appendix 4: CASTNET Laboratory Standard Operating Procedures, November 2009. http://epa.gov/castnet/javaweb/docs/qapp_v6_App_04_Laboratory_SOP.pdf
4. Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, Chapter IO-2, Integrated Sampling of Suspended Particulate Matter (SPM) in Ambient Air, http://www.epa.gov/ttn/amtic/inorg.html.
5. Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, Chapter IO-3, Chemical Species Analysis of Filter-Collected Suspended Particulate Matter (SPM), http://www.epa.gov/ttn/amtic/inorg.html.
6. Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, Chapter IO-4, Determination of Reactive Acidic and Basic Gases and Strong Acidity of Atmospheric Fine Particles in Ambient Air Using the Annular Denuder Technology, http://www.epa.gov/ttn/amtic/inorg.html

7. Measurement Principle and Calibration Procedure for the Measurement of Nitrogen Dioxide in the Atmosphere (Gas Phase Chemiluminescence), 40 CFR Part 50 Appendix F.