



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON D.C. 20460

August xx, 2008

EPA-CASAC-08-01x

OFFICE OF THE ADMINISTRATOR  
SCIENCE ADVISORY BOARD

The Honorable Stephen L. Johnson  
Administrator  
U.S. Environmental Protection Agency  
1200 Pennsylvania Avenue, NW  
Washington, DC 20460

Subject: CASAC Ambient Air Monitoring & Methods (AAMM) Subcommittee Peer  
Review of the Draft Federal Reference Method (FRM) for Lead in PM<sub>10</sub>

Dear Administrator Johnson:

EPA's Office of Air Quality Planning and Standards (OAQPS), within the Office of Air and Radiation, requested that the Agency's Clean Air Scientific Advisory Committee (CASAC) Ambient Air Monitoring & Methods (AAMM) Subcommittee (CASAC Subcommittee) conduct a peer review of EPA's "Draft Federal Reference Method (FRM) Lead in PM<sub>10</sub> (Pb-PM<sub>10</sub>)" — that is, lead (Pb) in particulate matter less than 10 micrometers in diameter (PM<sub>10</sub>) — dated June 15, 2008. The CASAC Subcommittee roster is attached as Enclosure A to this letter, Subcommittee members' individual written comments are found in Enclosure B, and the Agency's background and charge memorandum to the Subcommittee is provided in Enclosure C.

The Agency solicited CASAC's advice on this topic as part of EPA's current review of the National Ambient Air Quality Standards (NAAQS) for Lead. Several options being considered for the final Lead NAAQS would require the Agency to develop FRM and Federal Equivalent Method (FEM) criteria for the collection of Pb-PM<sub>10</sub> in ambient air, in order for monitoring data to be used in determining attainment with the NAAQS. The Agency has proposed a FRM for Pb-PM<sub>10</sub> based on the existing, low-volume PM<sub>10c</sub> sampler (*i.e.*, a PM<sub>10</sub> sampler that meets special requirements that are part of a PM<sub>10-2.5</sub> reference method sampler, as specified by Federal regulation), coupled with analysis by the x-ray fluorescence (XRF) analytical method.

The Agency released its Proposed Rule for the Revision of the NAAQS for Lead (40 CFR Parts 50, 51, 53 & 58) on May 1, 2008, and this was subsequently published in the *Federal Register* on May 20, 2008 (73 FR 29184–29291) as a Notice of Proposed Rulemaking (NPR). On July 14, 2008, the CASAC Subcommittee conducted its review of the proposed FRM for the measurement of Pb-PM<sub>10</sub> via a public advisory teleconference. EPA specifically requested the Subcommittee's comments both regarding the type of sampler to be used and the choice of the

1 multi-elemental analytical method for the Pb-PM<sub>10</sub> FRM — and, in particular, the low-volume  
2 PM<sub>10c</sub> FRM sampler and the XRF analysis method, respectively.

3  
4 The CASAC Subcommittee notes that the range of the level for the revised Lead NAAQS  
5 under consideration in this NPR is quite broad, extending from 0.1 to 0.5 µg/m<sup>3</sup>. The Subcom-  
6 mittee was therefore challenged in this peer review by not having a narrower “target” range for  
7 the final NAAQS for Lead, since the level and averaging time of the revised Lead standard sig-  
8 nificantly impact the suitability of candidate sampling and analytical methods. Without more  
9 guidance on EPA’s data quality objectives (DQOs) for Lead monitoring, the members of the  
10 CASAC Subcommittee are unable to provide definitive responses to Questions 2 and 4 that  
11 Agency staff posed to the Subcommittee as part of its review.

12  
13 Nevertheless, overall — and subject to addressing the CASAC’s previously-expressed  
14 concerns with transitioning to a Pb-PM<sub>10</sub> sampling indicator (reiterated below) — *the CASAC*  
15 *Subcommittee unanimously supports the use of the PM<sub>10c</sub> FRM sampler. In addition, it is the*  
16 *consensus recommendation of the Subcommittee in this peer review that EPA consider selecting*  
17 *inductively coupled plasma–mass spectroscopy (ICP-MS) as the Pb-PM<sub>10</sub> FRM analytical*  
18 *method and using XRF as an FEM.*

19  
20 The five charge questions from the Agency, along with a synthesis of the CASAC Sub-  
21 committee’s responses, are found immediately below:

22  
23 1. *What are your comments on the use of the low-volume PM<sub>10c</sub> FRM sampler as the*  
24 *Pb-PM<sub>10</sub> FRM sampler?*

25 If the EPA chooses to transition from a lead in total suspended particulate (Pb-TSP) sam-  
26 pling indicator to a Pb-PM<sub>10</sub> indicator, the CASAC Subcommittee is generally supportive of us-  
27 ing the PM<sub>10c</sub> FRM sampler. The rationale for such a selection is well laid-out in the draft FRM  
28 document that the Agency presented to the CASAC Subcommittee for its peer review, as well as  
29 in the individual written comments from Subcommittee members. However, as discussed below,  
30 the CASAC has previously noted that the choice of Pb-PM<sub>10</sub> as a sampling indicator should be  
31 conditional on a considerable tightening of the final Lead standard.

32  
33 2. *What are your comments on the use of XRF as the Pb-PM<sub>10</sub> FRM analysis method?*

34 By way of background, on March 25, 2008, the CASAC Subcommittee held a public ad-  
35 visory teleconference meeting to conduct a consultation with OAQPS on several ambient air  
36 monitoring issues related to the Lead NAAQS, including issues associated with alternative lead  
37 indicators. As is the CASAC’s customary practice, there was no consensus report from the  
38 CASAC as a result of that consultative meeting. However, Subcommittee members’ individual  
39 written comments were attached in Appendix B of the CASAC’s letter to the Agency (EPA-  
40 CASAC-08-010, dated April 14, 2008). During this March 25 consultation, while Subcommittee  
41 members generally indicated that XRF was an appropriate Pb-PM<sub>10</sub> FRM analysis method, some  
42 members commented that the Agency should consider using ICP-MS as an alternate analytical  
43 method for the FRM.

1 In addition, as mentioned above in this letter, this question is particularly difficult to an-  
2 swer without a clearer sense of the level of the revised NAAQS for Lead. Moreover, at present,  
3 the CASAC Subcommittee is unsure as to what the analytical requirements are for this method,  
4 as well as the Agency's associated data quality objectives. The Subcommittee understands that  
5 an analysis of the DQOs is underway — albeit in the face of uncertainty concerning both the  
6 level and the averaging time of the revised Lead NAAQS.

7  
8 That having been said, the CASAC Subcommittee considers XRF as possessing a number  
9 of potential benefits over competing approaches, although it also has some weaknesses. Specifi-  
10 cally, XRF is, overall, viewed positively by the Subcommittee, in that it: is reasonably cost-  
11 effective; is currently being used for analysis of the Speciation Trends Network (STN) filters;  
12 provides concentrations of elements other than lead; avoids the extraction procedures required by  
13 methods such as ICP-MS and atomic-absorption (AA) spectroscopy; and is non-destructive. On  
14 the other hand, in comparison with XRF, ICP-MS offers lower detection limits, more direct cali-  
15 bration against NIST-traceable references, transparent interpretation of results, and compatibility  
16 with the fiber filters used for high-volume TSP or PM<sub>10</sub> measurements. Importantly, the uni-  
17 formity of sample deposits across the face of low-volume PM<sub>10c</sub> filters would need to be more  
18 carefully investigated prior to selection of an XRF FRM, because XRF analyzes only a portion of  
19 the filter. The use of in-line filter holders appears to exacerbate this problem, and it is noted that  
20 some XRF methods (*e.g.*, the PANalytical instrument) slowly rotate the analysis holder during  
21 analysis, which allows the oval-shaped x-ray beam to scan over a much larger area, thus mini-  
22 mizing bias if there is any inhomogeneity of the filter deposit. Nonetheless, with whole-filter  
23 extraction methods such as ICP-MS, the uniformity of the deposit is no longer an issue, although  
24 completeness of recovery must still be confirmed.

25  
26 On balance, therefore, the issues of deposit uniformity and calibration standards associ-  
27 ated with XRF raise analytical concerns not found with ICP-MS with respect to EPA's accuracy  
28 goal of "an upper 95 percent confidence limit for the absolute bias of 10 percent." *Accordingly,*  
29 *the CASAC Subcommittee recommends that the Agency consider selecting ICP-MS as the FRM*  
30 *and using XRF as an FEM.*

31  
32 3. *What are your comments on the specific analysis details of the XRF analysis method*  
33 *contained in the proposed Pb-PM<sub>10</sub> FRM analysis method description?*

34 Whether XRF is used as the FRM or as an FEM, there are a number of issues that need to  
35 be addressed more thoroughly than currently appears in the Agency's draft FRM for Pb-PM<sub>10</sub>, in  
36 that the appropriate section of EPA's review document should be oriented more towards provid-  
37 ing specific details for the analysis of airborne lead. Whatever analytical method is used labora-  
38 tory and field blanks should be used to detect possible contamination in the filters and the overall  
39 system. It is recognized that different lots of filters may have dissimilar blank levels, so filters  
40 should be matched with blanks from the same lots. A relatively large number of laboratory  
41 blanks should be analyzed in each lot. Furthermore, field blanks, comprising approximately ten  
42 percent (10%) of all sample filters, should be deployed and analyzed as well.

1           4. *Do you think the precision, bias and MDL of the XRF method for the proposed Pb*  
2 *range will be adequate?*

3           Again, answering this question is sensitive to the choice of the form and level of the re-  
4 vised NAAQS for Lead, as implied by the question itself, and is made more difficult by not hav-  
5 ing DQOs available for the CASAC Subcommittee's review. The Subcommittee understands  
6 that there has been limited time to develop the DQOs, and that the Agency is also disadvantaged  
7 by having such a broad range for the level of the final Lead NAAQS under consideration, as well  
8 as the possible change in the averaging time of the standard. As discussed above, *XRF is a vi-*  
9 *able method, and should be able to meet the bias and method detection limit (MDL) require-*  
10 *ments. However, the lack of uniformity in the deposition of lead on filters could pose issues with*  
11 *meeting the precision requirements.* Accordingly, EPA should confirm that for the sampler be-  
12 ing used, non-uniformity in the deposition of lead particles does not compromise meeting the  
13 specified DQOs. Given its greater sensitivity, and concerns over the non-uniformity of deposi-  
14 tion impacting XRF results, a number of individuals on the Subcommittee specifically recom-  
15 mend that ICP-MS be selected as the analysis method for the FRM.  
16

17           5. *Are there any method interferences that we have not considered?*

18           In the judgment of the CASAC Subcommittee the Agency has adequately identified the  
19 potential interferences with XRF.  
20

21           Finally, the CASAC, in its letter dated January 22, 2008 (EPA-CASAC-08-007), had rec-  
22 ommended transitioning the sampling indicator for lead from TSP to a low-volume ambient air  
23 monitor for Pb-PM<sub>10</sub>. This transition to a new indicator was also supported by a majority of the  
24 members of the CASAC AAMM Subcommittee during its March 25, 2008 consultative telecon-  
25 ference (see EPA-CASAC-08-010). Notwithstanding, as discussed in the most recent letter from  
26 the CASAC (EPA-CASAC-08-016, dated July 18, 2008), the discussion leading up to this rec-  
27 ommendation assumed a significant tightening of the lead NAAQS. In particular, as the CASAC  
28 noted in its July 18 letter, a Lead NAAQS set at a level as high as 0.5 µg/m<sup>3</sup> using a Pb-PM<sub>10</sub>  
29 sampling indicator, could potentially allow TSP Pb levels as high as 1 µg/m<sup>3</sup> at sites near large  
30 sources with coarse-mode particulate lead emissions. Therefore, the CASAC clarified its rec-  
31 ommendation by stating that, if the level of the revised lead NAAQS approaches this upper end  
32 of the range, the current TSP indicator should *not* be changed — adding that, while transitioning  
33 from a Pb-TSP to a Pb-PM<sub>10</sub> sampling indicator would indeed be “preferable,” this change  
34 should only be effected if the level of the final NAAQS for Lead is established “conservatively  
35 below an upper bound of 0.2 µg/m<sup>3</sup> or lower.”  
36

37           In closing, the CASAC Subcommittee welcomes the opportunity to review EPA's pro-  
38 posed FRM for Pb-PM<sub>10</sub>, and reiterates that the choice of an appropriate FRM is crucial with re-  
39 spect to the timely development of a more health-protective Lead NAAQS. The Subcommittee  
40 stands ready provide additional advice and recommendations with respect to any air-quality  
41 monitoring issues, especially those related to the NAAQS. As always, we wish the Agency well  
42 in these important efforts to protect both human health and the environment.  
43  
44

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Sincerely,

*/Signed/*

*/Signed/*

Dr. Armistead (Ted) Russell, Chair  
CASAC AAMM Subcommittee

Dr. Rogene F. Henderson, Chair  
Clean Air Scientific Advisory Committee

cc: Marcus Peacock, Deputy Administrator  
Robert Meyers, Acting Assistant Administrator, OAR

Enclosures

**NOTICE**

This report has been written as part of the activities of the EPA's Clean Air Scientific Advisory Committee (CASAC), a Federal advisory committee independently chartered to provide extramural scientific information and advice to the Administrator and other officials of the EPA. The CASAC provides balanced, expert assessment of scientific matters related to issues and problems facing the Agency. This report has not been reviewed for approval by the Agency and, hence, the contents of this report do not necessarily represent the views and policies of the EPA, nor of other agencies within the Executive Branch of the Federal government. In addition, any mention of trade names or commercial products does not constitute a recommendation for use. CASAC reports are posted on the EPA Web site at: <http://www.epa.gov/casac>.

**Enclosure A – Roster of the CASAC Ambient Air Monitoring & Methods  
(AAMM) Subcommittee**

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**U.S. Environmental Protection Agency  
Clean Air Scientific Advisory Committee (CASAC)  
CASAC Ambient Air Monitoring & Methods (AAMM) Subcommittee**

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**Dr. Judith Chow**, Research Professor, Desert Research Institute, Air Resources Laboratory, University of Nevada, Reno, NV

**Mr. Bart Croes**, Chief, Research Division, California Air Resources Board, Sacramento, CA

**Dr. Kenneth Demerjian**, Professor and Director, Atmospheric Sciences Research Center, State University of New York, Albany, NY

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**Mr. Eric Edgerton**, President, Atmospheric Research & Analysis, Inc., Cary, NC

**Mr. Henry (Dirk) Felton**, Research Scientist, Division of Air Resources, Bureau of Air Quality Surveillance, New York State Department of Environmental Conservation, Albany, NY

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**Dr. Kimberly Prather**,\* Professor, Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA

**Dr. Jay Turner**, Visiting Professor, Crocker Nuclear Laboratory, University of California - Davis, Davis, CA

**Dr. Warren H. White**, Research Professor, Crocker Nuclear Laboratory, University of California - Davis, Davis, CA

**Dr. Yousheng Zeng**, Air Quality Services Director, Providence Engineering & Environmental Group LLC, Providence Engineering and Environmental Group LLC, Baton Rouge, LA

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\*Dr. Lumley and Dr. Prather did not participate in this CASAC AAMM Subcommittee activity.



**Enclosure B – Comments from Individual CASAC  
AAMM Subcommittee Members**

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This appendix contains the written comments of individual members of the Clean Air Scientific Advisory Committee (CASAC) Ambient Air Monitoring & Methods (AAMM) Subcommittee. The comments are included here to provide both a full perspective and a range of individual views expressed by Subcommittee members during the review process. These comments do not represent the views of the CASAC AAMM Subcommittee, the CASAC, the EPA Science Advisory Board, or the EPA itself. Subcommittee members providing written comments are listed on the next page, and their individual comments follow.

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**Mr. George Allen**

The following are written comments based on the Charge Questions in the EPA OAQPS memo to the SAB dated June 15, 2008. These comments also reflect discussion during the July 14 teleconference AAMM meeting on a peer review of the Draft Federal Reference Method (FRM) Lead in PM<sub>10</sub> (Pb-PM<sub>10</sub>). A copy of these comments is also being sent to Dr. Ted Russell, CASAC AAMM Subcommittee Chair.

Peer Review Charge Questions in **Bold**:

**1. What are your comments on the use of the low-volume PM<sub>10c</sub> FRM sampler as the Pb-PM<sub>10</sub> FRM sampler?**

The existing PM<sub>10c</sub> sampler is an obvious choice for a sampler since it is well characterized and commercially available from several vendors. Sequential (automated) PM<sub>10</sub> samplers should also be allowed, either as FRM or FEM samplers. The dichotomous sampler is another obvious candidate for an FRM or FEM sampler for PM-10 lead.

**2. What are your comments on the use of XRF as the Pb-PM<sub>10</sub> FRM analysis method?**

XRF is sufficient for routine analysis, but for the FRM, a more sensitive and specific technique should be used, such as ICPMS. If XRF is used, the method should be an FEM. If XRF remains the FRM analysis method, there are concerns of uniform deposit on the filter that may differ with different sizes (coarse vs. fine mode) of particles. Appropriate filter deposition testing would have to be done prior to promulgation of XRF as the FRM analysis method. There are also concerns regarding different XRF analytical methods and calibration techniques across different laboratories, the lack of a NIST thin-film XRF Pb reference standard, possible issues with heavy filter loading, the difficulty of generating spiked samples, and the possibility of interferences. ICPMS does not have any of these concerns.

**3. What are your comments on the specific analysis details of the XRF analysis method contained in the proposed Pb-PM<sub>10</sub> FRM analysis method description?**

The XRF analysis method description proposed here is well written and takes into account most of the issues raised above. It does not resolve the issues of non-uniform deposition or the lack of a NIST thin-film standard for Pb. A PM<sub>10</sub> filter can appear visually to have a uniform deposit, but in urban areas the visual appearance is often driven by fine-mode aerosol which may not reflect the deposition pattern of coarse mode Pb. Thus, visual inspection is only a crude first test for uniform deposition of PM-10 Pb. The issue of filter blanks needs more attention; blank values can vary by manufacturing lot. Thus, the blanks used for a set of samples must be from the same lot. The method description does not use field blanks; it is important to have 5% of filters used as field blanks. The method needs to include a section on how levels below the method's LOD or LOQ will be handled. I suggest reporting the blank-corrected data as measured (even if it is slightly negative), but flagging it as below the LOD.

**4. Do you think the precision, bias and MDL of the XRF method for the proposed Pb range will be adequate?**

The XRF MDL for Pb will be a function of XRF method and blank levels and variability. Although the MDL noted in this method description (1 ng/m<sup>3</sup> one-sigma) is adequate, it may or may not be achieved in the real world, since the MDL is a function of many things, including the number and stability of lab and field blank filters and the length of XRF analysis time. The bias and method detection limits in this draft are appropriate. I would suggest that the FEM precision be tightened from 15% to 10%.

**5. Are there any method interferences that we have not considered?**

Not that I am aware of.

**Dr. Judith Chow**

This memo addresses the twelve questions on which the Subcommittee members were asked to comment regarding Attachment 1, “Draft Federal Reference Method (FRM) for Lead in PM<sub>10</sub> (Pb-PM<sub>10</sub>), and Attachment 2, “Approaches for the Development of a Low-Volume Ambient Air Monitor for Lead in Total Suspended Particulate (Pb-TSP) Sampler.” This supplements prior comments to the first set of questions that was appended to the April 14, 2008 letter from Dr. Russell to Administrator Johnson.

**Questions for Attachment 1 [Draft Federal Reference Method (FRM) for Lead in PM<sub>10</sub> (Pb-PM<sub>10</sub>)]**

**Question 1: What are your comments on the use of the low-volume PM<sub>10c</sub> FRM sampler as the Pb-PM<sub>10</sub> FRM sampler?**

My prior comments in the April 14 letter recommended that EPA move toward Pb-PM<sub>10</sub>. These comments pointed out the lack of specificity and variability of inlet characteristics for the high-volume TSP sampler (Code of Federal Regulations, 2007a). High-volume TSP is a poor surrogate for inhalable particles and a poor surrogate for deposited particles. A true “Total Suspended Particulate” sampler that collects all of particles that remain in the air is of such large dimensions that it requires a small trailer and a large power supply to operate (Burton and Lundgren, 1987; Lundgren et al., 1984). The argument given in favor of retaining TSP in the April 14 letter was that large particles could contaminate surface areas and soils that might be ingested or resuspended. If toxic soils and house dust are of concern in addition to inhalable PM<sub>10</sub>, then these should be sampled and analyzed directly (Egami et al., 1989; Adgate et al., 1998; Farfel et al., 2001; Bai et al., 2003).

FRM sampler inlets have been wind-tunnel tested and have well-defined cut-points and slopes ( $10.2 \pm 1.41 \mu\text{m}$  for SA-246B inlet; Watson and Chow, 1993; 2001). Sampling systems coupled with these inlets provide accurate flow control, use low trace metal background PTFE Teflon-membrane filters, and yield precise mass measurements when coupled with appropriate laboratory weighing procedures. Low-volume PM<sub>10c</sub> FRMs (Appendix O to Part 50) are similar to PM<sub>2.5</sub> FRMs, which use the same PM<sub>10</sub> impactor inlet with the addition of WINS or very sharp-cut cyclone inlets (Kenny et al., 2000; 2004; Peters et al., 2001a; 2001b; 2001c). The low-volume PM<sub>10c</sub> FRM sampler is consistent with EPA’s proposed difference method for PM<sub>10-2.5</sub> (U.S.EPA, 2006) that uses identical filter media, sample collection, gravimetric analysis, and quality assurance [QA]/quality control [QC]) procedures for the side-by-side samplers.

Low-volume PM<sub>10</sub> and PM<sub>2.5</sub> samplers are commercially available, are widely deployed in many urban networks, and network operators are familiar with them. Costs for additional sampling and analysis should be reasonable. There is no need for a separate Pb-PM<sub>10</sub> network, although the existing low-volume PM<sub>10</sub> network might be expanded to suspected Pb hot-spots, as recommended by several committee members in the April 14 letter. The Pb-PM<sub>10</sub> network should be considered within the context of EPA’s integrated air monitoring strategy (Scheffe et al., 2007;

U.S.EPA, 2005) that intends to re-design the national monitoring system to attain multiple objectives beyond compliance (Chow and Watson, 2008).

**Question 2: What are your comments on the use of XRF as the Pb-PM<sub>10</sub> FRM analysis method?**

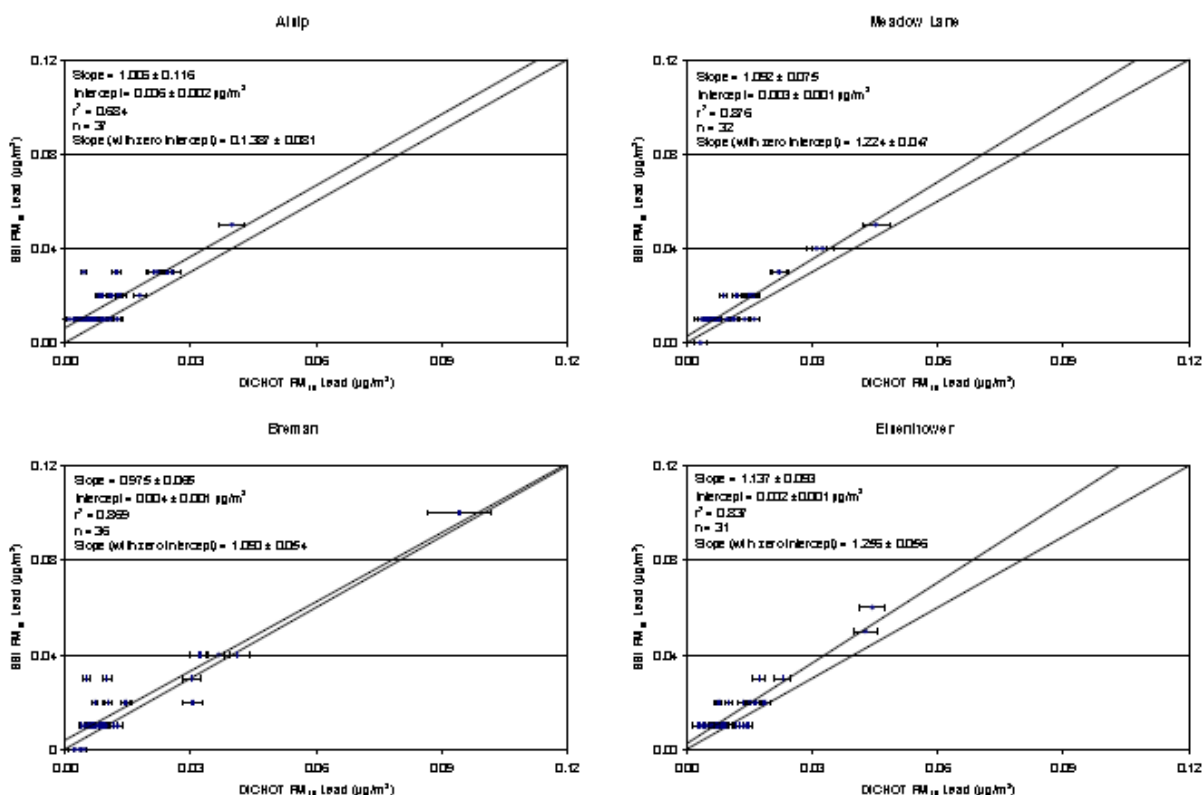
Energy dispersive x-ray fluorescence spectroscopy (XRF; NIOSH, 1998; U.S.EPA, 1999a; Watson et al., 1999a; RTI, 2004; DRI, 2007) is the most commonly used analytical method for multi-elemental analysis on Teflon-membrane filter samples, and the protocols always include Pb. XRF does not destroy the sample, so it can be archived and re-examined for stable particles by other methods (volatile aerosol components such as ammonium nitrate evaporate in XRF's evacuated sample chamber). XRF is currently used for PM<sub>2.5</sub> elemental analysis at urban locations in the Chemical Speciation Network (CSN), at non-urban locations in the Interagency Monitoring of PROtected Visual Environments (IMPROVE) network, and in many special studies.

Other methods have been proven to be equally sensitive, accurate, and precise for Pb measurements, including Proton Induced X-ray Emission Spectroscopy (U.S.EPA, 1999b), Atomic Absorption Spectroscopy (AAS) Code (Fernandez, 1989; NIOSH, 1994a; 1994b; U.S.EPA, 1999c; Code of Federal Regulations, 2007b), Inductively-Coupled Plasma Atomic Emission Spectroscopy (ICP-AES; U.S.EPA, 1999d; NIOSH, 2003a; 2003b; 2003c), Inductively-Coupled Plasma Mass Spectrometry (ICP-MS), and Anodic Stripping Voltametry (ASV; NIOSH, 2003d). These methods are commonly applied to air filters for Pb, especially in workplace environments and Hazardous Air Pollutant (HAPs) networks.

With adequate standard operating procedures (SOPs; such as those cited above), these methods give comparable results for a wide range of sample types and environments (Keppler et al., 1970; Gilfrich et al., 1973; Camp et al., 1974; 1978; Ahlberg and Adams, 1978; Nottrodt et al., 1978; Witz et al., 1982; Lin et al., 1993; Walder and Furuta, 1993; Pyle et al., 1996; Bettinelli et al., 1997; Reynolds et al., 1997; Watson et al., 1997; 1999b; 2000; Lemieux et al., 1998; Ashley et al., 1999; Rich et al., 1999; VanCott et al., 1999; Gigante and Gonsior, 2000; Sterling et al., 2000; Farfel et al., 2001; Harper et al., 2002; 2004; 2005; 2006; 2007; Menzel et al., 2002; Sus-sell and Ashley, 2002; Bai et al., 2003; Drake et al., 2003; Moreira et al., 2005; Ariola et al., 2006; Harper and Pacolay, 2006; Harris et al., 2006; Herner et al., 2006; Kilbride et al., 2006; Kim et al., 2007).

Figure 1 shows an example comparing Pb concentrations measured by AAS on high-volume PM<sub>10</sub> quartz-fiber filter analyzed by the Illinois Department of Environmental Quality with Pb by XRF on the summed fine and coarse Teflon-membrane filters from a collocated dichotomous sampler analyzed by DRI. The results are comparable, with a few outliers. These monitors from South Chicago were in a highly industrialized area with relatively high levels of arsenic (As), selenium (Se) and other potentially toxic elements. Refined Pb is amenable to a common acid extraction method, such as nitric acid and aqua regia, which is not the case for most minerals (and possibly not for Pb in its native ore prior to refining). The comparisons for other toxic elements in Watson et al. (2000) are not as good as those for Pb.

Although a method may be shown to yield quantities comparable with reference materials and analyses by other methods, it may be inadequate if the equipment and procedures are not up to the task. Each SOP should state its assumptions and include tests to indicate when deviations from those assumptions are excessive. The procedure should attempt to minimize the effects of interferences or sample deviations from the ideal. The ability of an XRF procedure to attain a  $1 \text{ ng/m}^3$  Pb detection limit depends on the filter mass (which affects the background count), sample volume, sample duration, and deposit area. It also depends on the Pb excitation radiation energy, intensity, beam area, and analysis time. The sensitivity and resolution of the SiLi detector is an important consideration, as well as peak overlap that will raise the background (which decreases the analysis precision). There are different, but analogous, considerations for the other methods cited above.



**Figure 1.** Comparison of PM<sub>10</sub> lead concentrations from an Andersen high-volume PM<sub>10</sub> on QMA quartz-fiber filters analyzed by AAS and a Sierra 241 dichotomous PM<sub>10</sub>/PM<sub>2.5</sub> sampler with Teflon-membrane filters analyzed by XRF (Watson et al., 1999a) at the four sites during the third year of the Robbins Particulate Study in South Chicago between 10/01/97 and 09/26/98 (Watson et al., 2000).

As long as the minimum detectable limits (MDLs;  $1.5 \text{ ng/cm}^2$ ), precision ( $\pm 15\%$  at 90% confidence level), and accuracy ( $\pm 5\%$ ) are within the EPA's specified levels, any of the methods cited above should be adequate. That said, XRF and/or proton induced x-ray emission (PIXE) can simultaneously acquire 40-50 elements without much additional cost (except for the cost of acquiring additional standards, performing instrument calibration, and data processing). If only Pb is desired, most of the multi-element excitation conditions can be dropped, thereby increasing

throughput and further lowering costs. The issues of extraction efficiency, use of different acid mixtures for extraction, matrix interferences, potential contamination, and sample destruction inherent in AAS, ICP-AES, ICP-MS, and ASV result in these methods being more costly, but they may be of use in some instances. For example, ICP-MS can quantify Pb isotopic abundances that might be of use in quantifying source contributions (Munksgaard and Parry, 1998).

**Question 3. What are your comments on the specific analysis details of the XRF analysis method contained in the proposed Pb-PM<sub>10</sub> FRM analysis method description?**

While the method description in Appendix Q to Part 50, “Reference Method for the Determination of Lead in Particulate Matter as PM<sub>10</sub> Collected From Ambient Air” covers many details, there are several points that need clarification:

Section 1.1 (Line 2). PM<sub>10</sub> should be collected on an “acceptance tested” 46.2 mm diameter polytetrafluoroethylene (PTFE) filter. Acceptance testing is performed to verify blank levels for Teflon-membrane filters. In the early 1970s, one batch of Teflon-membrane filters was contaminated with Pb from the manufacturer, and this compromised the study results (Chow, 1995a).

Section 1.1 (Lines 7 and 8). The definition of PM<sub>10</sub> should include a specific inlet efficiency curve with a 50% cut-point and slope, similar to the PM<sub>10</sub> FRM specification (U.S.EPA, 1987).

Section 1.4 (Line 1). Is it necessary to specify “electrically powered”? I don’t see any problem with other vacuum assisted suction methods as long as the flow rate specifications are attained. Photovoltaic cells and batteries are also sources of electricity.

Section 1.4 (Line 8). Change “Line intensity” to “photon energy”.

Section 2.1 (Line 3). The deposit area on ringed Teflon-membrane filters varies slightly from different speciation samplers (e.g., 11.76 – 11.78 cm<sup>2</sup>), and it is smaller than the 11.86 cm<sup>2</sup> estimated for the Pb-PM<sub>10</sub> FRM sampler. It would be better if the deposit area is measured from several samplers and sample batches to assure that the correct value is being used.

Section 2.2 (Lines 4-5). “The one-sigma detection limit for Pb is calculated as the average over-all uncertainty or propagated error for Pb, determined from measurements on a series of blank filters.” This should be more explicit, i.e., translate the square root of the number of counts from a series of blank filters near the Pb analysis energies into µg/m<sup>3</sup> using the XRF calibration factor (µg/count), sample volume, and deposit area. The one-sigma detection limit is best based on each batch of unexposed blank filters to account for batch-to-batch variations. Even though these variations are expected to be small, it is a better practice to ensure consistency among different batches of filters. This might be incorporated into the acceptance testing criteria.

Section 3.1 (Lines 1 and 3). Define “too much deposit” (Line 1) and “heavy deposit” (Line 3). This shouldn’t be a problem with XRF, because Pb has a strong energy and is not much af-



fectured by particle size or sample deposit (Criss and Birks, 1968; Hunter and Rhodes, 1972; Rhodes and Hunter, 1972; Dzubay and Nelson, 1975; Adams and Billiet, 1976). One could require a calculation of self-adsorption and the loading at which it might exceed the measurement tolerances using one or more of the cited methods.

Section 3.1 (Line 5). While an optimum PM<sub>10</sub> filter loading of 150 µg/cm<sup>2</sup> or 1.6 mg/filter is reasonable for a 46.2 mm filter with a low-volume (16.7 L/min) sampler, this value needs to be justified with a citation. The same is true for the minimum deposit of 15 µg/cm<sup>2</sup> (Line 7). An optimal loading estimate might be required to be part of the procedures, again using published formulae.

Section 3.1 (Lines 8-10). Deposit non-uniformity may occur if an in-line filter holder is used, but in-line filter holders are not part of PM<sub>10</sub> low-volume samplers. The deposits are very uniform with these samplers, as evidenced by their appearance. Modern XRF equipment also rotates the sample, and the incident beam is at an off-center angle, thereby lessening the effects of a non-uniform deposit. Deposit uniformity might be defined by a performance specification of some kind and be addressed in the SOP.

Section 3.2 (Line 11). “Energy resolution” should be defined as < 155-160 eV full-width at half maximum..

Section 4.1 (Line 4). A CV of 15% is high. Typically, precision can be much better than ±10%.

Section 6.1.2. (Lines 4-5). Selecting 50 out of 500 filters, or 10% of blank filters, for acceptance testing is more than is needed. Two filters out of a hundred are more reasonable and cost-effective.

Section 6.1.2 (Line 8). Where did 4.8 ng Pb/cm<sup>2</sup> come from? Based on the past records, 1-3 ng Pb/cm<sup>2</sup> seems to be a more adequate acceptance level, but this needs to be validated with a citation.

Section 6.2.1 (Lines 2 and 3). The method should not imply that Thermo and PANalytical, are the only units. UC Davis designed and operates its own system for IMPROVE samples, and it seems to work fine. I believe EPA is still using the old LBL workhorse in its RTP labs. Xenometrix (new owners of Jordan Valley, [www.xenometrix.com/index.htm](http://www.xenometrix.com/index.htm)) and Spectro ([www.spectro.com/pages/e/index.htm](http://www.spectro.com/pages/e/index.htm)) also have XRF units adaptable to this purpose.

Section 6.2.2 (Lines 1-4). Both 15 and 50 µg/cm<sup>2</sup> Pb thin film standards can be obtained from Micromatter Inc. (Arlington, WA). NIST (2008) also has a Pb standard solution, standard reference material (SRM) 3128 with certified Pb value of 9.987 ± 0.018 mg/g, or other SRMs in different matrices that might be applicable to assessing accuracy and precision.

Section 6.2.4 (Line 17). “Calibration is performed only when significant repairs occur or when a change in fluorescers, X-ray tubes, or detector is made.” Most XRFs are robust and may not need repairs for years. QA standards with each run monitor intensities and peak separations.

Nevertheless, it's a good idea to perform base calibrations at least once per year, and to use the  $L_{\beta}$  line as a secondary peak to verify Pb by the  $L_{\alpha}$  line.

Section 6.2.4.2 (Lines 3-4). Rather than keeping 20-30 filters as clean blank filters, it is better to retain 2% of every new batch of filters (i.e., 100 per batch) for acceptance testing (see above comment on Section 6.1.2).

**Question 4. Do you think the precision, bias and MDL of the XRF method for the proposed Pb range will be adequate?**

Yes, with the appropriate samples and procedures. Arsenic (As) and other spectral interferences can be estimated and corrected, and this is commonly done using the Pb  $L_{\beta}$  as well as the Pb  $L_{\alpha}$  to quantify Pb levels. A quick calculation shows that if As levels were so high as to overwhelm the Pb lines, then Pb exposure would not be the biggest problem. The deposit inhomogeneity reported by Bandhu et al. (2000) was caused by their use of in-line filter holders. Chow (1995b) shows pictures of samples from in-line filter holders, demonstrating that you don't need a lot of analysis to know when the deposit is non-uniform. The aerosol sampler (Fitz et al., 1989) used in the Southern California Air Quality Study (SCAQS) used in-line filter holders and required some extra effort to adjust the elemental data (Cahill et al., 1989; Chow et al., 1994; Matsumura and Cahill, 1991) for subsequent interpretation. None of the samplers under consideration use in-line filter holders, and all of them have a long-enough transition zone to assure a uniform deposit. The good comparability reported in most of the studies cited above could not be achieved if this were not the case.

**Question 5. Are there any method interferences that we have not considered?**

XRF spectrum processing methods are well-established for thin samples, and most of the newer analyzers have software that can implement several of the most common approaches to background subtraction, peak overlap correction, self-absorption (not really needed for Pb), coincidence counting, and deadtime corrections. The software implements well-established and non-proprietary methods (Bonner et al., 1973; Dzuby et al., 1977; Giaque et al., 1977; Grennfelt et al., 1971; Lubecki, 1969; Parkes et al., 1974; Russ, 1977; Statham, 1976; Statham, 1977) that can be applied to any digitized spectrum.

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**Mr. Bart Croes**

Overall, the documents provided to the Subcommittee continue the impressive responsiveness by U.S. EPA staff to CASAC and our Subcommittee's comments. Staff should be commended for taking a systematic approach towards implementation of a likely revised lead (Pb) National Ambient Air Quality Standard (NAAQS). I appreciate the opportunity to comment during several stages of the process, and agree with the basic approach taken by U.S. EPA. My comments address the consultation questions posed by Lewis Weinstock in his June 15, 2008 memo to Fred Butterfield. These comments also reflect input from California Air Resources Board (ARB) staff responsible for implementing U.S. EPA monitoring requirements and using the data in source apportionment and health studies.

**Charge Questions:**

Attachment 1 – Draft Federal Reference Method (FRM) Lead in PM<sub>10</sub> (Pb-PM<sub>10</sub>)

1. *What are your comments on the use of the low-volume PM<sub>10c</sub> FRM sampler as the Pb-PM<sub>10</sub> FRM sampler?*

Replacing the current, high volume FRM with a low volume sampler based on PM<sub>10c</sub> and PM<sub>2.5</sub> FRMs is desirable for the following reasons:

- Low volume sampling offers advantages in pressure/temperature flow correction for sample collection in local (actual) conditions.
- Low volume samplers have solid state electronic controls and data logging while high volume samplers utilize mechanical timers and have no data logging capability,
- Low volume samplers offer the opportunity for remote operation and data access where high volume samplers do not.
- Quartz and glass fiber filters used in high volume sampling have far higher background levels of Pb than Teflon filters used in low volume sampling.

Leaving the door open to potential FEMs is desired. For example, the ARB Toxics network (Xontech 924, low volume TSP, Teflon filter, ICP-MS) may or may not be equivalent, but California should have the opportunity to find out.

2. *What are your comments on the use of XRF as the Pb-PM<sub>10</sub> FRM analysis method?*

While it has problems with non-uniform deposits, XRF provides an efficient method of analysis and requires less sample preparation than other analytical methods. The other species will also allow source apportionment.

3. *What are your comments on the specific analysis details of the XRF analysis method contained in the proposed Pb-PM<sub>10</sub> FRM analysis method description?*

The description as written was adequate.

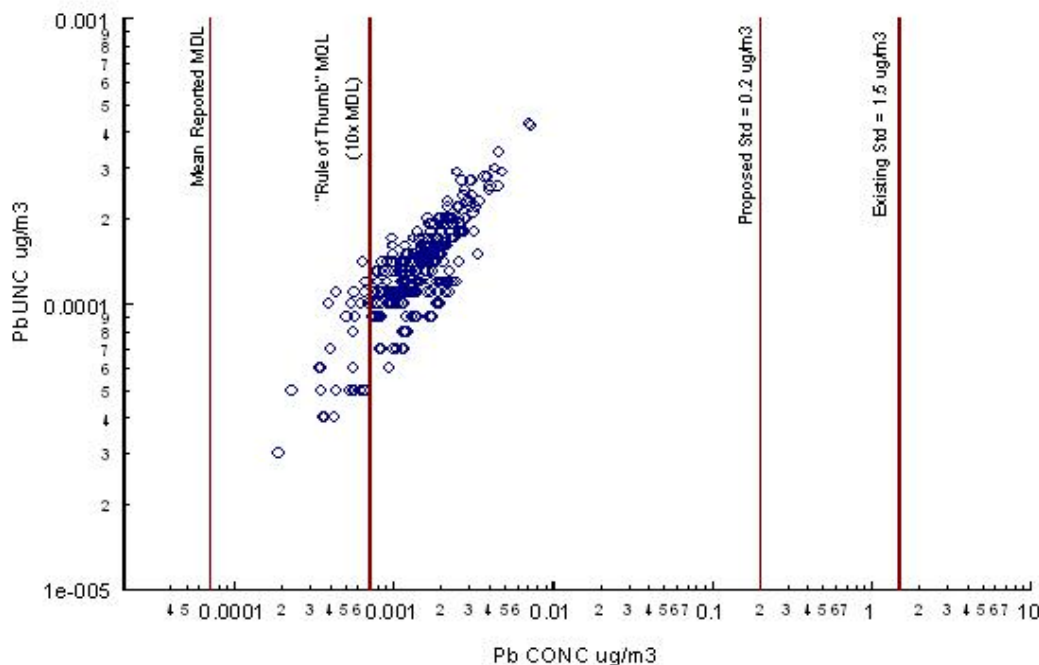
4. Do you think the precision, bias and MDL of the XRF method for the proposed Pb range will be adequate?

The MDL for Pb is well below  $0.001 \mu\text{g}/\text{m}^3$  (looking at California data) for a 24-hour sample, so there should be no problem with determining compliance for the new standard. Most of the lead samples at the (very clean) IMPROVE sites are valid.

Using IMPROVE XRF as an example, here are data from the Agua Tibia site, north of Escondido in northern San Diego County. The scatterplot of reported uncertainty vs. concentration shows good performance across the range of concentrations reported, with most concentrations in the well-quantified zone.

The vertical lines denote (left to right):

- The mean reported MDL.
- Warren White's "Rule of Thumb" MQL ( $10 \times \text{MDL}$ ).
- The proposed new standard ( $0.2 \mu\text{g}/\text{m}^3$ ).
- The old standard ( $1.5 \mu\text{g}/\text{m}^3$ ).



Based on this quick look, commercial XRF systems are capable of very good quantification near the proposed new standard.

5. Are there any method interferences that we have not considered?

Not to my knowledge.

**Dr. Kenneth Demerjian**

**Comments regarding monitoring methods for the measurement of PM lead in the atmospheric re: Draft Federal Reference Method (FRM) for Lead in Pb-PM<sub>10</sub>**

**1. What are your comments on the use of the low-volume PM<sub>10c</sub> FRM sampler as the Pb-PM<sub>10</sub> FRM sampler?**

The application of the PM<sub>10c</sub> FRM sampler is an acceptable approach for the monitoring of lead. It leaves open the possibility of missing Pb exposure from PM-Pb > 10 µm diameter particles. Measuring the concentration of PM-Pb as a function of particle size at a select number of representative monitoring sites would address this size cut issue and the data would likely be informative to the health community as well.

**2. What are your comments on the use of XRF as the Pb-PM<sub>10</sub> FRM analysis method?**

I do not agree with this choice. I recommend that ICP-MS be the FRM for the analysis of Pb and that XRF be considered as a FEM. The ICP-MS has better overall quality assurance and quality control (QA/QC) and traceable standards than the XRF method. In addition, the extraction and digestion of Pb compounds in ICP-MS analyses has proven to be quite effective and efficient (Qureshi, et al., 2006).

Among the issues raised regarding XRF, the uniformity of material on the filter collection surface and the potential role of large particle contributions to this non homogeneity remain of greatest concern. It would seem prudent to study these issues prior to formally committing to a decision on sampler type and the performance requirements of the analytical methods. The fact that the TSP Pb measurement has been of historical poor quality in terms of particle size sampling, should not be used as a rationalization that any incremental improvement in PM-Pb monitoring is better than the status quo.

**3. What are your comments on the specific analysis & details of the XRF analysis method contained in the proposed Pb-PM<sub>10</sub> FRM analysis method description?**

An effort should be made to archive and test filter blanks by batch number.

**4. Do you think the precision, bias and MDL of the XRF method for the proposed Pb range will be adequate?**

The approach described is adequate for characterizing the performance of the XRF analysis for Pb under ideal filter sample collection. It is clear from discussions among committee members that significant uncertainties remain with regard to XRF's quantification. These include potential effects of sampling inlets, Pb particle size and the uniformity of collected PM on the filter. D. Felton's comments, present data which indicate the extreme sensitivity in precision and accuracy with respect to ambient Pb concentration levels and certainly makes the case for the

need to reconsider the statistical measures for precision and accuracy for the low Pb concentrations typical observed in urban areas (e.g. figure 1 below)

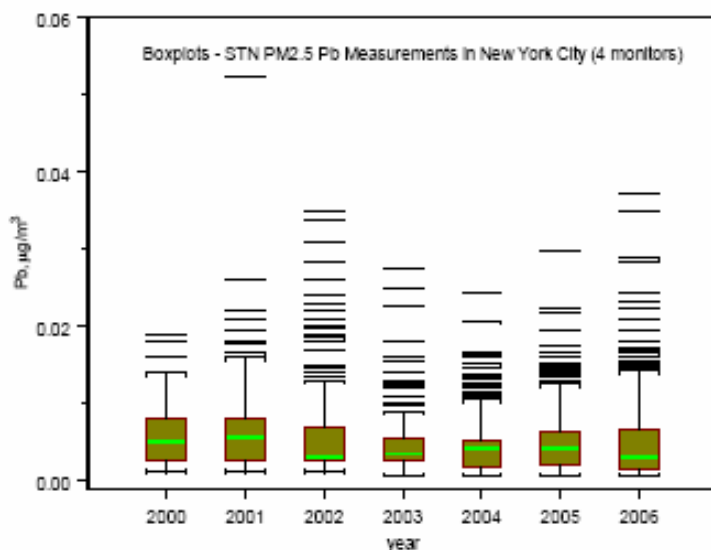


Figure 1. Boxplots STN PM2.5 Pb Concentrations in New York City

##### 5. Are there any method interferences that we have not considered?

All standard sources of interference have been identified. The low levels ambient PM Pb in the atmosphere will continue to be a challenge and require maintaining filter blank quality and monitoring the integrity of sample handling and potential contamination sources within the sample collection system.

Qureshi, S., V. A. Dutkiewicz, K. Swami, K. X. Yang, L. Husain, J. J. Schwab, and K. L. Demerjian, 2006. Elemental Composition of PM<sub>2.5</sub> Aerosols in Queens, New York: Solubility and Temporal trends, *Atmospheric Environment*, 40, S238-S251.



**Dr. Delbert Eatough**

Comments on Draft Federal Reference Method (FRM) for Lead in Pb-PM<sub>10</sub>

**What are your comments on the use of the low-volume PM<sub>10c</sub> FRM sampler as the Pb-PM<sub>10</sub> FRM sampler?**

I fully support the suggestion. The sampler is well characterized, available and compatible with other instruments in existing networks. For reasons stated in Section 2., I do not believe that basing the standard on a low volume TSP sampler is a good idea at this time.

**What are your comments on the use of XRF as the Pb-PM<sub>10</sub> FRM analysis method?**

I am not an expert on XRF but concur with the points made by others that the establishment of ICP-MS as the FRM with XRF as a FEM is a reasonable direction to go. The reasons given for going this direction as discussed in the call included: 1) Availability of the technique in many states; 2) Ease of extraction and sensitivity of analysis for the techniques; and 3) Avoidance of the issues inherent with XRF if the deposit on the filter is not uniform.

**What are your comments on the specific analysis & details of the XRF analysis method contained in the proposed Pb-PM<sub>10</sub> FRM analysis method description?**

**Do you think the precision, bias and MDL of the XRF method for the proposed Pb range will be adequate?**

**Are there any method interferences that we have not considered?**

As I am not an expert on XRF analysis, I defer to the comments made by members of the committee who are.

Mr. Dirk Felton

**Peer Review of the Draft Federal Reference Method (FRM) for Pb-PM<sub>10</sub>: Attachment 1 - Draft Federal Reference Method (FRM) Lead in PM-10 (Pb-PM<sub>10</sub>)**

Background and Summary: In order for monitoring data to be used in determination of attainment with the NAAQS, the data must be collected with a FRM or FEM. A number of options under consideration for the Pb NAAQS indicator would require the EPA to develop a FRM and FEM criteria for the measurement of Pb in PM<sub>10</sub>. The EPA has proposed language for a FRM for Pb- PM<sub>10</sub> based on the existing FRM sampler for low volume PM<sub>10c</sub> in Appendix O to Part 50 of the Code of Federal Regulations (CFR) coupled with analysis by x-ray fluorescence (XRF). The attached document includes the proposed regulatory text for the FRM for Pb in PM<sub>10</sub>.

Charge Questions:

*What are your comments on the use of the low-volume PM<sub>10c</sub> FRM sampler as the Pb-PM<sub>10</sub> FRM sampler?*

The PM<sub>10c</sub> sampler is adequate for use as the Pb-PM<sub>10</sub> FRM sampler. Many States already use this sampler for NATTS PM<sub>10</sub> metals sampling. The sequential versions of the samplers should also be designated as FRMs because future Pb PM<sub>10</sub> FEM evaluations should use the FRM samplers and protocols most predominantly utilized in the national network. Future FEM evaluations should be designed with the identical sample collection interval (midnight to midnight) and filter handling procedures as followed by the majority of the data providers for the national network.

*What are your comments on the use of XRF as the Pb-PM<sub>10</sub> FRM analysis method?*

Specifying XRF would make analytical problems stemming from non-uniform loading, spectral overlap and non-ideal filter loading densities an inherent part of the FRM. ICPMS should be the analysis method for the FRM and for the PEP audit samples. ICPMS is more accurate and it does not require the filter to be uniformly loaded. XRF should be designated as a cost effective FEM that is routinely compared to ICPMS through the periodic collocation of the PEP audit program.

It should also be noted that gravimetric mass determination of the sample filter is not required for Pb analysis.

*What are your comments on the specific analysis details of the XRF analysis method contained in the proposed Pb-PM<sub>10</sub> FRM analysis method description?*

The section on background measurement and correction states that 20–30 clean blank filters are kept in a sealed container and are used exclusively for background measurement and correction. These should be replaced with filters that are representative of the “batches” of filters that are used for the current measurements. It is likely that filter

qualities such as thickness, density and contaminant concentrations will change over time.

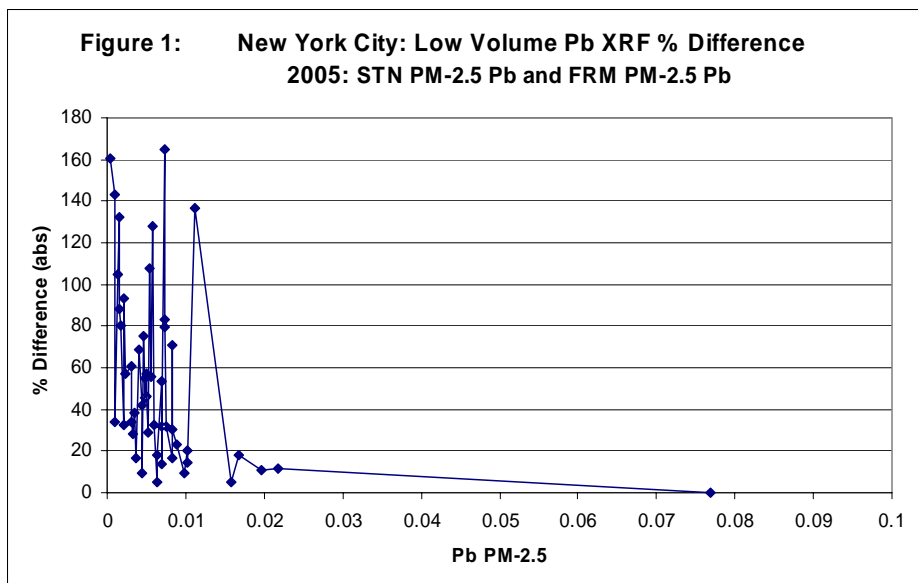
*Do you think the precision, bias and MDL of the XRF method for the proposed Pb range will be adequate?*

XRF is not the most accurate method for use in a Pb FRM and if selected it should be viewed as a compromise between cost effectiveness and accuracy at concentrations below about  $0.01 \mu\text{g Pb/m}^3$ . For low concentration measurements, it is preferable to use ICPMS which is more accurate and does not require the filter to be uniformly loaded for the FRM. XRF should be designated as an FEM and be permitted for use unless accuracy at very low concentrations is necessary for specific monitoring objectives.

The MDL for Pb XRF as stated in the draft Reference Method is  $0.001 \mu\text{g/m}^3$ . At this concentration the Pb data is not accurate enough to be used reliably for anything other than to demonstrate that the amount of Pb in the air is low. The EPA should consider establishing a minimum reporting level for XRF Pb no lower than  $0.005 \mu\text{g/m}^3$ . Levels below this can be reported but flagged as between detection limit and reporting limit or set to zero if they are below  $0.001 \mu\text{g/m}^3$ .

The draft  $\text{PM}_{10}$  method references the procedures in Appendix A, Part 58 for use in precision calculations. CFR Appendix A, Part 58 (1997 – section 5.3.1.1) states that the concentrations of both collocated pairs of Pb data must be above  $0.15 \mu\text{g/m}^3$  in order for the data to be used in precision calculations. This concentration will be too high for most of the sites in the new Pb monitoring network. A lower value can be selected but the precision of the measurement will decrease rapidly at lower concentrations. In Figure 1 below, STN  $\text{PM}_{2.5}$  Pb is compared to data from a collocated  $\text{PM}_{2.5}$  FRM in which the filters were analyzed for Pb by XRF. This data should emulate what we would expect to see for the precision calculations for a clean site in the proposed low volume  $\text{PM}_{10}$  Pb network. As we can see, the Percent Difference rapidly increases below about  $0.02 \mu\text{g Pb/m}^3$ . This is only one example but it serves to demonstrate that the proposed method's precision determination will have to account for XRF's increase in error at low concentrations.

The EPA may have to revise the way statistics are calculated for Pb or other NAAQS developed in the future for individual components of PM. The typical ambient concentrations of Pb are of course much lower than those for gravimetric mass and are closer to instrument and method detection limits. The statistics used to determine precision and accuracy may have to be specified as a range; looser at low concentrations where much of the ambient data will be and tighter at higher concentrations closer to the Pb NAAQS.

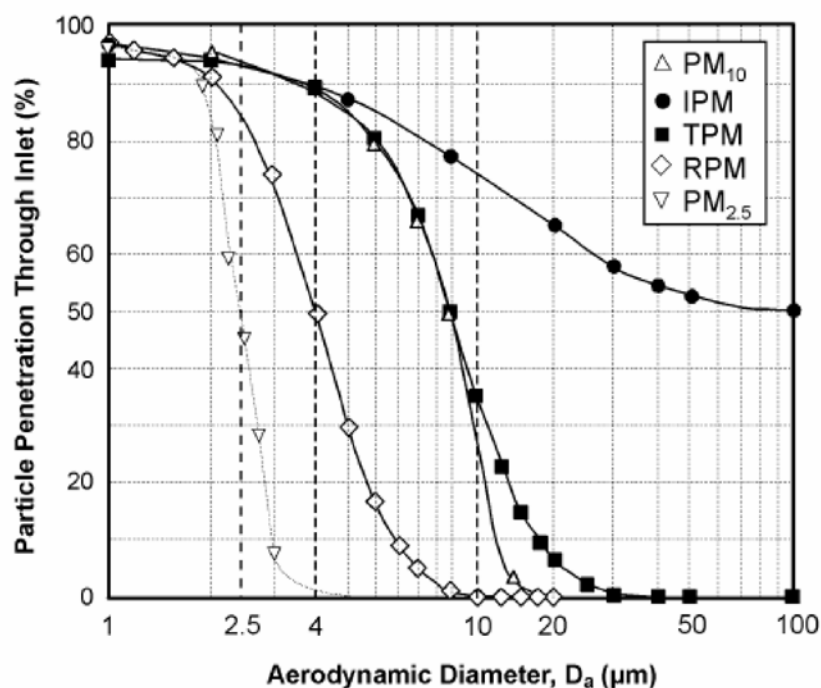


*Are there any method interferences that we have not considered?*

The sampler components and the shipping and handling materials for the filter samples must be free of Pb that can affect the integrity of the sample. The metal used to produce the sampler inlet is of particular concern and there should be a specified limit for the amount of trace Pb that is permissible for any component of the sampler including o-rings and greases. It would also be advisable to restrict the use of brass upstream of the sample filter or in any part that experiences wear and is exposed to the sampler exhaust such as in cooling fans and motor brushes.

## Dr. Philip Hopke

A stumbling block for the development of a new sampler from “scratch” is what are the criteria that would be desired in such a sampler. My suggestion is that if we are concerned about a combination of inhaled risk including deposition in the head airways that would result in transport to the GI tract as well as hand-to-mouth behavior, then we should look at developing a sampler that would meet the “inhalable” curve defined by industrial hygienists. Figure 1 presents the penetration curves for the typical PM size fractions.



Clearly such development would take some time so I would suggest a multi-pronged approach. There are at least three commercially available low-volume TSP heads currently on the market (Thermo, BGI, and URG). These could be tested by Dr. Kenny in the UK or there are wind tunnels at universities where sufficient testing is possible even if it does not fully meet 40 CFR 58 requirements. Depending on the outcome of these tests, it might be possible to denote one or more of these as sufficiently close to the IPM curve to move ahead with these. If none of the heads provide adequate response characteristics, then an effort can be initiated to design an inlet that meets the established criteria.

It should be noted that any TSP head is going to be sensitive to wind speed. They are cylindrically symmetric and thus, wind direction invariant.

**Dr. Kazuhiko Ito**

**General Comment:**

I understand that, because of the schedule for the proposed new FRM for Pb-PM<sub>10</sub>, we are asked specific charge questions at this point. However, based on the conversations that took place during the July 14<sup>th</sup> conference call, it seems to me that there are some important uncertainties that need to be investigated or characterized further even after the new method and alternative low-volume TSP samplers are considered. Specifically, as Dr. Hopke pointed out, it seems unclear if the Pb-PM<sub>10</sub> (or perhaps even Pb-TSP) is the most appropriate indicator of Pb exposure if the relevant route of exposure is ingestion of surface deposited Pb.

**Charge Questions and comments:**

**• Attachment 1 Draft Federal Reference Method (FRM) Lead in PM<sub>10</sub> (Pb-PM<sub>10</sub>)**

***What are your comments on the use of the low-volume PM<sub>10c</sub> FRM sampler as the Pb-PM<sub>10</sub> FRM sampler?***

To the extent that we are interested in Pb in PM<sub>10</sub> size fraction, the PM<sub>10c</sub> sampler is acceptable and appropriate for Pb-PM<sub>10</sub> FRM, given the performance shown in the past tests.

***What are your comments on the use of XRF as the Pb-PM<sub>10</sub> FRM analysis method?***

I imagine the information on the issues associated with Pb analysis by XRF is available from the nationwide PM<sub>2.5</sub> speciation data collected since 2000. Analysis of such data would be informative.

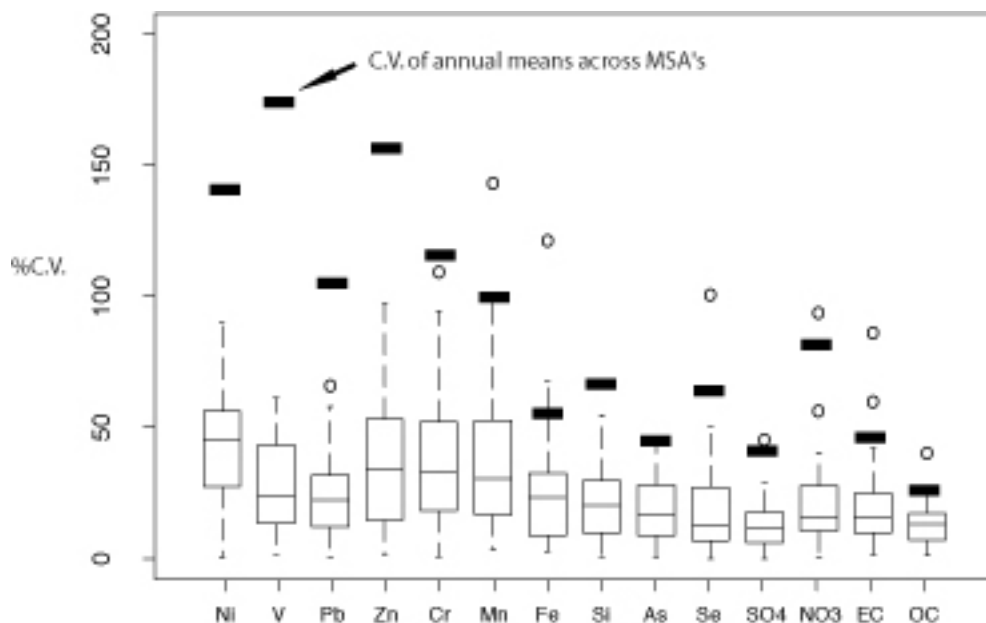
***What are your comments on the specific analysis details of the XRF analysis method contained in the proposed Pb-PM<sub>10</sub> FRM analysis method description?***

The document describes potential spectral interferences and spectral overlaps, but it does not give us a sense of the extent of this problem in the real data. It would be helpful if the document could also describe likely extent of this issue. Again, how serious a problem was this in the nationwide PM<sub>2.5</sub> chemical speciation data?

***Do you think the precision, bias and MDL of the XRF method for the proposed Pb range will be adequate?***

I think this answer depends on the extent of spatial variation of Pb-PM<sub>10</sub> in the locations of interest as well as the actual NAAQS level for Pb. The goal for a 15% precision for co-located monitors may be adequate if a coefficient of variation of annual means for multiple monitors within an area of interest is, say, 50%, but this would vary from city to city. I happened to look at within-city variation of several PM<sub>2.5</sub> chemical species including Pb in 28 MSAs several years ago for a different reason (I was comparing within-city vs. across-city variation of PM

components). Figure 1 shows the coefficient of variation (CV) for the across-MSA variation vs. distributions of CV's of within-MSA variation for the 28 MSAs where there were multiple monitors for years 2000–2003. For Pb, the CV ranges from nearly zero to 60% with the median of ~25%. Therefore, the adequacy of precision of 15% may be OK for the cities where high Pb levels occur (I imagine Pb-PM<sub>10</sub> variation would be larger than that for Pb-PM<sub>2.5</sub>).



**Figure 1.** Comparison of coefficient of variation (C.V.) of annual (multi-year, '00-'03) means across MSAs (denoted with bold "-") and distribution of within-MSA C.V. of annual means in the 28 MSAs where multiple monitors were available. "o" represents extreme value.

*Are there any method interferences that we have not considered?*

I don't know of any.

**Dr. Donna Kenski**

**Comments on the Peer Review for Pb NAAQS**

**1. What are your comments on the use of the low-volume PM<sub>10c</sub> FRM sampler as the Pb-PM<sub>10</sub> FRM sampler?**

The PM<sub>10c</sub> FRM sampler is the obvious and best choice for a Pb-PM<sub>10</sub> FRM sampler.

**2. What are your comments on the use of XRF as the Pb-PM<sub>10</sub> FRM analysis method?**

I don't see the logic in selecting XRF over ICP/MS as the analysis method. ICP/MS is more sensitive and not subject to the interferences that are documented in Joann Rice's memo. NIST-traceable standards can be used for calibration and many states have in-house labs that can perform the analysis. And, it does not require uniform filter loading. XRF is perfectly suitable for an FEM, but I recommend that ICP/MS be selected as the FRM analytical method.

**3. What are your comments on the specific analysis details of the XRF analysis method contained in the proposed Pb-PM<sub>10</sub> FRM analysis method description?**

The description as written was adequate.

**4. Do you think the precision, bias and MDL of the XRF method for the proposed Pb range will be adequate?**

The MDL as specified is fine if determination of compliance with the NAAQS is the only issue. But since health professionals, EPA, and others have a valid interest in determining concentrations at levels far below the NAAQS, it seems shortsighted not to measure Pb with higher accuracy at the (more common) low concentrations as well. With the (presumed) lowering of the Pb NAAQS, and with generally lower ambient concentrations across the country, the MDL should be lower than the 0.001 µg Pb/m<sup>3</sup> that is proposed. As this is easily achievable and already being accomplished by other national networks, it ought to be part of the FRM method.

**5. Are there any method interferences that we have not considered?**

Not that I know.



**Dr. Peter McMurry**

Comments regarding measurement methods for particulate lead in atmospheric aerosols —  
Comments on Draft Federal Reference Method (FRM) for Lead in Pb-PM<sub>10</sub>

**What are your comments on the use of the low-volume PM<sub>10c</sub> FRM sampler as the Pb-PM<sub>10</sub> FRM sampler ?**

I think it is a good idea. This sampler is readily available, is familiar to monitoring agencies, and has been well-tested. Furthermore, the Pb samples would be sampled in the same way as PM<sub>10</sub> mass, so the fraction of mass that is Pb would be well defined.

**What are your comments on the use of XRF as the Pb-PM<sub>10</sub> FRM analysis method?**

Chemical analysis is not my primary area of expertise. Therefore, the views expressed here represent my synthesis of comments from today's telephone conversation.

I think very compelling arguments were made to use an extraction method such as ICP-MS rather than XRF as the FRM analysis method. These include the (1) the confidence that Pb can be effectively extracted with efficiencies that approach 100%, (2) the availability of NIST traceable standards for liquid solutions of Pb that can be used to calibrate analytical instruments used to analyze dissolved extracts and the corresponding lack of such standards for deposited Pb, (3) the availability of instruments, such as ICP-MS in states and the corresponding unavailability of XRF instruments, (4) the sensitivity of XRF to spatial distributions of deposits on filters, which are unlikely to be uniform (especially for coarse particles) and the corresponding insensitivity of extraction methods to such non-uniformities, (5) the use of proprietary software for analyzing XRF data, which shields the public from a clear understanding of how concentrations of lead are determined, and (6) the superior sensitivity of methods such as ICP-MS. I question whether XRF would meet the accuracy and precision goals required for a standard.

Because XRF is inexpensive and nondestructive, I think it makes sense to use it as a FEM.

**What are your comments on the specific analysis & details of the XRF analysis method contained in the proposed Pb-PM<sub>10</sub> FRM analysis method description?**

I will defer to other members on the committee on this.

**Do you think the precision, bias and MDL of the XRF method for the proposed Pb range will be adequate?**

Again, I will defer to those members of the committee who are more knowledgeable than I on this topic. I was left with the sense there are compelling arguments for using another analytical method as the FRM.

**Are there any method interferences that we have not considered?**

Not to my knowledge.

**Mr. Richard Poirot**

**Comments on Proposed Pb PM<sub>10</sub> FRM - Appendix Q Part 50**

An important prefacing comment is that the CASAC Lead Panel has advocated a transition of the Pb indicator from TSP to PM<sub>10</sub> Pb if, and only if, the level of the standard is set lower than 0.2 µg/m<sup>3</sup>. If a level equal to or higher than 0.2 µg/m<sup>3</sup> is selected, the CASAC Pb panel is unanimously opposed to a reduction in the indicator particle size range from TSP to PM<sub>10</sub>.

***What are your comments on the use of the low-volume PM<sub>10c</sub> FRM sampler as the Pb-PM<sub>10</sub> FRM sampler ?***

Assuming the level of the Pb standard is set below 0.2 µg/m<sup>3</sup>, the PM<sub>10c</sub> sampler would be an appropriate choice for a Pb-PM<sub>10</sub> FRM sampler.

***What are your comments on the use of XRF as the Pb-PM<sub>10</sub> FRM analysis method?***

XRF should be an adequate analytical method for a Pb NAAQS set toward the middle to upper end of the range of levels recommended by EPA staff and the CASAC Pb Panel. If the level is set toward the low end of that recommended range (0.02 µg/m<sup>3</sup>), a more accurate analytical method like ICP-MS, with lower detection limits and smaller analytical errors, would be preferable. Consideration should also be given to specifying ICP-MS as the FRM and establishing XRF as a FEM.

***What are your comments on the specific analysis & details of the XRF analysis method contained in the proposed Pb-PM<sub>10</sub> FRM analysis method description?***

I think it should be useful and possible to tighten up some of the specific details relating specifically to the determination of Pb by EDXRF. Much of the description sounds more like cautionary guidance rather than prescribed details of specific procedures, and also seems to pertain to XRF analysis of elemental species other than Pb. This raises a related point that it would be best to be very clear up-front about analytical and data reporting procedures for (readily detectable) XRF elements other than Pb that may result at little or no extra cost from the Pb XRF analysis (and would also represent an important reason in favor of the choice of XRF as part of the Pb FRM). Arguably this “supplemental data” would have value for quality assurance and source attribution of the Pb measurements, and if significant additional costs are not incurred, analytical and data reporting procedures could be specified. Similar considerations would also apply if (multi-elemental) ICP-MS were selected as the Pb FRM. Along similar lines, clear guidance should also be provided on whether (or not) there should be PM<sub>10</sub> mass measurements conducted on the Pb FRM filters. Possibly the Agency would want to provide for an optional national analytical contractor, as has proved effective for IMPROVE and STN networks. Alternatively, some consideration should be also given to coordination with the evolving NAATS metals sampling program which generally (but not always) utilizes PM<sub>10c</sub> samplers combined with ICP-MS analyses (at most but not all sites), and which would benefit from greater internal consistency.

***Do you think the precision, bias and MDL of the XRF method for the proposed Pb range will be adequate?***

The precision, bias and MDL of the XRF method should be adequate for a Pb NAAQS in the currently proposed range of 0.1 to 0.3  $\mu\text{g}/\text{m}^3$ , although a  $\text{PM}_{10}$  sampling method is not recommended if the level is greater than or equal to 0.2  $\mu\text{g}/\text{m}^3$ . The XRF precision, bias and MDL could pose problems for a NAAQS set at the lower end of the EPA staff-recommended range of 0.02, and may result in uncertainties in spatial patterns and temporal trends at population-oriented monitoring sites where levels are likely to fall well below the proposed NAAQS range. The indicated XRF  $\text{PM}_{10}$  Pb MDL of 0.001  $\mu\text{g}/\text{m}^3$  would be only 1% of the lower bound level of the proposed NAAQS and unlikely to have a significant influence on compliance determinations. I also think it's likely that this MDL could be further reduced. For example the current MDL for  $\text{PM}_{2.5}$  Pb in the IMPROVE network is closer to 0.0001  $\mu\text{g}/\text{m}^3$ .

Current Pb precision comparisons are limited to concentrations above 10% of the current NAAQS (i.e., 0.15  $\mu\text{g}/\text{m}^3$ ). This limit will need to be lowered to reflect the hopefully much lower level of the currently revised NAAQS. Also, since it generally appears likely that the Administrator may select a level (and form) of the standard which are less stringent than are warranted by the Agency's Risk/Exposure Assessment and Staff Paper, some consideration should be given to collection of accurate and precise data at levels below and possibly well below the level of the NAAQS selected in this review cycle.

**Are there any method interferences that we have not considered?**

None that I'm aware of – related to XRF analysis of Pb on  $\text{PM}_{10\text{C}}$  filters. However, it should be recognized that XRF is not very well suited for analysis of fiberglass TSP or hi-volume Quartz  $\text{PM}_{10}$  filters. ICP-MS would be a better choice for an FRM analytical method that could be used across all potential filter types, and would provide a better basis for comparative sampling to develop better information on Pb particle size distributions, sources etc. — especially in the event that TSP (and/or hi-vol  $\text{PM}_{10}$ ) are retained (or specified as FEM).

**Other minor comments on Pb  $\text{PM}_{10}$  FRM:**

p. 3, para 1, line 6: The hyphenated “24-hour sample” is correct here, but all other instances of the number “24” in this document are also (incorrectly) attached by hyphen to the words that follow. These include “24-hours” in line 3 and “24-cubic meters” in line 5 of this paragraph and 2 instances of “24- $\text{m}^3$ ” in 2<sup>nd</sup> and 3<sup>rd</sup> paragraphs on page 5.

p. 6, para 1: You present optimal (150  $\mu\text{g}/\text{cm}^2$ ) and minimal (15  $\mu\text{g}/\text{cm}^2$ )  $\text{PM}_{10}$  mass loading levels (roughly 75 and 7.5  $\mu\text{g}/\text{m}^3$  respectively) for XRF Pb quantification, but also indicate potential distortion with “unusually heavy deposits”. Why not also provide the  $\text{PM}_{10}$  mass level that would be considered unusually heavy (i.e. an upper bound to go along with the ideal and minimal loading levels). Also, unless mass measurements are required, how will it be known whether the filter loading is above, below or within the range where distortion-free measurements are expected?

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p. 6, para 2, line 3: You could add “S/P” to this list of XRF interferences.

p. 7, para 2, line 6: This effect is “especially significant and more complex for PM<sub>10</sub> measurements...” than for what?

p. 8, section 6.1.2, last line: Just for curiosity, what is the basis for your selection of this blank Pb limit of 4.8 ng/cm<sup>2</sup>? This (x 11.86 cm<sup>2</sup> of exposed filter / 24 m<sup>3</sup> of air sampled) would yield an implied ambient Pb concentration of 0.002 µg/m<sup>3</sup> — or about twice the indicated Pb XRF MDL - or about 1% of a standard of 0.2 µg/m<sup>3</sup> (are you giving us a hint about the intended level of the NAAQS?).

p. 9, section 6.2.3, line 2: What do you mean “Filters are typically archived in cold storage”? For what current analyses is this cold storage procedure “typical”? Will it be required for Pb sampling? What elements, if any, which are quantifiable by XRF do you expect to see volatilized from filters if they are not kept in cold storage prior to analysis? Certainly you don’t expect any loss of Pb, do you?

Dr. Jay Turner

Peer Review: Draft Federal Reference Method (FRM) Lead in PM<sub>10</sub> (Pb-PM<sub>10</sub>)

Charge Questions

1. *What are your comments on the use of the low-volume PM<sub>10c</sub> FRM sampler as the Pb-PM<sub>10</sub> FRM sampler?* The low-volume PM<sub>10c</sub> FRM sampler is an appropriate choice as the Pb-PM<sub>10</sub> FRM sampler. It is an adaptation of the PM<sub>2.5</sub> FRM sampler which now has nearly ten years of use and refinement, including both single-event and sequential configurations. There are also operational and cost advantages to placing measurements for multiple NAAQS on the same sampler platform. For sites specified for both PM<sub>10</sub> and Pb-PM<sub>10</sub> compliance monitoring, filter samples collected using the low-volume PM<sub>10c</sub> FRM sampler could be subjected to both gravimetric analysis and Pb elemental analysis, providing compliance data for both standards from a single sample.
2. *What are your comments on the use of XRF as the Pb-PM<sub>10</sub> FRM analysis method?* I prefer the use of ICPMS (or GFAAS) as the FRM with an expectation that XRF would be given FEM status. While ICPMS does have the added complexity of a sample digestion step, it can be more easily calibrated than XRF. Our recent experience with ICPMS has demonstrated high recovery for both coal fly ash and urban particulate matter NIST Standard Reference Materials (SRM) from quartz filters using a nitric acid and hydrochloric acid extraction solution (following the NATTS PM<sub>10</sub> metals sampling and analysis protocol developed by ERG). The Pb-PM<sub>10</sub> method would use Teflon filters and ERG has also developed a protocol for this case which could be used as a starting point for the analysis method specifications.<sup>1</sup>
3. *What are your comments on the specific analysis details of the XRF analysis method contained in the proposed Pb-PM<sub>10</sub> FRM analysis method description?* I defer to the XRF experts for a critique of the analysis method details. Given the variations in instrument hardware and software, all labs reporting compliance data based on XRF should participate in an audit program which includes analyses of samples with traceability to ICPMS.
4. *Do you think the precision, bias and MDL of the XRF method for the proposed Pb range will be adequate?* These questions are best addressed after completion of the DQO process. Perhaps the required MDL could be relaxed depending on the NAAQS concentration value, although a detection limit that is much lower than the standard is desirable to simplify the data handling for concentrations below the MDL. Precision should be determined using data with Pb concentrations above a defined threshold value since the precision reported as a percentage CV will degrade as the MDL is approached. In general, we should be prepared for both ICPMS and XRF data being reported to AQS, and these methods will have very different detection limits. This will add complexity to certain non-compliance data analyses; including trends analyses studies on Pb health effects.

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<sup>1</sup> “Standard Operating Procedure for the Determination of Metals in Ambient Particulate Matter Analyzed by Inductively Coupled Plasma/Mass Spectrometry (ICP/MS)”, prepared by ERG for EPA under Work Assignment 5-03, ERG No.: 0143.04.005, EPA Contract No.: 68-D-00-264, September 2005.

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5. *Are there any method interferences that we have not considered?* I defer to the XRF experts on the issue of method interferences.

**Dr. Warren H. White**

COMMENTS ON PROPOSED FRM FOR PM<sub>10</sub> LEAD —  
Use of low-volume PM<sub>10c</sub> FRM sampler

As noted in our previous consultation, the uniformity of this sampler's collected deposit needs to be established if XRF is used as the analytical method. Attachment 1 illustrates the need for such a determination with an example of a non-uniform sample collected with a different (non FRM) sampler. The elements Pb and Fe, presumed associated with different particle size classes, show quite different deposition patterns in this example. As the x-ray beam fluoresces only the central portion of the filter, the ratio of reported loading to ambient concentration varies accordingly.

XRF analysis of filters from this sampler would thus respond differently to fine Pb particles from fume sources and coarse Pb particles from dust sources.

XRF as method of analysis

XRF is cost-effective, is sensitive enough for the levels under NAAQS consideration (see below), and fits well with other aspects the Agency's monitoring strategy and infrastructure. It has not previously been used for a NAAQS, however, and this first application raises issues of calibration (see below), standardization (see below), and sample uniformity (noted above) that wet-chemical methods do not present. I think Dirk Felton's suggestion to establish XRF as an FEM with ICP-MS as the FRM is worth considering, with the caveat that methods requiring extraction and digestion raise their own accuracy issues.

Adequacy of XRF bias, precision, and detection limit

The adequacy of XRF measurement capabilities depends on the MQOs (measurement quality objectives) established for the analytical method, which in turn depend on the DQOs (data quality objectives) established for compliance monitoring. In today's discussion it was noted that DQOs required to protect public health will themselves depend on the level and form eventually chosen for the NAAQS. With all these considerations yet to be finalized, there are nevertheless certain points that are already clear.

**Detection:** The NAAQS level proposed in the Federal Register is in the range 0.1-0.3 ug/m<sup>3</sup>. The existing CSN and IMPROVE networks demonstrate reliable (95% probability) XRF detection of non-spurious Pb at filter loadings of 5-7 ng/cm<sup>2</sup> (Attachment 2). For the low-volume PM<sub>10c</sub> FRM sampler, this corresponds to a real detection limit of about 0.003 ug/m<sup>3</sup>, more than an order of magnitude below the lowest contemplated NAAQS level.

**Precision:** The declared goal for collocated precision is a 15% CV at 90% confidence. Quality assurance for IMPROVE includes regular XRF reanalyses of a fixed collection of about 70 representative ambient samples. Over 20 reanalyses have been performed of each sample at approximately monthly intervals, yielding some 70 well-determined analytical CVs. The typical



(median) CV obtained for Pb has been 13% ([Trzepla-Nabaglo and White, 2008](#)). These results do not reflect flow and other sampling uncertainties but do include observations at all concentrations, with a (relatively low) mean loading of about 12 ng/cm<sup>2</sup>. As Dirk Felton observed, precision for collocated samples will be sensitive to the minimum concentration included in the calculations.

**Bias:** The declared goal is a system bias within 10% at 95% confidence. Demonstrating attainment of these tolerances with XRF is likely to be a challenge. The need to verify that the sample deposit is uniform has already been noted. The other main difficulty will be the absence of a suitable NIST-traceable standard for calibration. NIST (2002) offers “air particulate on filter media” as SRM 2783, with a certified Pb loading of about 32 ng/cm<sup>2</sup>, but gives a 95%-confidence uncertainty of about 17% for this value. I am not aware of any peer-reviewed examination of the claimed accuracies of commercially available calibration foils, or even consistency among different foils.

#### Specific analysis details in the FRM

Some aspects of XRF analysis require more prescriptive detail than the draft FRM gives them. The most important are two that relate to method accuracy.

**Audit filters:** Bias is to be assessed “through an audit using spiked filters.” The preparation of spiked standards for XRF analysis is significantly more complicated than simply depositing a known quantity of standard solution on a glass-fiber hi-vol filter and letting it dry, as is now done. Deposit uniformity is needed for quantitative XRF, as noted above. Achieving this uniformity in a liquid deposit on a Teflon membrane is likely to require attention to surface phenomena. The most relevant spiked filter would be created by actually sampling a pure Pb-containing aerosol and determining the Pb loading from the weight gain. XRF results for such a filter could be compared directly with those for ambient samples, but the production of such filters would require development and validation.

**Protocols:** The principals of EDXRF are universal but there is no standard protocol for implementing them, as the Agency discovered two years ago in its effort to “harmonize” XRF reporting from different labs used by their PM<sub>2.5</sub> speciation networks ([Gutknecht et al., 2006](#)). Different instrument systems use different x-ray spectra generated by different configurations of source anode, secondary target, and spectral filter, different geometries of irradiation and detection, and different spectral decomposition software based on different interpretive strategies. Much of the spectral processing in commercial instrument systems is proprietary and invisible to the user, making it difficult to confirm which lines are used and how they are de-convoluted. Will the Agency undertake to certify certain commercial systems for use?

For whatever analytical method is used, field blanks should be routinely exposed and analyzed to detect possible contamination in the field and laboratory. CSN and IMPROVE both report loadings below 3.5 ng/cm<sup>2</sup> in 95% of their routine field blanks (Attachment 2), significantly exceeding the FRM’s proposed filter acceptance criteria (requiring 90% to be less than 4.8 ng/cm<sup>2</sup>).

### Method interferences

I know of no additional method interferences.

**Attachment 1:** material excerpted and annotated from Nuclear Instruments and Methods in Physics Research B 160 (2000) 126-138

Elemental composition and sources of air pollution in the city of Chandigarh, India, using EDXRF and PIXE techniques

H.K. Bandhu, Sanjiv Puri, M.L. Garg, B. Singh, J.S. Shahi, D. Mehta, E. Swietlicki, D.K. Dhanwan, P.C. Mangal, Nirmal Singh

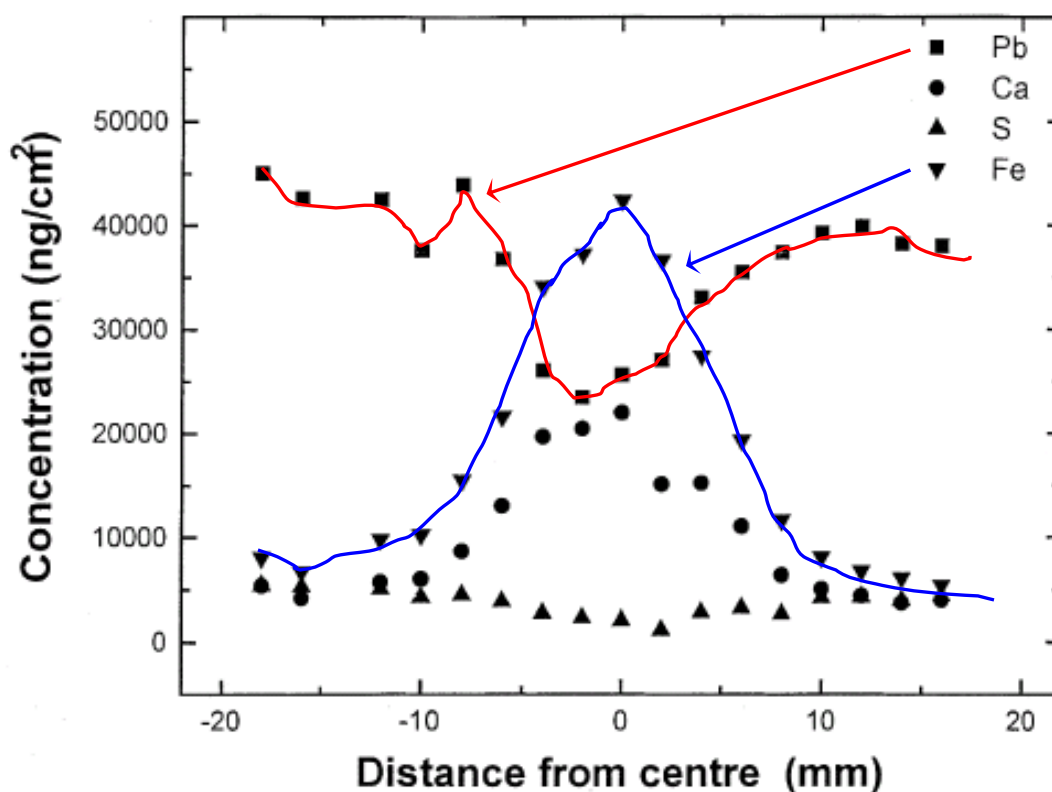


Fig. 5. Aerosol loading distribution for different elements as a function of distance from the center measured using 2 mm proton beam.

Samples were collected on 47 mm diameter, 0.8  $\mu$ m pore size, cellulose nitrate filter papers (Microdevices, Ambala, India). Filter paper was mounted in an aerosol filter holder (Millipore, Cat No. xx50 04700) having an inlet dispersion chamber to produce optimum particle distribution on the surface of the filter. The air through the filter paper was sucked at a flow rate of 12 l min<sup>-1</sup> with the help of diaphragmatic vacuum pump (Millipore, Cat. No. xx55 22050) and critical orifice (Millipore, Cat. No. xx50 000 00). The flow rate was monitored periodically for each sam-

ple with a rotameter and no cases of reduction of flow rate due to filter clogging were experienced during the sampling. The collection surface was directed downward to prevent particle collection by sedimentation and the filter holder was protected with a rain cover. All the sampling sites chosen for sampling were located on the flat roof of building tops 40-60 feet high.

**Attachment 2:** material excerpted and annotated from Environ. Sci. Technol. 2008, 42, 5235–5240

An empirical approach to estimating detection limits using collocated data  
Nicole P. Hyslop and Warren H. White

**TABLE 1. Summary of STN and IMPROVE  $L_c$  estimates,  $L_D$  estimates**

element	network	$L_c$ 95th percentile (90–99th percentiles) (ng cm <sup>-2</sup> )	$L_D$ 95% detection probability (92–97% probability) (ng cm <sup>-2</sup> )
Pb	STN	3.5 (1.8–8.1)	6.5 (6.3–7.0)
	IMPROVE	3.1 (2.6–4.2)	5.1 (4.8–6.0)
		↑ From field blanks	↑ From collocated sampling

To avoid type I errors a *critical limit*  $L_c$  is set such that measurements above that limit indicate the analyte is present with a high level of confidence. For a given probability  $\alpha$  of type I error,  $L_c$  is the minimum value satisfying the inequality

$$\Pr(\hat{L} > L_c | L = 0) \leq \alpha \quad (1)$$

To avoid type II errors, a *limit of detection*  $L_D$  is set such that atmospheric concentrations of the analyte at or above that threshold will be detected with a high level of confidence.  $L_D$  is dependent on  $L_c$  because the analyte must be measured above  $L_c$  to be considered present. For a given probability  $\beta$  of type II error,  $L_D$  is the minimum value satisfying the inequality

$$\Pr(\hat{L} < L_c | L = L_D) \leq \beta \quad (2)$$

**Dr. Yousheng Zeng**

***Charge Question 1: What are your comments on the use of the low-volume PM<sub>10c</sub> FRM sampler as the Pb-PM<sub>10</sub> FRM sampler?***

I support the EPA proposal to use the low-volume PM<sub>10c</sub> FRM sampler as the Pb-PM<sub>10</sub> FRM sampler. The PM<sub>10c</sub> FRM sampler is better defined and better understood than the earlier PM<sub>10</sub> sampler. This method will also provide consistency with PM<sub>10</sub> and PM<sub>2.5</sub> monitoring network; data comparability for evaluation of Pb-PM<sub>10</sub> and PM<sub>10</sub> inhalation pathway; and monitoring operation efficiency (same samplers for both PM<sub>10</sub> and Pb-PM<sub>10</sub>).

However, I share the same concern with some committee members. With this method, the monitoring results will be naturally lower because PM<sub>10</sub> samples, not TSP samples, will be collected for Pb analysis. If the revised Pb NAAQS is not set low enough to account for the absence of Pb associated with particles larger than 10  $\mu$ , the new Pb NAAQS may not provide additional protection to human health.

***Charge Question 2: What are your comments on the use of XRF as the Pb-PM<sub>10</sub> FRM analysis method?***

I support the approach proposed by Mr. Dirk Felton to use ICPMS (or AA as he mentioned during previous consultation meeting) as FRM for sample analysis and use XRF as FEM. A similar approach has worked well for SO<sub>2</sub> where a manual method is the reference method and instrumental methods are FEM and widely used in day-to-day monitoring operations.

***Charge Question 3: What are your comments on the specific analysis details of the XRF analysis method contained in the proposed Pb-PM<sub>10</sub> FRM analysis method description?***

I don't have comments on this issue.

***Charge Question 4: Do you think the precision, bias, and MDL of the XRF method for the proposed Pb range will be adequate?***

At this point, we really don't know what will be the final Pb NAAQS. It appears that the proposed analysis method (either XRF or ICPMS) should be adequate to produce needed monitoring data. However, it is highly recommended to use the Data Quality Objective (DQO) model that EPA used for evaluation of PMc in 2004. During the public conference call on July 14<sup>th</sup>, 2008, EPA indicated that EPA was working on a DQO model for Pb. It would be most desirable to use the DQO model to help finalize these parameters (precision, bias, and MDL).

***Charge Question 5: Are there any method interferences that we have not considered?***

I don't have comments on this issue.

**Dr. Barbara Zielinska**

**Charge questions regarding FRM for Lead in Pb-PM10:**

1. What are your comments on the use of the low-volume PM10c FRM sampler as the Pb-PM10 FRM sampler?

As stated in my comments from March 23, 2008, regarding previous consultation on this subject, I support the use of the low-volume PM10c FRM sampler as the Pb-PM10 FRM sampler. This sampler has been well-tested, has well-defined cut-points and slopes and is readily available.

2. What are your comments on the use of XRF as the Pb-PM10 FRM analysis method?

Although XRF method has many advantages (is nondestructive, sensitive, relatively simple and inexpensive), it presents some problems related to the uniformity of material on the filter collection surface. ICP-MS method is extremely sensitive for lead, has traceable standards and the uniformity of material is not an issue. I would recommend ICP-MS as an FRM for the analysis of lead and XRF as an FEM (or one of the FEMs).

3. What are your comments on the specific analysis details of the XRF method contained in the proposed Pb-PM10 FRM analysis method description?

The XRF analysis method is well described in this document. Specific analysis details were addressed during the advisory teleconference meeting and are reflected in the lead discussants memos.

4. Do you think the XRF method precision, bias and MDL for the proposed Pb range will be adequate?

The method MDL, precision and bias seem to be adequate. However, for very low ambient concentrations of Pb, it may be challenging to achieve the required precision.

5. Are there any method interferences that we have not considered?

I am not aware of any additional interference.

**Enclosure C – Agency’s Background and Charge Memorandum to the  
CASAC AAMM Subcommittee**

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**UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
RESEARCH TRIANGLE PARK, NC 27711**

June 15, 2008

**MEMORANDUM**

**SUBJECT:** CASAC Peer Review and Consultation on Monitoring Issues for Lead National Ambient Air Quality Standard (NAAQS)

**FROM:** Lewis Weinstock  
Acting Group Leader  
Ambient Air Monitoring Group  
Office of Air Quality Planning and Standards (C304-06)

**TO:** Fred Butterfield  
Designated Federal Officer  
Clean Air Scientific Advisory Committee  
EPA Science Advisory Board Staff Office (1400F)

Attached are materials for review by the Clean Air Scientific Advisory Committee’s (CASAC) Ambient Air Monitoring and Methods (AAMM) Subcommittee. These materials will be the subjects of a peer review and consultation by the AAMM Subcommittee, scheduled for a teleconference to be held on July 14, 2008. I am requesting that you forward these materials to the AAMM Subcommittee to prepare for the peer review and consultation.

This project, entitled *Lead (Pb) National Ambient Air Quality Standards (NAAQS) Review: Monitoring Issues*, has been requested by EPA’s Office of Air Quality Planning and Standards (OAQPS), within EPA’s Office of Air and Radiation, in anticipation of potential revisions to the Pb NAAQS. The peer review will cover the proposed Federal Reference Method (FRM) for the measurement of Pb in particulate matter less than 10 micrometers in diameter (Pb-PM<sub>10</sub>). The consultation will cover the need and approach for development of a low-volume Pb in total suspended particulate (Pb-TSP) method as an FRM or Federal Equivalent Method (FEM). Charge questions associated with both the peer review and the consultation are provided below.

The upcoming consultation will support the EPA by providing scientific advice as the EPA Administrator considers potential revisions to the Pb NAAQS; a notice of final rulemaking is to be signed by September 15, 2008. We are requesting an expedited schedule to assist EPA in

meeting the September 15, 2008 deadline for finalizing the Pb NAAQS review.

We appreciate the efforts of you and the Subcommittee to prepare for the upcoming meeting and look forward to discussing this project in detail on July 14, 2008. Questions regarding the enclosed materials should be directed to Mr. Kevin Cavender, EPA-OAQPS (phone: 919-541-2364; e-mail: [cavender.kevin@epa.gov](mailto:cavender.kevin@epa.gov)).

**Document Associated with Subcommittee's Peer Review:**

- **Attachment 1 – Draft Federal Reference Method (FRM) Lead in PM<sub>10</sub> (Pb-PM<sub>10</sub>)**

**Background and Summary:** In order for monitoring data to be used in determination of attainment with the NAAQS, the data must be collected with a FRM or FEM. A number of options under consideration for the Pb NAAQS indicator would require the EPA to develop a FRM and FEM criteria for the measurement of Pb in PM<sub>10</sub>. The EPA has proposed language for a FRM for Pb-PM<sub>10</sub> based on the existing FRM sampler for low volume PM<sub>10c</sub> in Appendix O to Part 50 of the Code of Federal Regulations (CFR) coupled with analysis by x-ray fluorescence (XRF). The attached document includes the proposed regulatory text for the FRM for Pb in PM<sub>10</sub>.

**Charge Questions:**

*What are your comments on the use of the low-volume PM<sub>10c</sub> FRM sampler as the Pb-PM<sub>10</sub> FRM sampler?*

*What are your comments on the use of XRF as the Pb-PM<sub>10</sub> FRM analysis method?*

*What are your comments on the specific analysis details of the XRF analysis method contained in the proposed Pb-PM<sub>10</sub> FRM analysis method description?*

*Do you think the precision, bias and MDL of the XRF method for the proposed Pb range will be adequate?*

*Are there any method interferences that we have not considered?*

**Document Associated with Subcommittee's Consultation:**

- **Attachment 2 – Options for the Development of a Low Volume Lead in Total Suspended Particulate (Pb-TSP) Sampler**

**Background and Summary:** Problems with the current high-volume Pb-TSP sampler have been highlighted as part of the on-going Pb NAAQS review. As part of the NAAQS review, EPA proposed network design requirements that could result in the need for a significant expansion and/or reallocation of Pb monitors. Due to the concerns over the existing high-volume Pb-TSP sampler, EPA requested comments on the need for a FRM or FEM low-



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volume Pb-TSP sampler. The attached document discusses options for the development of a low-volume Pb-TSP sampler for use in the Pb network.

### **Charge Questions:**

*Would a low-volume Pb-TSP sampler be an improvement over the existing high-volume Pb-TSP sampler? What advantages and disadvantages do you see associated with a low-volume Pb-TSP sampler?*

*What inlet designs would be best suited for a low volume Pb-TSP sampler? What designs are not appropriate for a low-volume Pb-TSP sampler?*

*What is your preferred approach for the development of a low-volume Pb-TSP sampler, and why?*

*If the EPA were to develop a low-volume Pb-TSP FRM, how important is it that the sampling capture efficiency be characterized for varying particle sizes?*

*If the EPA were to develop a low-volume Pb-TSP FRM, should the new FRM replace the existing high-volume Pb-TSP FRM, or should the EPA maintain the existing FRM?*

*Is it appropriate to accept alternative sampler and inlet designs as FEM?*

*Are the proposed FEM testing criteria for Pb methods adequate to ensure equivalence of alternative sampler and inlet designs? If not, what additional testing requirements should be considered?*

### Attachments

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