Clean Air Scientific Advisory Committee (CASAC)
Ambient Air Monitoring and Methods Subcommittee (AAMMS)
Individual Preliminary Comments on EPA's White Paper,
Approach for Development of a New Federal Reference Method (FRM) for Lead in Total Suspended Particles (Pb-TSP)

(as of September 13, 2010)

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Comments from Mr. George A. Allen

General background.

This charge to the AAMMS does not include the sample collection method for the Pb FRM -- that remains the Hi-Volume sampler with quartz or glass-fiber filters at this time. The issues discussed here are related to analysis of these filters for Pb and related issues, in the context of revising the Pb FRM's analytical method to better suite the new and much (10 times) lower PB NAAQS that is now in effect. As EPA notes, this large drop in the NAAQS requires revision of the analytical method to insure that data of high quality can be reported at these much lower concentration loadings on the FRM Hi-Vol filter. These lower loadings require assessment of both the filter extraction process and the analysis method used for the Pb FRM. Analytical methods have also changed dramatically since the Pb FRM was last revised; this process allows the FRM to be updated to take advantage of these newer technologies.

It is important to note that for these components of the Pb FRM, there are likely to be FEM methods approved that may be more practical for routine use. Still, it is important to have a robust and well characterized FRM in place even though analysis of Pb from Hi-Vol filters by any reasonable method with sufficient sensitivity is probably much more robust than the uncertainties inherent in the existing Pb FRM Hi-Vol sampling method. This process updates the "back end" of the method; I strongly encourage EPA to continue development of a "larger particle Lower-Vol" Pb FRM sampler that can provide accurate and reproducible samples to better harmonize the improvements in the Pb-FRM filter analysis being discussed here.

Charge Question 1. "What are the panel's views on the two extraction method options of heated ultrasonic and graphitic hot block with nitric/hydrochloric acid for the extraction of Pb from TSP?"

Either extraction method should meet the needs of a revised Pb FRM, and both of these methods are currently approved by EPA as FEM methods for Pb extraction off a Hi-Vol filter. Assuming their performance is similar across the expected lower range of Pb filter loadings, I would recommend using the simpler method, which in this case appears to be the graphitic hot block with nitric acid, Method EQL-0710-192. It is worth noting here that a graphitic hot block may not be necessary; aluminum has been shown to work well and is a simpler approach. While the other method (sonication and both acids, EQL-0510-191) may be needed for extraction of other metals, it is not needed for Pb, and this is a Pb FRM, not an FRM intended for wider use. Sonication adds complexity to the method especially if "trace" analysis protocols are used; quartz fiber filters produces a "filter mush" that requires an extra step to remove the filter material from the liquid, usually with a centrifuge. Glass fiber filters may also need this treatment after sonication.

Charge Question 2. "What are the panel's views on ICP-MS as the analysis method for Pb-TSP?"

For the Pb-FRM, ICP-MS is clearly the preferred analysis technique. It is a highly sensitive and specific method for Pb; there are no other obvious candidate methods.

Charge Question 3. "What are the panel's views on the approach described for evaluating and testing the method prior to proposal as a new FRM for Pb-TSP?

The described approach is rigorous. The description of the "archived" field (real samples?) filters needs to be clarified -- where are the samples from, what are the loadings, etc. This use of real samples for assessing extraction, especially at lower Pb loadings, is an important part of the evaluation since dry loading combined with a large amount of other material may effect the extraction process. The information in Table 1 (dry NIST SRMs) needs clarification. How will the dry SRM be applied to the filter? What does the "minimum weight" column mean?

There is an assumption here that quartz filters would be used since they have lower blank levels for some metals of interest other than lead. But again, this is an FRM for Pb - not other metals - and glass fiber filter Pb blanks are very low. An agency would presumably use glass fiber filters for Pb since that media is much less fragile than quartz fiber filters. If other metals were of interest, I'd expect that they would be done using a low-volume PM10-FRM Teflon filter sampler, usually using either XRF and/or ICP-MS. I would not expect agencies to routinely do other metals off a Hi-Vol filter sample, and thus I would suggest that EPA simplify the Pb FRM evaluation by constraining tests to glass fiber filters. For (PM10) "trace metals", the Hi-Vol sampler is not the sampling method or filter media of choice. Trace level analysis requires "trace level" protocols across the entire method, and a low-vol PM10 FRM Teflon sampling method is better suited for this.

Charge Question 4. "Inter-laboratory testing of the method will be done to assess between laboratory variability (CV) at the 95% confidence interval. What are the panel's views on a reasonable level of inter-laboratory variability?

Inter-laboratory method testing is an important component of the FRM assessment, since it will better reflect the real-world performance of the method -- which is usually somewhat degraded from ideal testing conditions. For an acceptable level of inter-lab variability that includes variability from filter extractions, a starting point for this value might be the recovery range noted in the white paper: "The SRMs are expected to be recovered within 80 to 120% of the certified value per method 6020A". If initial test results show a tighter recovery range, then the inter-lab criteria could be tightened. I would expect much of the inter-lab variability to be from the extraction process, since a well-controlled ICP-MS analysis for Pb should have reasonably tight inter-lab variability at these levels.

Comments from Dr. Judith Chow

This memo addresses the four questions on which the Subcommittee members were asked to comment regarding "the White Paper on the Approach for the Development of a New Federal Reference Method (FRM) for Pb in Total Suspended Particulates (TSP)." This supplements prior comments to the first set of questions that was appended to the August 12, 2008 letter from Dr. Russell to Administrator Johnson.

1. QUESTIONS FOR WHITE PAPER ON THE APPROACH FOR THE DEVELOPMENT OF A NEW FEDERAL REFERENCE METHOD (FRM) FOR PB IN TOTAL SUSPENDED PARTICULATES (TSP)

1.1. Question 1: What are the panel's views on the two extraction method options of heated ultrasonic and graphitic hot block with nitric/hydrochloric acid for the extraction of Pb from TSP?

Both the heated ultrasonic water bath (with 1.02 M nitric acid [HNO3]/2.23 M hydrochloric acid [HCl]) and graphite hot block (with 3.5 % HNO3 [v/v] at 95 ± 5 °C) are adequate methods to extract PM deposits on glass-fiber or quartz-fiber filters. It is assumed that blank filters have been acceptance-tested to assure that Pb blank levels are negligible. The procedure for the heated ultrasonic HNO3/HCl method is more cumbersome and requires a centrifuge to complete the extraction. This method adds 15.0 ± 0.15 ml of the HNO3/HCl solvent to the filter aliquot, followed by 1 hr of ultrasonic extraction at 80 ± 5 °C in a loosely capped 50 ml extraction tube. After cooling, 25.0 ± 0.25 ml of distilled deionized water (DDW) are added to bring the volume to 40 ± 0.4 ml in a tightly capped extraction tube. This tube is then centrifuged for 20 minutes at 2500 RPM. Note that the water level in the ultrasonic bath also needs to be set above the level of the extraction solution in the tubes but below the level of the extraction tube caps to minimize contamination. Some of the solvent volume may be lost during the ultrasonic heating stage, because the caps are left loose. The use of HCl in the extract adds another potential source of contamination and produces a more complex analytical matrix; HNO3 by itself is an effective Pb solvent (U.S. EPA, 2007).

The hot block digestion method is simple and straightforward. It involves transferring a 20 ml aliquot of diluted HNO3 (1:19 v/v) from concentrated HNO3 (67 – 70%) to each extraction vessel, ensuring that the filter strip is covered with HNO3 extract, placing the vessel on the hot block, covering it with ribbed watch glass or a cap with a central vent, and heating it at 95 ± 5 °C for 60 min. The extract is to be brought to a final volume of 50 ml by dilution with reagent grade DDW. Given the simpler matrix and reduced sample handling of the hot block digestion method, one could reasonably expect to achieve more consistent results (i.e., better precision). There is a possibility that deviations from procedures could produce insoluble lead chloride.

1.2. Question 2: What are the panel's views on ICP-MS as the analysis method for Pb-TSP?

As stated in the white paper, Pb can be analyzed by ICP-MS, just as it can be analyzed by atomic absorption spectrometry (AAS) with a graphite furnace and ICP-atomic emission spectroscopy (ICP-AES) once it is in solution. It can be accurately quantified to several orders of magnitude below the necessary working range. The ICP-MS should support a method detection limit (MDL) of 0.0075 µg/m3. The instrument will be well within its capabilities, resulting in accurate and precise results.

The analysis method for Pb should be performance-based. As long as the MDL, precision (±15% at 90% confidence interval), and accuracy (±5%) are within the EPA's specified levels, other analytical methods (e.g., AAS with graphite furnace, ICP-AES, X-ray fluorescence [XRF], or proton-induced X-ray emission [PIXE]) should be available as options. Unless the state or local agency is already set up for ICP-MS, it will be costly to initially identify, procure, and set-up for acid digestion (~$5,000 – 10,000; e.g., hot block, flow hood) and ICP-MS (~$200,000). An advantage of ICP-MS is the ability to quantify different isotopic abundances for Pb, which may be related to their sources (Herner, et al., 2006; Huggins, 2002; Moreira, et al., 2005; Oehme and Lund, 1979).

1.3. Question 3: What are the panel's views on the approach described for evaluating and testing the method prior to proposal as a new FRM for Pb-TSP?

The white paper states the proposed approach for determining method performance (i.e., analysis of standard reference materials [SRMs], verification of filters spiked with a known concentration of NIST traceable Pb salts solution, examination of interference and filter matrix effects, determination of MDL, and intra-laboratory method performance [e.g., assess bias within ±10% and precision within ±15%, evaluation of glass and quartz-fiber filter matrices, analysis of spiked filter strips, SRMs, and real-world samples, tests for small variations in extraction temperature and time, and evaluation of extract storage stability]).

Additional tests need to be planned and conducted to ensure 100% extraction efficiency. Extraction of spiked-samples with NIST traceable Pb salt or SRMs does not necessarily verify the extent of a complex matrix of ambient or source samples.

1.4. Question 4: Inter-laboratory testing of the method will be done to assess between laboratory variability (CV) at the 95% confidence interval. What are the panel's views on a reasonable level of inter-laboratory variability?

Inter-laboratory testing as listed in the white paper (e.g., method performance assessment of the four participating laboratories, analysis of spiked filter samples and actual filter samples) is adequate. It would be worthwhile to examine previously published composition for Pb analyses. It would also be helpful to specify the concentration range representing the measured and calibrated concentration range. The total number of samples to be performed for each type of

analysis should be more than 10 pairs by each participating laboratory to obtain a statistically significant analysis.

In addition to the calculation of coefficient of variation (CV) at the 95% confidence interval, equivalence and comparability should be established for the inter-laboratory comparison as defined in Mathai et al. (1990). The U.S. EPA criteria for equivalence between Federal Equivalent Methods (FEM) and FRM for PM2.5 mass concentration, such as: 1) linear regression slope of 1 ± 0.05; 2) linear regression intercept of 0 ± 1 μg/m3; and 3) linear regression correlation coefficient (r) of >0.97 can be modified and adapted for "equivalence." The following criteria can be considered for "comparability" within the stated precision: 1) the slope (by either ordinary least squares [OLS] or effective variance [EF] weighting) equals unity within three standard errors, or average ratios (y/x) equal unity within one standard deviation; 2) the intercept does not significantly differ from zero within three standard errors; and 3) the correlation coefficient exceeds 0.9 (Berkson, 1950; Kendall, 1951; Madansky, 1959). This is a less demanding definition than equivalence because it considers the reported precisions of the two measurements being compared; these may be larger than the requirements for an FEM used to determine compliance, but still sufficient to discern concentration differences (Watson and Chow, 2002).

References

Berkson, J. (1950). Are there two regressions? J. Am. Stat. Assoc., 45:164-180.

Herner, J.D.; P.G. Green; and M.J. Kleeman (2006). Measuring the trace elemental composition of size-resolved airborne particles. Environ. Sci. Technol., 40(6):1925-1933.

Huggins, F.E. (2002). Overview of analytical methods for inorganic constituents in coal. International Journal of Coal Geology, 50(1-4):169-214.

Kendall, M.G. (1951). Regressions, structure and functional relationship, Part I. Biometrika, 39:96-108.

Madansky, A. (1959). The fitting of straight lines when both variables are subject to error. J. Am. Stat. Assoc., 54:173-205.

Mathai, C.V.; J.G. Watson; C.F. Rogers; J.C. Chow; I.H. Tombach; J.O. Zwicker; T.A. Cahill; P.J. Feeney; R.A. Eldred; M.L. Pitchford; and P.K. Mueller (1990). Intercomparison of ambient aerosol samplers used in western visibility and air quality studies. Enivron. Sci. Technol., 24(7):1090-1099.

Moreira, F.R.; R.M. Borges; and R.M. Oliveira (2005). Comparison of two digestion procedures for the determination of lead in lichens by electrothermal atomic absorption spectrometry. Spectrochimica Acta Part B-Atomic Spectroscopy, 60(5):755-758.

Oehme, W. and W. Lund (1979). Comparison of digestion procedures for the determination of heavy metals (cadmium, copper, lead) in blood by anodic stripping voltammetry. Fresenius Z. Anal. Chem., 298:260-268.

U.S. EPA (2007). 40 CFR Ch. I; Appendix G to Part 50 - Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air. Federal Register, 50:57-61.

Watson, J.G. and J.C. Chow (2002). Comparison and evaluation of in-situ and filter carbon measurements at the Fresno Supersite. J. Geophys. Res., 107(D21):ICC 3-1-ICC 3-15.

Comments from Dr. Delbert Eatough

1. What are the panel's views on the two extraction method options of heated ultrasonic and graphitic hot block with nitric/hydrochloric acid for the extraction of Pb from TSP?

EPA is proposing to replace the current extraction method described in Appendix G of 40 CFR Part 50 with one of the two methods listed above. The essence of the three methods, as I see it, are compared in the following Table.

Method	Current Method	Ultrasonic Bath	Hot Block Reflux
Fraction Analyzed	3/4" x 8" strip	3/4" x 8" strip	3/4" x 8" strip
Solution	15 mL, 3 M HNO_3	15 mL, 1 M HNO_3, 2 M HCl	20 mL, 1:19 v/v HNO_3
Extraction	30 min, boiling	60 min, 80 °C	60 min, 95 °C

From a chemical extraction point of view, the three methods should be nearly equivalent for the extraction of Pb from particles collected on either a glass or quartz fiber filter. As pointed out in the EPA material provided for the consultation, the HCl added to the Ultrasonic Bath technique will assist in the extraction of more refractory metals from the sample, but is not needed for the recovery of Pb. From, a personal point of view, I prefer the Ultrasonic Bath technique because it minimizes the temperature to which the concentrated nitric acid solution is heated. However, the more important question is the blank, Pb recovery, and precision of each technique. These points cannot be established from the material provided. The two newer techniques proposed by EPA for evaluation are covered in two reports referenced in the white paper, e.g. EQL-0510 191, Determination of Lead in TSP by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with Heated Ultrasonic Nitric and Hydrochloric Acid Filter Extraction and EQL-0710-192, Heated Nitric Acid Hot Block Digestion and ICP-MS Analysis for Lead (Pb) on TSP High-Volume Filters. The first is a report from RTI to EPA on the indicated method and the second a method description from U.S. EPA Region 9. Neither are complete scientific reports, giving details on the data behind the various statements in the documents. The above listed important points of method blank, Pb recovery and precision of the techniques cannot be established from these report.

Likewise, there are no studies from any given laboratory which allow comparisons of the three techniques. Such a limited study from a single quality laboratory would do much to better define important elements which should be part of the EPA evaluation and testing program.

Finally, I would like to suggest that all three methods, and not just the two outlined in the white paper should be evaluated on an equal footing. This will provide a tie to previous analyses and give an indication as to whether a change from the older analytical scheme is needed with respect to the extraction method.

2. What are the panel's views on ICP-MS as the analysis method for Pb-TSP?

The analytical techniques used for the determination of Pb in the various extract solutions to be evaluated, as outlined in charge question 1 is required, as outlined by EPA to have a MDL for Pb of 5% of the NAAQS (0.15 $\mu g/m^3$), or 0.008 $\mu g/m^3$. As recently summarized by Cavender (EPA, OAQPS) in a presentation at the March 2, 2009 National Air Quality Conference in Addison, TX, expected MDLs for Pb in TSP and PM_{10} methods are:

Estimated MDL: ($\mu g/m^3$)	**Sample Analysis Methods**
0.002 to 0.00005 [a,c]	Graphite Furnace Atomic Absorption (GFAA)
0.0007 [b]	Energy-dispersive X-Ray Fluorescence (EDXRF)
0.00006 [c]	Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
0.0003 [c]	Inductively Coupled Plasma Atomic Emission spectrometry (ICP-AES/OES)

[a] Estimated MDL retrieved from AQS
[b] 40 CRF Part 50, Appendix Q
[c] Estimated MDLs reported in the Inorganic (IC) Compendium of Methods for the Determination of Inorganic Compounds in ambient Air, EPA/625/R-96/01a, July 1999

Each of the methods listed above are capable of given data within the required MDL. While ICPMS has the anticipated lowest MDL in the Table, this extra level of lower detection is not needed for the purposes of the NAAQS for Pb as currently outlined. While evaluating the ICP-MS method as an alternate method for data analysis would be warranted, I see no reason to dump the long standing GFAA method for which we have decades of experience. Moving ahead with both methods in the evaluation proposed by EPA would seem warranted. The comparison of the two methods will enhance our understanding of both precision and accuracy in the determination of Pb under the current standard. Since both methods will use the various extract solutions outlined in charge question 1, there is not practical impediment to this approach.

I would like to make a few final points in regards to the above Table. All of the techniques, except for EDXRF analysis are ideally suited for analysis of solutions, such as those produced by the procedures highlighted under charge question 1. However, the procedures required to produce those solutions are laborious, expensive and prone to sample contamination introduction. The solution extraction approach is required under the current FDM technique for Pb in TSP. But making an effort to move any from this requirement would be highly desirable. EPA has put in place the possibilities for both low volume TSP samplers or the acceptance of a

PM_{10} value for Pb measurements in the future in the 40 CFR 50 document. These were both directions the AAMMS urged EPA to move in the past and I encourage EPA to actively incorporate evaluation of these methods into some phases of the development of FRMs for Pb. It such a path. is not taken, then comparison data which would allow the incorporation of either a low volume TSP sampler or a PM_{10} metric in the future will not be obtained and moving one of these directions will not be possible. Either technique would allow the use of EDXRF (or equivalent methods) for the direct analysis of collected samples without an extraction step. This would be highly desirable.

3. What are the panel's views on the approach described for evaluating and testing the method prior to proposal as a new FRM for Pb-TSP?

As outlined in the charge questions and in the white paper, the approach which EPA will take to validate any new methods for analysis of TSP PB is based on the guidance documents and references provided with the charge questions. Particular weight is given to information contained in Validation and Peer Review of U.S. Environmental Protection Agency Chemical Methods of Analysis, prepared for The EPA Forum on Environmental Measurements (FEM); FEM Document Number 2005-01, October 14, 2005. The approach to be used includes the analysis of Standard Reference Materials (SRMs) and NIST-traceable Pb salt solutions; assessment of method detection limits (MDLs), bias, precision; and inter-laboratory testing to assess between laboratory variability. The approach is reasonable, well thought out and based on solid guidance to EPA. I urge EPA to keep in focus the point that the lowest MDL is not the prime factor which should be considered in making a decision. As long as any analytical technique has a MDL within the requirements of the standard, it should be evaluated on an equal footing with the methods with the lowest MDL. There are three important modifications I would suggest to the approach outlined in the white paper:

(1). Complete a single laboratory evaluation of the three extraction methods outlined in 1. above to better inform the process and set the protocols as EPA moves into multilaboratory evaluations.

(2). Include a minimum of both ICP-MS and GFAA in both the single laboratory study and multi-laboratory evaluations so that there is a solid basis for either retaining the GFAA method in the FRM (along with ACP-MS if adopted) or switching to only the ICP-MS method. I urge this evaluation because of the legacy in both data and laboratory experience with the current analytical method.

(3). Include comparison measurements with both a low flow TSP sampler and a PM_{10} sampler to develop a data set which would allow EPA to consider moving away from the high volume TSP sampling procedure in the future. I particularly urge EPA to include the PM_{10} measurements and direct analysis of the collected filter material to allow the Pb program to become more consistent with sampling for the PM standard in the future.

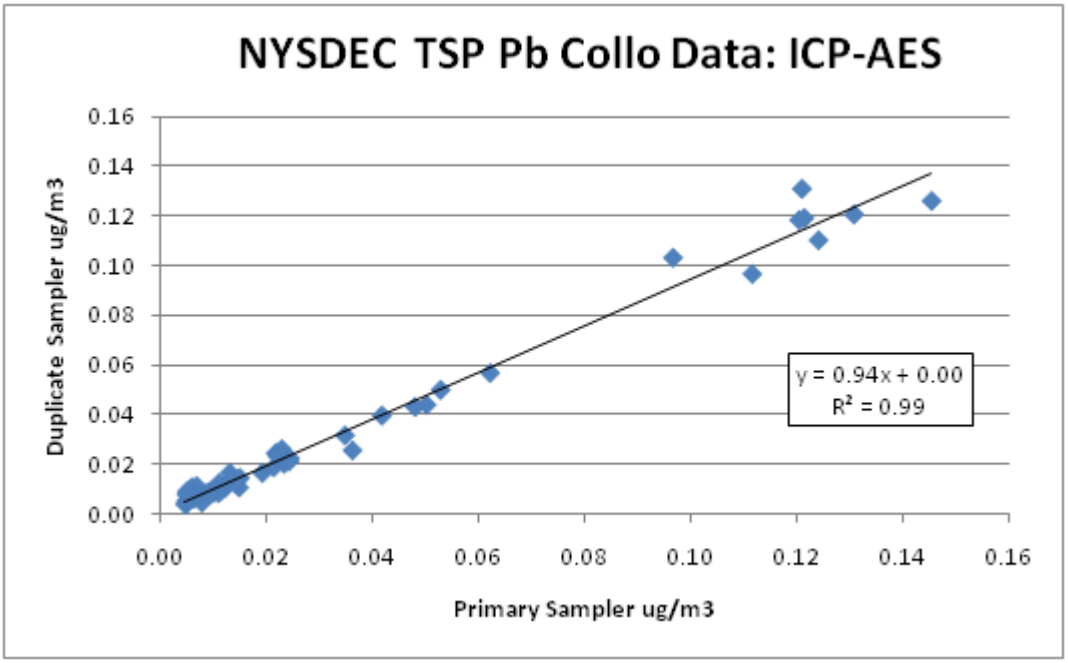
4. Inter-laboratory testing of the method will be done to assess between-laboratory variability (CV) at the 95% confidence interval. What are the panel's views on a reasonable level of inter-laboratory variability?

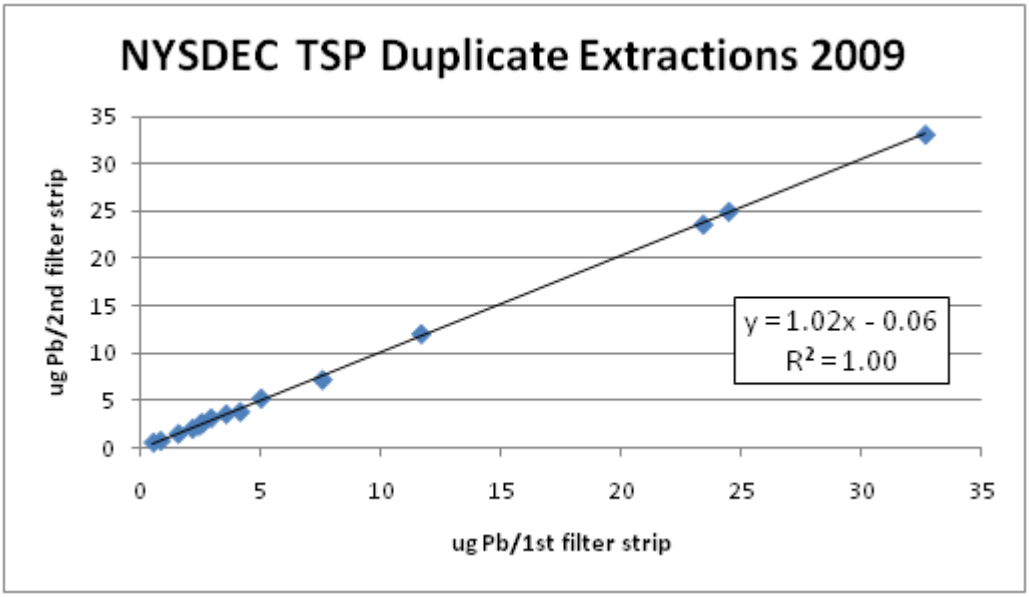
I would like to give this question more thought before responding and defer for now to others on this point.

Comments from Mr. Dirk Felton

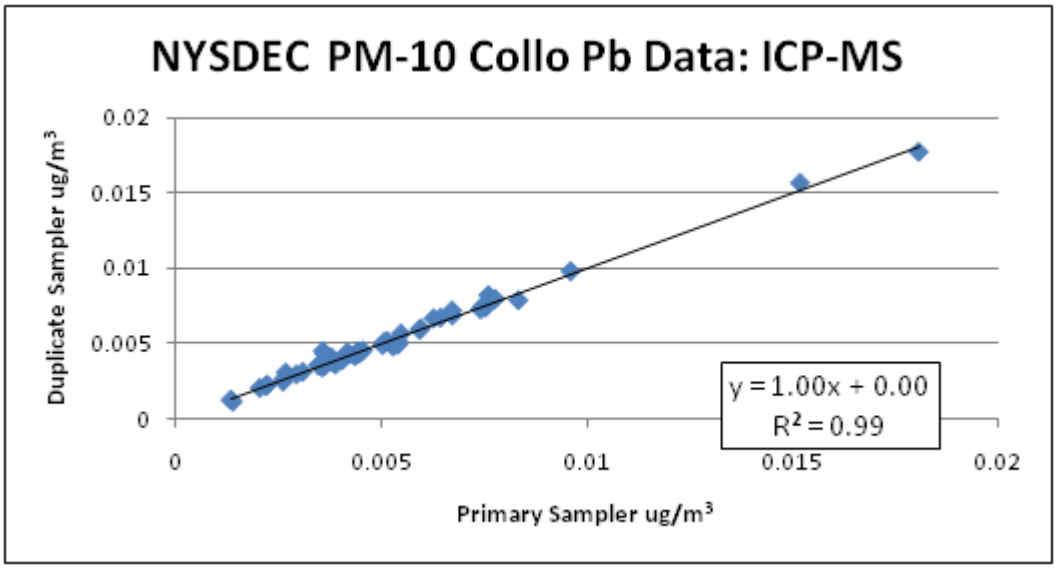
General Comment

The FRM for TSP Pb suffers from relatively high measurement uncertainties at the higher concentrations near the NAAQS. This error is apparent from the field precision data which includes variability due to sampler collection efficiency. The high volume TSP samplers specified for use in the NAAQS program have variable collection efficiency due to wind direction and wind speed. These sampler related collection errors are proportionally larger as the concentration of Pb in the air increases. The graph below shows that when the ambient Pb concentration nears the new NAAQS, the difference in concentration between the primary and duplicate samplers increases. This increase in error is not related to extraction efficiencies which are summarized in the next plot. Duplicate extractions are performed by extracting and analyzing a second strip from the same filter. The 2009 Pb QA data provided by the NYSDEC indicates that the current extraction and analysis methods are adequate but the field collection of Pb samples needs improvement.





ICPMS is used by most monitoring agencies in the NATTS program for the analysis of low-volume PM-10 filters for toxics metals including Pb. The data for this program is used for trends determinations and risk assessments so data accuracy is important throughout the concentration range. The accuracy and sensitivity of the analysis must be much better than for the Pb high volume analysis because of the smaller sampling volume for these samplers. The results from the collocated non-source oriented NATTS site in New York demonstrate that the low volume field samplers with ICPMS analysis produce very high quality data.



Initial Response to Charge Questions

1. What are the panel's views on the two extraction method options of heated ultrasonic and graphitic hot block with nitric/hydrochloric acid for the extraction of Pb from TSP?

> **Either extraction method is acceptable for NAAQS Pb monitoring. Monitoring Agencies are likely to prefer one method over another because it is either cost effective or because it is better suited for the analyses of other elements.**
>
> **Since Pb is relatively easy to extract, it would be preferable to have a range of acceptable extraction parameters such as acid types and concentrations, temperatures, heating methods and filtration included in the FRM. Performance standards for extraction efficiency could be included to ensure that the method selected by specific laboratories is adequate for compliance data. This approach would not only make the samples collected for Pb NAAQS monitoring useful for other programs but will also make the samples collected for other programs such as air toxics eligible for use in comparison to the Pb NAAQS.**

2. What are the panel's views on ICP-MS as the analysis method for Pb-TSP?

> **The method is acceptable but is more accurate than is necessary for high volume TSP filter analysis. The advantage of making this method a FRM is that it is also suitable for use with low volume PM-10 filters. The FAAS method is adequate for high volume sample analysis and is performed in-house by many State and Local monitoring agencies. The FAAS method should be retained as an FEM but limited to use for high volume samples.**

3. What are the panel's views on the approach described for evaluating and testing the method prior to proposal as a new FRM for Pb-TSP?

> **The approach looks adequate though some of the evaluation criteria are not very tight. Recoveries, inter-method precisions and bias at high concentrations should be better than the criteria set forth in the white paper. The criteria should be tightest at the level of the NAAQS.**
>
> **The sampled filters should also be selected to look for real world interferences. The white paper mentions that filters will be selected to cover a range of Pb but they should also cover a range of other factors such as heavy crustal or EC loadings that may potentially interfere with the analysis results.**

4. Inter-laboratory testing of the method will be done to assess between-laboratory variability (CV) at the 95% confidence interval. What are the panel's views on a reasonable level of inter-laboratory variability?

The comparisons between labs should include criteria that indicate performance at low concentrations, high concentrations and of course at the level of the NAAQS. The evaluation should also emphasize the performance for real world samples.

The use of the CV for the assessment is useful for comparing labs participating in the evaluation of the two methods, however it may not be as useful for monitoring agencies attempting to estimate method accuracy. The CV is based on the number of samples in the study which may not provide much information for individual sample variability. The results could be summarized to indicate single sample expected accuracy as well as the relative accuracy over a period relevant for the NAAQS such as over three months of sampling.

Comments from Dr. Philip Hopke

1. What are the panel's views on the two extraction method options of heated ultrasonic and graphitic hot block with nitric/hydrochloric acid for the extraction of Pb from TSP?

The methods proposed appear to be adequate for extracting lead from TSP samples, but they have failed to evaluate modern extraction techniques. There is no discussion of microwave digestion where you can automate multiple samples. There are systems that can run up to 40 samples at a time with monitoring of the temperature of each extraction cell to ensure uniform extraction. Thus, the Agency has missed an opportunity to permit efficient, uniform extraction that would make the analyses faster, more uniform and simpler to run in large numbers.

2. What are the panel's views on ICP-MS as the analysis method for Pb-TSP?

ICP-MS is an appropriate method.

Comments from Dr. Jay Turner

It is appropriate that the Agency revise the FRM for Pb-TSP to provide for suitable sample analyses to determine compliance with the Pb NAAQS revisions promulgated in November 2008. Advice has been solicited concerning the extraction and analytical methods, method validation and testing, and target for inter-laboratory variability.

Charge Questions and Responses

1. What are the panel's views on the two extraction method options of heated ultrasonic and graphitic hot block with nitric/hydrochloric acid for the extraction of Pb from TSP?

The two methods (EQL-0510-191 and EQL-710-192) are reasonable candidate methods. They are consistent with current laboratory equipment and practices. Our group's recent experience with graphite hot block sample digestions for air toxics PM_{10} metals (including but not limited to Pb) has been very positive.

Is the intent to eventually designate one of these methods (perhaps with modifications subject to the forthcoming evaluation) as the FRM but to also potentially designate the other method (again, perhaps with modifications) as an FEM method? If so, what approach will be taken to determine equivalency? There is a Method Comparison entry in the Text Matrix table appended to the White Paper – would this be the only method comparison performance criterion for a candidate FEM method (in additional to meeting all of the other criteria in the table)? Also, would the inter-laboratory tests be required?

How do these two candidate extraction methods compare to the PM_{10} metals extraction method used the National Air Toxics Trends Station (NATTS) network? *Pb is one of the target analytes for NATTS (albeit PM10 and not TSP) and there might be advantages to harmonizing the NAAQS and NATTS analytical methods either through the FRM or FEM methods.*

The extraction description in EQL-710-192 concludes with the step "Shake the extract vigorously for 5 seconds (with the filter strip in the extraction vessel) and let settle for at least an hour. The sample is now ready for analysis." What are the provisions for storing the sample(s) for some length of time between extraction and analysis? Also, does the one hour of settling time guarantee that no filtration of the extract is required? A filtration step is included in EPA Compendium Method IO-3.1 (Selection, Preparation, and Extraction of Filter Material), the metals extraction SOP posted under the air toxics section of the EPA AMTIC web site (http://www.epa.gov/ttnamti1/files/ambient/airtox/metalsop.pdf), and the Technical Assistance Document for the National Air Toxics Trends Station Program (Revision 2, April 2009; http://www.epa.gov/ttn/amtic/files/ambient/ inorganic/mthd-3-5.pdf).

What are the plans for the initial demonstration of performance for each analytical laboratory? While the candidate methods will be evaluated using the Text Matrix appended to the White Paper, would there be advantages to having each analytical laboratory perform tests with SRM or some other standardized samples as part of an initial demonstration of performance? This is not addressed in the candidate SOPs.

2. What are the panel's views on ICP-MS as the analysis method for Pb-TSP?

ICP-MS is appropriate as the reference method. It has suitable sensitivity and minimal issues with interferences. In additional to contract laboratories. many state and local agencies are already performing ICP-MS analysis for air toxics PM_{10} metals (see e.g. Table 8 in National Air Toxics Trends Stations Quality assurance Annual Report, Calendar Year 2007; http://www.epa.gov/ttnamti1/files/ambient/airtox/NATTS2007QAAnnualReport.pdf). Again, there might be advantages to harmonization with the NATTS method which is EPA Compendium Method IO-3.5 (Determination of Metals in Ambient Particulate Matter Using Inductively Couple Plasma/Mass Spectrometry). Does the agency plan to evaluate and possibly designate FEM methods based on other instruments?

3. What are the panel's views on the approach described for evaluating and testing the method prior to proposal as a new FRM for Pb-TSP?

The approach is sound. Tests and criteria have been defined in the Test Matrix appended to the White Paper. I have some concerns about the broad range for the SRM recoveries (80-120%). While this recovery range is a commonly used criterion, should it be tighter for NAAQS compliance measurements? Also, should recovery tests be performed at even higher concentrations? The NAAQS is based on a three-month rolling average. For 1-in-6 day sampling this is nominally 15 samples and thus a few very high concentration samples could lead to a violation and it would be important to have accurate measurements at high concentrations since the NAAQS is an arithmetic average.

4. Inter-laboratory testing of the method will be done to assess between-laboratory variability (CV) at the 95% confidence interval. What are the panel's views on a reasonable level of inter-laboratory variability?

The target performance for interlaboratory variability should take into consideration the overall measurement quality objectives and the performance achieved by the method(s) from the intra-laboratory method performance evaluation. I will likely provide more-detailed feedback in my final comments.

Comments from Dr. Warren White

As usual, I am impressed by the care and consideration the Agency gives to defining its compliance measurements. I would also like to commend the authors of this white paper for their inclusion of hyper-links to relevant Agency documents (on pages 1 and 2), which can sometimes be hard for outsiders to locate.

I bring no specific personal expertise to this review, having no direct experience with either hi-vol (TSP) sampling or ICP-MS analysis. My comments accordingly focus on the statistical aspects of the inter-laboratory testing, responding to charge question #4.

The experimental design for inter-laboratory testing is said to follow, generally, that of Long et al. (1979). For tests on sampled filters, it anticipates selecting 28 = 7x2x2 archived hi-vol filters. This will provide 7 ambient levels on each of 2 filter media (glass and quartz), for extraction by 2 different procedures (heated ultrasonic and heated block). Each hi-vol filter will be sectioned into eight strips; four pairs of adjacent strips will be distributed to four different laboratories.

In the Long et al. inter-laboratory evaluation, the role of the paired strips was to provide matched tests of the alternative extraction procedures: "Each laboratory was requested to extract one strip of each pair with the boiling HNO3 procedure and the other with the ultrasonic HNO3 procedure." This matching provided more statistical power for testing the equivalence of the two extraction procedures. The present white paper instead envisions that "Each laboratory will receive 7 pairs for the heated block method and 7 pairs for the heated ultrasonic method." This means that the two extractions will be tested on unmatched samples, making their equivalence more difficult to assess.

It seems to me that the statistical design would be improved by splitting each pair between the two extraction procedures, as was done by Long et al. This return to the earlier design would also reduce the required number of archived filters (and lab analyses) by one-half, to 14. Precision would still be evident from the planned triplicate analyses of each extract.

On the charge question of "a reasonable level of inter-laboratory variability", we can note that Long et al. judged that two observations by different laboratories using the previous FRM would not differ by more than 28% of the concentration level more than 5% of the time due to chance alone. Alternatively, if 10% bias and 15% precision are tolerated for each lab, then differences of $50\% = 2.77 \times (10\%^2 + 15\%^2)^{1/2}$ could be expected 5% of the time. [The factor 2.77 is the two-sided 5% critical value for the normal distribution (1.96), multiplied by the square root of two to account for the independent uncertainties in two observations.]

Whether these are "reasonable" levels of variability requires a consideration of data quality objectives: "The U.S. Environmental Protection Agency (EPA) has developed the Data Quality Objectives (DQO) Process as the Agency's recommended planning process when environmental data are used to … derive an estimate of contamination." (http://www.epa.gov/quality/qs-docs/g4-final.pdf) Given the epistemic uncertainties in our exposure and risk assessments for lead, a 50% uncertainty may be acceptable, but this is not a strictly scientific judgment.

Comments from Dr. Yousheng Zeng

Charge Question 1: What are the panel's views on the two extraction method options of heated ultrasonic and graphitic hot block with nitric/hydrochloric acid for the extraction of Pb from TSP?

EPA has presented two options for lead extraction from TSP filters – Option 1: heated ultrasonic nitric and hydrochloric acid filter extraction, and Option 2: heated nitric acid hot block digestion. I don't have experience with these two specific extraction procedures. However, based on my past experience with acid digestion of TSP samples, the mixture of nitric acid and hydrochloric acid provides more aggressive and thorough extraction of metals than nitric acid alone. More aggressive extraction may or may not be important for lead. It certainly makes difference for extracting some other metals. With ICP-MS, multiple metal analyses will be easier than the current FRM using FAAS. Multiple metal analyses will provide more useful information for source identification and apportionment. With the ease and value of having multiple metals analyses, it is anticipated that more agencies would analyze multiple metals beyond lead. Therefore, a procedure that has stronger digestion and extraction power for not only lead, but also other metals is beneficial.

In addition to hydrochloric acid, Option 1 uses a slightly higher nitric acid concentration than Option 2 (64.4 mL of concentrated nitric acid in 1000 mL vs. 50 mL in 1000 mL). Option 1 also uses ultrasonic waves to provide agitation and to aid extraction.

Overall, Option 1seems to be a stronger method than Option 2. Unless Option 1 is more susceptible to interference due to presence of hydrochloric acid or chlorides, I would favor Option 1. As part of EPA's further evaluation of the two candidate methods before final selection of the FRM, I would suggest that EPA address vulnerability between the two methods in terms of potential interference in the two methods, *i.e.*, does the presence of hydrochloric acid make the subsequent ICP-MS analysis more susceptible to interference in the context of a typical ambient TSP samples as the matrix? As stated in Section 7.2 of SW-846 Method 6020A, "many more molecular-ion interferences are observed when hydrochloric and sulfuric acids are used". This question may have been investigated and answered, but not included in the materials provided for this subcommittee review.

Charge Question 2: What are the panel's views on ICP-MS as the analysis method for Pb-TSP?

EPA has cited the advantages of using ICP-MS over the current FRM analytic method (FAAS). I agree that ICP-MS should be a significantly better method than FAAS. My only comments are

1. Potential interferences (including isobaric elemental interferences, physical and chemical interferences, and interferences that may be caused by introduction of hydrochloric acid as discussed above;) should be addressed as part of EPA's evaluation.
2. If possible, EPA should consider some secondary objectives to leverage and maximize the benefits of conducting the evaluation. These secondary evaluations may include:
    a. Analyzing other elements in addition to Pb. If the results are favorable, they can be used to support monitoring agencies' effort to analyze multiple elements at a small incremental cost and acquire valuable data for other programs such as air toxics studies, source apportionment, etc.
    b. Analyzing samples using the current FRM (*i.e.*, FAAS) and XRF method in parallel to the evaluation of the candidate ICP-MS methods so that comparisons can be made. A comparison with FAAS may help understand the past monitoring data and bridge the past and future data. A comparison with XRF may be useful because a large body of data has been and can be generated by XRF.
3. The candidate FRM methods are designed for analyzing TSP filters collected by high volume samplers. With a large number of PM_{10} samplers in operations, it would be desirable to evaluate suitability of applying the candidate ICP-MS methods to the PM_{10} filters collected by more widely used PM_{10} samplers. If the new ICP-MS based FRM is also suitable for analyzing the PM_{10} filters collected by common PM_{10} samplers, it will make it easier for monitoring agencies to analyze these filters for Pb and other metals, not necessarily for lead NAAQS attainment determination but for other air programs.

Charge Question 3: What are the panel's views on the approach described for evaluating and testing the method prior to proposal as a new FRM for Pb-TSP?

The proposed approach seems to be comprehensive. I don't have specific comments at this time.

Charge Question 4: Inter-laboratory testing of the method will be done to assess between-laboratory variability (CV) at the 95% confidence interval. What are the panel's views on a reasonable level of inter-laboratory variability?

The proposed inter-laboratory variability level seems to be reasonable. I don't have specific comments at this time.