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Highlights of the Emissions Measurement Center's Activities for 2004/2005

U.S. Environmental Protection Agency
Office of Air and Radiation
Office of Air Quality Planning and Standards
Emissions, Monitoring, and Analysis Division
(www.epa.gov/ttn/emc)

Below are highlight items involving emission test method development, evaluation, validation, publication and other **Emissions Measurement Center (EMC)** activities during the past twelve months. The information is organized by publication category or organizational activities.

A. New and Revised 40 CFR Part 60, Appendix A, Test Methods

1. **Instrumental Test Methods Revisions** - Methods 3A, 6C, 7E, 10, and 20 of 40 CFR Part 60, Appendix A are instrumental test methods that we are revising to harmonize equipment and performance criteria. Inconsistent acceptance criteria for performance tests and calibration gas quality are being made uniform. Other improvements address low-concentration measurements and alternative performance evaluating techniques. Revisions to these methods were proposed on October 10, 3003 (68 FR 58838). Sixty one public commenters submitted over 700 comments on the proposal. We are presently addressing the comments and resolving the issues raised and we anticipate promulgation of the method revisions in the summer of 2005. **(Foston Curtis 919/541-1063 and Terry Harrison 919/541-5233)**

2. **Method 18 Revisions -** Method 18 of 40 CFR Part 60, Appendix A utilizes gas chromatography coupled with various sampling procedures to measure gaseous organic emissions from stationary sources. In January of 2004, we met with interested stakeholders to discuss their concerns with real-life application of Method 18 and to hear other suggestions for improvements in the method. At last years Stationary Source Sampling and Analysis of Air Pollutants Conference, we presented our technical perspective on stakeholder recommendations. We have just obtained the resources to begin work on a regulatory package to propose revisions to Method 18 and expect to propose these revisions by the end of 2005. **(Rima Howell 919/541-0443 and Gary McAlister 919/541-1062)**

3. **Method 24 Revisions** - Method 24 describes procedures for determining the volatile matter content, water content, density, volume solids, and weight solids of surface coatings, typically referencing ASTM procedures for conducting these analyses. In an EPA-sponsored study, we completed a round-robin sampling and

analysis evaluation of a new procedure for determining the volatile organic content of water-based coatings and drafted a method revision based on the results. We are working with the Adhesive Council which conducted a round-robin evaluation of a headspace procedure for water-based coatings. The Adhesive Council has drafted a final method and is working to get it accepted by ASTM. As it is presently under the ASTM balloting process, we expect to be able to propose it as an addition to Method 24 sometime in 2005. **(Candace Sorrell 919/541-1064)**

B. New and Revised 40 CFR Part 60, Appendix B, Performance Specifications for Continuous Opacity and Gaseous Monitoring Systems

1. Performance Specification 11 - Specifications and Test Procedures for Particulate Matter Continuous Emission Monitoring Systems at Stationary Sources (PS-11) - These requirements for particulate matter (PM) continuous emissions monitoring systems (CEMS) were promulgated on Monday, January 12, 2004 (69 FR 1786). PS-11 is used for evaluating the acceptability of a PM CEMS at the time of or soon after installation, and whenever specified in a source's applicable regulation(s). This performance specification requires site-specific correlation of the PM CEMS response against manual gravimetric Reference Method measurements (e.g., Methods 5, 5B, 5i, or 17, 40 CFR 60, Appendix A). PS-11 outlines the procedures and acceptance criteria for installation, operation, calculations, and reporting of data generated during a PM CEMS correlation. Currently, development of a guidance document for PM CEMS is underway; it should be available by early summer 2005. **(Dan Bivins 919/541-5244)**

2. Performance Specification 12A - Specifications and Test Procedures for Total Vapor Phase Mercury Continuous Emission Monitoring Systems in Stationary Sources (PS-12A) - The EMC is currently conducting a new long-term field test program to demonstrate the performance and reliability of four commercially available mercury CEMS at a coal-fired utility boiler controlled by selective catalytic reduction technology, an electrostatic precipitator, and a wet scrubber. The knowledge obtained during this demonstration is being used to inform finalization of proposed the Agency mercury monitoring requirements proposed on January 30th (68 FR 4652) and March 16th (69 FR 12398) of 2004 with standards for electric utility boilers. **(Bill Grimley 919/541-1065 and Robin Segall 919/541-0893)**

3. Draft Performance Specifications for Predictive Emissions Monitoring Systems (PEMS) (PS-16) - Performance Specification 16 will provide performance criteria for evaluating and accepting PEMS. PEMS are typically used to predict emissions from combustion processes (e.g., NO_x from gas boilers, turbines, and internal combustion engines) through the monitoring of process parameters. Predictive systems are being allowed on the State level and the EPA

has allowed their use in recently-promulgated rules. We expect to propose PS-16 in the Spring of 2005. **(Foston Curtis 919/541-1063)**

4. **Draft Performance Specifications and QA/QC for Continuous Parameter Monitoring Systems (PS-17)** - Our newer emissions standards (e.g., MACT and NSPS) frequently include requirements for monitoring of process or control device operational parameters and for having the operator to stay within site-specific or rule-specific operating ranges. We recognized the need for performance specifications for installing, operating and maintaining these parametric monitoring systems (e.g. temperature, pressure, pH, liquid flow, conductivity) and have begun work on drafting performance specifications and quality assurance requirements. We expect to propose PS-17 for public comment review in the summer of 2005. **(Barrett Parker 919/541-5635)**

C. New and Revised 40 CFR Part 60, Appendix F, Quality Assurance Procedures (for Continuous Monitoring Systems)

1. **Procedure 3 - Quality Assurance Requirements for Continuous Opacity Monitoring Systems at Stationary Sources** - As a result of the comments received after re-opening the comment period for the rulemaking formerly known as "Method 203," which includes requirements for ongoing quality assurance and quality control evaluations of COMS used as continuous compliance monitoring systems, we decided to form a stakeholders' group to undertake the task of re-writing this rule package. The stakeholders' group was comprised of opacity monitor manufacturers, State/local agencies, EPA region personnel, as well as representatives from owners/operators. Method 203 has been rewritten as Procedure 3, and was re-proposed as an addition to 40 CFR part 60, appendix F in the Federal Register on May 8, 2003 (68 FR 24692); we expect to promulgate it by the end of 2005. **(Solomon Ricks 919/541-5242)**

2. **Procedure 2 - Quality Assurance Requirements for Particulate Matter Continuous Emission Monitoring Systems at Stationary Sources** - As an accompaniment to PS-11 for PM CEMS we promulgated ongoing quality assurance and quality control requirements for using PM CEMS as continuous compliance monitoring systems (69 FR 1786, 1/12/04). **(Dan Bivins 919/541-5244)**

D. New and Revised 40 CFR Part 63, Appendix A, Test Methods

1. **Method 301** - Method 301 is the field data validation protocol promulgated on December 29, 1992. The method provides a framework and performance criteria for validating emissions test data (and methods) when no EPA method is available or when proposing an alternative to an existing test method. Comments and questions from the user community have prompted preparation of technical revisions and clarification to the method. The proposed amendments to Method

301 appeared in the Federal register on December 22, 2004. The comment period closed on February 22, 2005. One of the important changes we proposed was to allow the tester to evaluate candidate alternatives to existing reference methods by analyte spiking procedures as well as by direct comparison to the reference method. We also proposed to add a discussion of detection limits, delete the practical limit of quantitation procedure, tighten the acceptable precision limits, and correct deficient equations and other technical errors. We expect to finalize the amendments sometime next Spring. **(Gary McAlister 919/541-1062)**

2. **Method 323-Measurement of Formaldehyde Emissions from Natural Gas-Fired Stationary Sources - Acetyl Acetone Derivatization Method** - We proposed the industry-developed acetyl acetone colorimetric method (first published as CTM-037) for formaldehyde as part of the combustion turbine MACT ~~in~~ on Tuesday, January 14, 2003 (68 FR 1925). It utilizes a chilled midget impinger train for sampling. Method 323 was cited in the June 15, 2004 internal combustion engine MACT promulgation, but the method itself has not been promulgated. (It was originally proposed with the combustion turbine MACT, but was determined not appropriate after proposal and was removed from the promulgation package and we failed to add it into the internal combustion engine MACT package.) **(Terry Harrison 919/541-5233)**

3. **Method 324-Determination of Vapor Phase Mercury Emissions from Stationary Sources Using Dry Sorbent Trap Sampling** - As part of its field testing programs to demonstrate the effectiveness of commercially available mercury CEMS at coal-fired utility boilers, EMC has also evaluated a long-term integrated mercury monitoring method using sorbent trap sampling. This method was proposed along with PS-12A on January 30, 2004 (68 FR 4652) as part of the electric utility MACT. Comments have been received and considered and promulgation of a mercury rule for electric utility boilers is expected in March 2005. **(Bill Grimley 919/541-1065 and Robin Segall 919/541-0893)**

E. New and Revised 40 CFR Part 51, Appendix M, Test Methods

1. **Promulgation of Methods 203A, B, and C - Visual Determination of Opacity of Emissions from Stationary Sources for Time-Averaged, Time-Exception, and Instantaneous Limitation Regulations -**These methods are intended to provide State and Local agencies with an expanded array of data reduction procedures to determine compliance with various types of State Implementation Plan (SIP) opacity regulations. The data reduction procedures and the procedures for fugitive emissions observation in Methods 203A, 203B, and 203C of Appendix M of Part 51 (Requirements for Preparation, Adoption, and Submittal of Implementation Plans) constitute the primary difference between these methods and Method 9 of Appendix A of 40 CFR, Part 60 (Standards of Performance for New Stationary Sources). These methods were proposed in 1994

and are expected to promulgated by early summer 2005. **(Solomon Ricks 919/541-5242)**

F. Conditional Test Methods (CTM) - These methods, which are published on the EPA website at: www.epa.gov/ttn/emc, have been evaluated by EPA and may be applicable to one or more categories of stationary sources. The EPA confidence in a CTM is based upon review of technical information including field and laboratory validation studies. EPA understanding of the most significant quality assurance (QA) and quality control (QC) issues; and EPA confirmation that the method addresses these QA/QC issues sufficiently to identify when the method may not be acquiring representative data. For State and local programs to use a CTM for Title V permits, State Implementation Plans (SIP), etc., they must be subject to an EPA Regional SIP approval process or permit veto opportunity and public notice and comment; CTM may be used without EPA oversight for other non-Federal applications including state permitting programs and scientific/engineering studies. For a source to use them to meet Federal requirements under 40 CFR Parts 60, 61, and 63, A CTM must be approved as an alternative test method.

1. CTM-036 Method for Measurement of Toluene Diisocyanate (TDI) and Methylenediphenyl Diisocyanate (MDI) Stack Emissions - This method was submitted by Bayer Polymers, LLC along with laboratory and field validation data. We reviewed the method and validation data and subsequently posted the method as CTM-036 in April of 2002. We since received additional data from Bayer in support of application of the method to additional compounds (1,6-hexamethylene diisocyanate (HDI), HDI biuret, HDI trimer, and isophorone diisocyanate (IPDI)) and agreed, upon review of the data, that the method was appropriate for measuring those compounds also. The updated method will be added to the EMC website in the next several weeks. **(Gary McAlister 919/541-1062)**

3. CTM-040 Method for Determination of PM10 and PM2.5 Emissions (Constant Sampling Rate) - This method combines Method 201A (40 CFR 51, Appendix M) with the PM2.5 cyclone from a conventional five-stage cascade cyclone train that includes five cyclones of different diameters in series. The PM2.5 cyclone is inserted between the PM10 cyclone and the filter of the Method 201A train. Stack gas is sampled at a predetermined constant flowrate through the in-stack cyclones and filter. Once the sample is obtained, the uncombined water is removed and gravimetric analysis is used to determine the mass of particulate for each size fraction. This method was previously posted as PRE-004 on the EMC web site and has recently been moved to the Conditional Test Method category. **(Tom Logan 919/541-2580)**

4. CTM-041 Determination of Volumetric Gas Flow in Rectangular Ducts or Stacks Taking Into Account Velocity Decay Near the Stack or Duct Walls -

With EPA's Clean Air Markets Division (CAMD) we undertook a project to identify a method suitable for inclusion in alternative method requests by the Part 75 regulated community for flow measurements in rectangular ducts. EPA's current Method 2H, while addressing wall effects in circular ducts, does not address wall and corner equal area flow measurement problems in rectangular ducts. The final evaluation report was reviewed by EMC and CAMD and the candidate method was found to be suitable. It was posted on the EMC website as CTM-041 in December 2003, and can now be used as a common basis for making requests for approval of such an alternative method. **(John Schakenbach 202-564-9158, Bill Grimley 919/541-1065, or Tom Logan 919/541-2580)**

F. Other Emissions Measurement Projects

1. Development of Optical Remote Sensing Method to Determine Emission Flux from Fugitive Emission Sources - No standard protocol exists for making measurements of air emission flux from fugitive or nonpoint sources. Current estimation techniques based on emission factors are imprecise and may overestimate. Earlier point measurement or remote sensing approaches that rely on reverse dispersion modeling are prone to modeling errors. This project, begun in 2002, seeks to demonstrate a path-integrated optical remote sensing (PI-ORS) technique utilizing multiple beam paths and optimizing algorithms to yield a time-averaged, mass-equivalent concentration field across a contaminant plume from which, using wind data, the emission rate can be determined. During 2002 and 2003 extensive field validation testing using open path FTIR and controlled releases of various gases was conducted. For this project, funded by DoD's Environmental Security Technology Certification Program, we are serving as a regulatory advisor to the Air Force and its contractor, ARCADIS. We plan to have the draft protocol for conducting these measurements peer-reviewed and then publish it as a Conditional Test Method in late Spring 2005. **(Robin Segall 919/541-0893)**

2. Development of an Acrolein Method for Stationary Source and Ambient Air Applications – In the past, both the stationary source and ambient air methods for acrolein have demonstrated poor recoveries. The current stationary source method (Method 0011, SW-846) for aldehydes and ketones uses an acidified solution of 2, 4-dinitrophenylhydrazine (DNPH) to derivatize and stabilize compounds containing the carbonyl functional group. Though it performs well for a number of the other aldehydes and ketones, Method 0011 has consistently shown poor recoveries for acrolein. The EPA's Office of Research and Development is currently testing a new compound, Dansyl Hydrazine (DNSH) to determine whether it can yield high recoveries of acrolein for ambient air samples. EPA EMC recently investigated whether this new compound, DNSH, could yield high recoveries of acrolein under stationary source measurement conditions, thereby allowing EPA to potentially develop a new stationary source

method for acrolein. A mixing chamber was used to simulate stack conditions in the laboratory and tests were performed sampling a known concentration of acrolein using (1) DNSH solution and (2) modified DNPH coated beads. In addition, an extractive Fourier Transform Infrared (FTIR) measurement system was evaluated as well. The testing showed that DNSH and DNPH will yield poor recoveries for acrolein under source conditions. The FTIR did identify and quantify the acrolein in the test chamber; however, the detection limit was ~ 1.0 ppm which is not low enough for anticipated applications. Further testing using an FTIR with a longer pathlength cell is being evaluated at this time. **(Dennis Mikel 919/541-5511)**

3. **Stationary Source Audit Program (SSAP)** - EMC has implemented an electronic Stationary Source Audit Program (SSAP) database. Federal, State, Local, and Tribal Agency personnel now use this database to electronically order audit samples. The database compiles the audit results in several report formats that allow the QA Team and Agency staff to review the results of a particular audit. The audit sample results are input into the database by the person who initially requested the audit sample and a pass/fail notice is automatically issued . For security, access to the database is limited to registered Federal, State, Local & Tribal Agency users. **Registration requests can be submitted to Candace Sorrell at the e-mail address or telephone number below.** The request should include name, non-P.O. Box address, Agency affiliation, phone number, and e-mail address and you will receive further instructions via return e-mail. Currently, there are audit materials for Methods 6, 7, 8, 12, 13A and 13B, 18, 23, 24 (inks and solvents), 25, 26, 26A, 29, 101A, and 315. The EMC QA team also conducts teleconference calls on the first Tuesday in every month from 1:30-3:30 pm (EST) to discuss audit and other emission testing issues. Agendas and minutes for these conference calls can be obtained by contacting Candace. **(Candace Sorrell 919/541-1064)**

4. **ASTM Activity** - EMC participates in Subcommittee D22-03 of ASTM primarily to encourage development of new stack test methods for cases where we anticipate a future need that is not met by a current EPA method. D6831-02 Standard Test Method for Sampling and Determining Particulate Matter in Stack Gases Using an In-Stack, Inertial Microbalance and D6784-02 Standard Test Method for Elemental, Oxidized, Particle-Bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method) are successful examples falling into this category. We participate at a more advisory level when D22-03 is developing a method for which EPA already has an acceptable method with our principal goal being to provide input such that we will be able to accept the method as an alternative to the EPA method in future regulatory actions. For example, ASTM D6522-00 Standard Test Method for the Determination of Nitrogen Oxides, Carbon Monoxide, and Oxygen Concentrations in Emissions from Natural Gas-Fired Reciprocating Engines, Combustion Turbines, Boilers and Process Heaters Using Portable Analyzers has

been cited as an alternative to EPA Method 3A for oxygen and Method 10 for carbon monoxide from natural gas fired units as part of the combustion turbine, internal combustion engine and boiler and process heater MACTs as well as for Method 3A, and Methods 7E and 20 (nitrogen oxides) in the NSPS subpart GG revision. **(Terry Harrison 919/541-5233, John Bosch 919/541-5583)**