**EPA's Reference and Equivalent Methods Research Program: Supporting NAAQS Implementation through Research, Development, and Analysis**

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**Abstract**

One of the key responsibilities of the U. S. Environmental Protection Agency is to protect public health and welfare through a framework of regulations governing allowable concentrations of pollutants in multiple media (air, water, solid waste, etc.), combined with a vigorous monitoring and enforcement program to prevent damage to human health and the environment. Enforcement of environmental laws and regulations cannot be accomplished without monitoring pollutants to determine where, when, and if violations are occurring. EPA has an extensive network to monitor air pollutants, supported by an active research and development program ensuring deployment of consistent, accurate, and technologically viable air pollution monitoring systems. Work to support monitoring partners, assess and improve current methods, develop new methods, and method designation review is conducted in EPA's Reference and Equivalent Methods Research Programs (REMRePs). Here we describe the method designation application and review process, along with current and future methods development research within the program.

**Introduction**

Under the Clean Air Act (CAA) of 1970, as amended, the US Environmental Protection Agency (EPA) is mandated under Section 103 to, "…conduct a program of research, testing, and development of methods for sampling, measurement, monitoring, analysis, … of air pollutants"[1]. Under Section 103, the program must consider "…individual, as well as complex mixtures of air pollutants … a national network to monitor, collect, and compile data … to ensure comparability of air quality data collected in different States …"[1]. To implement this legislative mandate, EPA developed and deployed, in conjunction with states, tribal lands, and US territories, a network of air pollution monitors focused on determining ambient levels of six criteria pollutants regulated by National Ambient Air Quality Standards (NAAQS): Carbon Monoxide (CO); Lead (Pb); Ozone ($O_3$); Sulfur Dioxide ($SO_2$); Nitrogen Dioxide ($NO_2$), and Particulate Matter ($PM_{10}$ and $PM_{2.5}$). The NAAQS provides the maximum concentration levels of these six criteria air pollutants that should be found in a given 'area of interest', e.g., city, state, metropolitan statistical area [MSA], etc.[2].

Monitoring ambient air quality to determine compliance with the NAAQS requires use of either Federal Reference Methods (FRMs) or Federal Equivalent Methods (FEMs), as specified in Section 2.1 of Appendix C to 40 Code of Federal Regulations (CFR) Part 58. FRMs designated by EPA are federally approved sampling and/or analytical methods used for making NAAQS compliance decisions. FRMs for the six criteria pollutants are defined in the appendices to **40 CFR Part 50** as follows: **i)** $SO_x$ ($SO_2$) – Appendix A and A-1; **ii)** CO – Appendix C; **iii)** $O_3$ – Appendix D; **iv)** $NO_x$ ($NO_2$) – Appendix F; **v)** Pb – Appendix G; **vi)** $PM_{10}$ and $PM_{2.5}$ – Appendices J and N respectively. Methods described in these appendices ensure that reference methods are developed, tested, and are fully compliant with the regulations. FEMs

are based on different technologies than FRMs, but have passed rigorous equivalency testing as outlined in **40 CFR Part 53**.

EPA's Office of Air and Radiation (OAR), through its Office of Air Quality Planning and Standards (OAQPS), manages the regulatory, data collection, data analysis, system operations, and quality assurance programs related to EPA's air pollution monitoring program. EPA's Office of Research and Development (ORD) supports OAQPS's mission by maintaining research and development programs to assess, develop, and validate FRMs and FEMs. EPA's REMRePs are the sole research programs specifically focused on development, analysis, and modification of air pollution monitoring equipment, sampling equipment, and laboratory/field analysis and calibration protocols for air pollution monitoring systems. EPA's REMRePs are implemented based on the applicable 40 CFR Part 50 – 59 regulatory directives governing NAAQS compliance through ambient air monitoring.

Through the REMRePs, EPA is able to:

- Review and assess the technical feasibility and scientific accuracy of samplers, monitors, analyzers, and measurement devices/systems designed to determine the ambient concentrations of the six NAAQS criteria air pollutants;
- Provide scientific and technical guidance to OAQPS in its management and implementation of EPA's air pollution monitoring program;
- Provide technical guidance to manufacturers of samplers, monitors, analyzers, and measurement devices/systems who submit their systems for consideration as either FRMs or FEMs;
- Develop or analyze new reference or equivalent methods (FRMs or FEMs), measurement and/or calibration protocols/procedures/techniques, and analysis methods in support of legislative, judicial, and/or regulatory changes to the NAAQS;
- Determine the impact of changes to the NAAQS on air pollution monitoring systems, based on knowledge of the current state of the art capabilities of the FRMs and FEMs, and;
- Provide technical guidance on NAAQS monitoring to states, tribes, other Federal agencies, EPA Regional offices, and key EPA program offices.

**Research and Development of FRM and FEM Technologies**

The technologies used in reference and equivalent methods research are divided into two distinct categories: 1) current technologies and; 2) future (target) technologies. Current technologies are those that are presently designated as the FRM for a given NAAQS pollutant. Future (target) technologies are those that are being investigated to replace existing FRM technologies. Research and development for current and future technologies is underway to ensure availability of robust and comparable methods. Examples of current technologies (specifically ozone [$O_3$] and $PM_{2.5}$ monitors) and future technologies (specifically lead [Pb], and $NO_2/NO_x$) are discussed in more detail below. The current list of designated reference and equivalent methods can be found online[3].

**Application Submission and Review Process for FRMs and FEMs**

The application process for submitting new candidate methods (or changes to existing reference and equivalent methods) is outlined here. Whenever new or modified reference and equivalent methods are proposed, usually by manufacturers of air pollution monitoring equipment (samplers, analyzers, etc.) and associated field and laboratory analysis protocols, the individual or organization suggesting the change(s) must submit their data supporting the change through a formalized application process. The proposed method or modification must adhere to the rigorous equivalency testing procedures in **40 CFR Part 53** (including **Part 53.2**, **53.3**, **Subpart B**, and **Subpart C**)[4]. In circumstances where **40 CFR Part 53** does not specifically address a proposed candidate method, EPA REMReP scientists develop guidance matching the nature of the candidate method to provisions stated in **40 CFR Part 53**. The proposed candidate reference methods (manual and automated) for each of the six criteria air pollutants must use the definitions, analysis, and test procedures found in the applicable appendices in **40 CFR Part 50** and in **40 CFR Part 53** (**53.2 [a]** and **53.2 [b]**), including **Subpart A**, and **Subpart B**[3]. The proposed candidate equivalent methods for each of the six criteria air pollutants must use the definitions, analysis, and test procedures found in **40 CFR Part 53** (**53.3 [a]** and **53.3 [b]**), including **Subparts A**, **B**, **C**, **D**, **E**, and **F**[4].

Applications for candidate methods should include, but not be limited to the following elements to ensure that those candidate reference and equivalent methods can be fully validated against the applicable **40 CFR Part 50 – 59** regulations:

- User/operator manual;
- Statements addressing:
    - Designation/identification protocol;
    - Measurement range;
    - Compliance (with applicable regulation);
    - Representativeness (of method, sampler, analyzer);
    - Quality control protocol (ensuring all analyzers operate like test article);
    - Durability (expected length of operation under typical operating conditions);
    - Standard adjustments required for test article (if any), and;
    - Statement that test article was not replaced during validation testing for candidate method application;
- Drawings/schematics illustrating component locations, electrical, gas, data/information, and control flows, etc.;
- Calibration data from test, and;
- Test data (**40 CFR Part 53**, **Subpart B** and **C**, etc.).

Applicants are encouraged, though not required, to submit questions and requests for test plan approvals in writing. Application packages for candidate reference and equivalent methods should be organized in a logical manner facilitating review by scientists in EPA's REMRePs. All Confidential Business Information (CBI) and proprietary processes, trade secrets, etc., should be clearly and prominently indicated in the application package to protect it from inadvertent disclosure to third parties. Duplicate applications should be sent to the following address (es): Mailing Address - Director, National Exposure Research Laboratory, Process Modeling

Research Branch (MD E205-03), United States Environmental Protection Agency, Research Triangle Park, North Carolina 27711; Commercial Delivery (Shipping) Address - Director, National Exposure Research Laboratory, Process Modeling Research Branch (MD E205-03), United States Environmental Protection Agency, 4930 Old Page Road, Durham, NC 27703.

After applications are submitted and received, EPA scientists are required to review all application packages for reference and equivalent methods and send a response to the applicant within 120 days. If the package is incomplete, or if there are questions on the application, the applicant is required to provide a revised application package. A new 120 day review time period begins with the receipt of the revised application package.

**Examples of Current Technologies**

**Ozone.** The current FRM for $O_3$, ethylene chemiluminescence, is not widely used. Research is being implemented in 2012 and 2013 to address this issue. In a majority of monitoring locations, the current FEM (UV photometric method) is used in place of the FRM. However, the equivalent method is limited because it is susceptible to interference from water vapor, VOCs, and other chemical species that absorb UV radiation[5]. There is a newly-approved FEM (NO chemiluminescence) that can be used instead of the FRM. The current options under consideration are to continue with the current FRM or adopt a more widely used method as the FRM. During 2012 and 2013, there will be an intercomparison between the two FEMs to determine their feasibility for replacing the FRM.

**$PM_{2.5}$.** Continuous methods for measuring $PM_{2.5}$ are increasingly being considered by states as replacements for the filter-based $PM_{2.5}$ FRM because they are less expensive and require less labor to operate. Comparability between FRM and FEM measurement performance for $PM_{2.5}$ is an extremely important consideration for states considering use of the FEM. EPA is actively engaged in research and collaborating with key stakeholders to conduct ongoing assessments of FEM data quality to identify and mitigate factors adversely affecting FRM and FEM data comparability in routine $PM_{2.5}$ monitoring networks[6].

**Examples of Future/Target Technologies**

**Lead (Pb).** The limitations of the high-volume Total Suspended Particulate (TSP) method as the FRM for Pb sampling have long been recognized and include: **i)** inconsistent flow control and leak check functionality; **ii)** particles being collected during periods where sampling is not occurring; **iii)** filters cannot be analyzed by standard non-destructive techniques (e.g., XRF), and; **iv)** ability to collect and separate different particle sizes is negatively impacted by, wind speed and direction, wide range of sampler flow rates and inlet geometries[5].

To address these limitations, EPA is currently considering replacing TSP samplers with ones providing greater precision and reduced error in measuring Pb concentrations. In particular, a newly developed sampler should display fewer wind speed and wind direction dependencies as a function of particle size. One option for a new FRM for Pb involves replacing TSP with $PM_{10}$ as the Pb metric. This strategy leverages existing $PM_{10}$ sampling and analysis methodologies and provides Pb concentration measurements which may be more biologically relevant than TSP sampling. Alternatively, a new FRM sampler could be developed providing known size

selective collection characteristics as a function of sampling conditions, resulting in reduced measurement uncertainty as compared to the current FRM.

**Nitrogen Dioxide ($NO_2$)**. Evaluation of the current $NO_2$ FRM is another high priority issue. The current $NO_2$ FRM (gas phase chemiluminescence) uses a heated metal catalyst to convert $NO_2$ to nitric oxide (NO), and measures NO by the light produced from the reaction with ozone. $NO_2$ is then calculated as the difference between the $NO_x$ (sample passes through converter) and NO channels. This $NO_2$ reference method has been the FRM since 1976, measures $NO_2$ indirectly, and is susceptible to interferences by various oxides of nitrogen. While potential interferences are expected to minimally affect monitors located in urban areas[7], recently developed technologies offer more selective and direct measurement of $NO_2$. These technologies include photolytic conversion of $NO_2$ to NO (before detection of NO by chemiluminescence), and direct optical measurements based on the attenuation of light by $NO_2$ in the spectral region around 400 nm. Ambient intercomparison testing with a number of different instruments supporting $NO_2$ analysis, along with laboratory experiments and atmospheric chamber testing will be used to compare the current FRM to recently developed technologies. Results from these tests will influence future FRM designations.

**Summary**

EPA's REMRePs are research and development programs based on the **40 CFR Part 50**, **40 CFR Part 53,** and **40 CFR Part 58** regulations. These programs facilitate EPA's ability to accurately measure ambient concentrations of the six NAAQS criteria air pollutants so the agency can assess the ambient concentration levels of these air pollutants and determine if specific geographic areas are in compliance with the NAAQS. The REMRePs support EPA's ability to determine the impact of the six NAAQS criteria air pollutants on public health and ecosystem health.

The research and analyses conducted by EPA scientists in the reference and equivalent methods research programs provide support for: **i)** Operation of EPA's ambient monitoring networks; **ii)** Conducting health related research (e.g., linking health outcomes to $PM_{2.5}$ concentrations), and; **iii)** Providing information EPA decision makers use to formulate policy affecting the NAAQS. States, tribes, and other federal agencies also use information from the REMRePs in their decision making activities. The cyclical nature of the NAAQS reviews (5 year cycle) for the six criteria air pollutants along with the continuing requirement to review candidate reference and equivalent methods justifies the need for an ongoing, research and development program to support these activities. EPA's Reference and Equivalent Methods Research Programs provide the technical support and organizational resources to support these critical activities required by the Clean Air Act.

**Disclaimer**

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