

**UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON D.C. 20460**



OFFICE OF THE ADMINISTRATOR  
SCIENCE ADVISORY BOARD

DATE

The Honorable Lisa P. Jackson  
Administrator  
U.S. Environmental Protection Agency  
1200 Pennsylvania Avenue, N.W.  
Washington, D.C. 20460

Subject: CASAC Review of EPA's White Paper, "Approach for the Development of a New Federal Reference Method (FRM) for Lead in Total Suspended Particulates (Pb-TSP)"

Dear Administrator Jackson:

In November 2008, EPA published the final rule for the National Ambient Air Quality Standard (NAAQS) for lead, revising the primary standard an order of magnitude, from  $1.5 \mu\text{g}/\text{m}^3$  to  $0.15 \mu\text{g}/\text{m}^3$ . The indicator for the Lead NAAQS, lead in total suspended particulates (Pb-TSP), did not change. As a result of the lowering of the Lead NAAQS and improvements in analytical measurement technologies, EPA has developed the white paper, *Approach for the Development of a New Federal Reference Method (FRM) for Lead in Total Suspended Particulates (Pb-TSP)*, which outlines the approach for the development of a new FRM for Pb-TSP. EPA requested that the Ambient Air Monitoring and Methods Subcommittee (AAMMS, or the Subcommittee) of the Clean Air Scientific Advisory Committee (CASAC) provide a peer review of the white paper. As part of the peer review, the Subcommittee held a public teleconference on September 15, 2010 and discussed comments in response to EPA's four charge questions, which centered on extraction methods, analytical methods, validation and testing, and inter-laboratory variability. The CASAC and AAMMS membership is listed in Enclosure A. The Subcommittee's consensus responses to the Agency's charge questions are presented in Enclosure B. Individual review comments from the Subcommittee are compiled in Enclosure C. Major highlights of the report are presented below.

EPA's white paper presents a new Pb-TSP FRM consisting of two extraction methods, ultrasonic bath with a nitric acid/hydrochloric acid solution and hot block reflux with nitric acid, followed by analysis using inductively coupled plasma-mass spectrometry (ICP-MS). The white paper also presents EPA's plan for method evaluation and testing, including intra- and inter-laboratory testing. The Subcommittee finds that the two extraction methods are generally appropriate. However, there are additional, applicable extraction methods, such as microwave digestion, that should be included in the FRM assessment for adoption either as an FRM or

1 Federal Equivalent Method (FEM). With regards to the analytical method, the Subcommittee  
2 finds ICP-MS to be appropriate, yet recommends a strategy that provides flexibility, such that  
3 other agencies can use other methods, such as Graphite Furnace Atomic Absorption  
4 Spectrometry (GFAAS), with relative ease. The white paper suggests that evaluation of the  
5 FRM include other metals. This may not be necessary, since PM<sub>10</sub> FRM Teflon filter samples  
6 are much better suited for this purpose and they avoid issues with the high-volume sampler size  
7 cut and possible blank contamination of the high-volume filters for trace metal analysis. With  
8 regards to the method evaluation and testing, the Subcommittee notes that the current FRM can  
9 still provide reliable results, and could be retained as an FRM or FEM, along with the additional  
10 methods being assessed. During the teleconference, EPA indicated that this avenue is being  
11 investigated. EPA should consider allowing the various methods for extraction to be used with  
12 either ICP-MS, the new method being assessed, or Flame Atomic Adsorption Spectroscopy  
13 (FAAS), the current technique being used for analysis. Similar to our past recommendations,  
14 EPA should consider developing performance-based standards to define FRMs, in this case for  
15 both extraction and analysis. The Subcommittee finds a range of weaknesses in the proposed  
16 method evaluation and testing and makes several recommendations to strengthen it. The  
17 Subcommittee is generally comfortable with the comprehensiveness of the planned inter-  
18 laboratory testing, but recommends that EPA consider decoupling the extraction methods from  
19 the analytical methods in the evaluations. The Subcommittee does not recommend a specific  
20 level of acceptable inter-laboratory variability, but recommends identifying and taking into  
21 consideration the data quality objectives of the overall measurement.

22  
23 During the meeting, the Subcommittee also discussed the merits of alternative sampling  
24 methods, although EPA's white paper did not discuss sampling issues. EPA should consider,  
25 again, the use of lead in PM<sub>10</sub> (Pb-PM<sub>10</sub>) as the indicator for lead exposure. In the prior NAAQS  
26 review, it was unclear that Pb-PM<sub>10</sub> would comprehensively characterize the many routes of  
27 exposure to ambient air lead. Source characteristics have changed over the years, and if studies  
28 show that Pb-PM<sub>10</sub> is an appropriate indicator for characterizing lead exposure, low-volume  
29 PM<sub>10</sub> sampling has further advantages, including their widespread use and ability to measure  
30 multiple compounds in addition to lead. As applicable field studies are conducted, the use of Pb-  
31 PM<sub>10</sub> should be evaluated to lay the foundation for consideration of its use as the Pb indicator in  
32 future NAAQS reviews. The AAMMS previously provided advice and recommendations on  
33 using Pb-PM<sub>10</sub> sampling in 2008 and the Agency is referred to the August 26, 2008 CASAC  
34 AAMMS report for further details. If the agency determines that Pb-PM<sub>10</sub> is not appropriate,  
35 we encourage the development of a more robust larger particle sampler. Low-volume TSP  
36 sampling would allow the use of alternative filter substrates than are currently used in high-  
37 volume TSP samplers. EPA has noted the possibility of developing a medium-volume sampler  
38 for Pb that would have a well-characterized size cut of approximately 18-20 microns.



**NOTICE**

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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. 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>.

1 **Enclosure A – Rosters**

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5 **Ambient Air Monitoring and Methods Subcommittee (AAMMS)**  
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28 \* Did not participate in the review  
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\* Roster to be updated

## Enclosure B

### CASAC AAMMS Consensus Responses to Charge Questions on EPA's White Paper, *Approach for the Development of a New Federal Reference Method (FRM) for Lead in Total Suspended Particulates (Pb-TSP)*

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 major aspects of the three methods are compared in the following Table. 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 white paper, the hydrochloric acid 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.

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 <sub>3</sub>	15 mL, 1 M HNO <sub>3</sub> , 2 M HCl	20 mL, 1:19 v/v HNO <sub>3</sub>
Extraction	30 min, boiling	60 min, 80 °C	60 min, 95 °C

Although many versions of the traditional extraction approach using heated ultrasonic water bath with nitric/hydrochloric acids have been used successfully, they do not represent the current state-of-art extraction approaches (e.g., microwave digestion). Compendium Method IO-3.1 (USEPA, 1999a) describes a validated microwave digestion method that EPA originally developed in 1989. Qureshi, et al. (2006) describe a more contemporary approach to microwave digestion. A survey of the recent literature should permit an easy update of EPA's Compendium Method IO-3.1. Thus, it would be straightforward to incorporate microwave digestion in the intercomparison tests and determine its equivalence to the other proposed methods. It has the advantage of handling a greater sample throughput with the potential for reduced sample-to-sample variability, given the features of current generation microwave digestion systems. Thus, the Subcommittee recommends moving forward with the ultrasonic bath and hot block reflux methods, but adding microwave digestion as an additional option. Given the variety of potential methods available which appear to perform well, another approach would be to develop performance-based standards (quantification of extraction efficiency) to define acceptable extraction procedures for the FRM.

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

The Subcommittee views that inductively coupled plasma-mass spectrometry (ICP-MS) is an appropriate analytical method for the Pb-TSP FRM. ICP-MS has superior sensitivity and specificity for Pb, which is a key criterion for the FRM. Furthermore, the method can generate data for multiple elements and, depending on the sensitivity of the instrument, can generate data

1 for the isotopic composition of Pb, which can provide insight into source attribution. Many  
2 state/local agencies are already operating ICP-MS instruments, as demonstrated by the data  
3 reported to EPA for PM<sub>10</sub> air toxics metals (including Pb) under the National Air Toxics Trends  
4 Stations (NATTS) program.

5  
6 There are advantages to designating a single analytical method as the FRM, especially if  
7 it has sufficiently high performance that it would remain a suitable method, should revisions be  
8 made to the Pb NAAQS. That said, the Subcommittee recommends a strategy that provides  
9 flexibility, such that agencies can use other methods such as Graphite Furnace Atomic  
10 Absorption Spectrometry (GFAAS), if they are deemed suitable. One approach would be to  
11 designate a performance-based FRM, which would define key performance criteria for minimum  
12 detection limit (MDL), precision, accuracy, linearity, and tolerance for interference. An FRM  
13 based solely on performance, however, has the drawback that each monitoring agency would  
14 have to demonstrate the ability to meet these performance criteria, which could be burdensome.  
15 Alternatively, a single analytical method could be designated as the FRM and performance  
16 criteria could be defined to serve as the basis for Federal Equivalent Method (FEM) designations.  
17 In this case, the Subcommittee strongly recommends that the proposed evaluation of candidate  
18 FRM methods also include analytical methods beyond ICP-MS (including, but perhaps not  
19 limited to, GFAAS) with the intent that methods meeting the performance criteria would be  
20 directly designated as an FEM. In effect, EPA would have completed the FEM process for any  
21 monitoring agencies that would like to use these qualified methods. This approach should be  
22 more cost effective and provide a high level of consistency because all candidate methods are  
23 evaluated by the same labs using the same procedures.

24  
25 The Subcommittee also recommends that EPA consider:

- 26  
27 • Evaluating and possibly designating as an FRM or FEM commonly used ICP-MS  
28 based analytical methods, such as EPA Compendium Method IO-3.5 (USEPA,  
29 1999b) which is already used by many monitoring agencies for NATTS sample  
30 analysis.
- 31 • Including low-volume PM<sub>10</sub> samples collected on Teflon filters with analysis by X-  
32 Ray Fluorescence (XRF) as part of the candidate FRM testing. While this advisory  
33 response focuses on the Pb-TSP method, EPA promulgated an FRM for the  
34 determination of Pb in PM<sub>10</sub> (CFR, Appendix Q to Part 50) and in the future may  
35 consider the feasibility of low-volume TSP sampling.
- 36 • Including the current FRM analytical method (FAAS) in the evaluation of candidate  
37 FRM methods to assess comparability and help bridge past and future data.
- 38 • Including the analysis of other elements in the candidate FRM tests. Since the  
39 monitoring agencies would be able to analyze for multiple elements at a small  
40 incremental cost (at least for methods such as ICP-MS), the documentation of method  
41 performance for multiple elements would assist the agencies in prudent use of such  
42 data for air toxics, studies, source apportionment, etc. However, it should be noted  
43 that the high-volume TSP method (sampler and filter media) are less suitable for  
44 other metals than a PM<sub>10</sub> Teflon filter sample due to the limitations inherent in the  
45 TSP sampler as well as potential limitations of TSP filter media for trace metal  
46 analysis.

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

4 The overall approach to validation and testing needs to include a comparison to the  
5 existing extraction and analytical methods. A satisfactory comparison to the existing methods  
6 will ensure that the data collected using a new FRM will be consistent with the older Pb database.  
7 This is not likely to be an issue, but it is good practice and should prevent any unexpected  
8 changes in the resultant dataset.  
9

10 The test matrix, as outlined in the white paper, sets a low bar for validation of the  
11 proposed methods for extraction and analysis of Pb from glass and quartz fiber filters. It also  
12 does not include enough detail on issues such as how the spiked samples will be prepared, which  
13 lab will determine the accuracy and precision of the spiked samples, and whether the sampled  
14 filters will include potential interferences (such as heavy and light loadings of metals, and other  
15 pollutants such as elemental carbon). To address these issues, the test protocol should include a  
16 description of how the test strips are prepared and include an analysis of a subset of the prepared  
17 strips by an acceptable reference laboratory. The selection process for the sampled filters should  
18 be more clearly specified and should include some potential interferences for the extraction and  
19 analytical processes. Archived filters are available and it is likely that state and local monitoring  
20 agencies can assist with the selection of appropriate filters.  
21

22 EPA has based the development of the Pb analytical FRM on the Office of Solid Waste's  
23 SW-846 Method 6020A (USEPA, 2007). This method does not have adequate Quality  
24 Assurance for analysis of samples used in a compliance oriented air monitoring network. The  
25 following recommendations address some of the criteria that are specified in the test matrix in  
26 the white paper, but need to be strengthened for a Pb FRM.  
27

- 28 • The Low Level Calibration Verification (LLCV ) should be  $\pm 10\%$ .
- 29 • The Low Level Quality Control Sample (LLQC ) is not really that low since it is 30%  
30 of the NAAQS. The recovery limits should be at minimum  $\pm 15\%$ .
- 31 • The recoveries of Standard Reference Material (SRM) spiked on unexposed filter  
32 strips at all concentrations should be  $\pm 10\%$ .
- 33 • The 3 non-sequential results should not be averaged in the bias calculation. This will  
34 not provide an indication of single sample bias, which is how actual samples are  
35 analyzed. In general  $\pm 10\%$  bias is too loose, but 5% may be too stringent. A  
36 precision of 10% seems reasonable, because it includes the uncertainty due to  
37 potentially uneven loadings from sampled filters.
- 38 • The replicate analysis, as specified in EPA 6020A, only requires one replicate  
39 analysis per batch. The batch size must be specified in the method since new  
40 extractors can accommodate up to 96 samples. One replicate for every 20 samples  
41 should be considered to be a minimum.  
42

43 The Pb FRM development program should include Teflon filter media, as well as an  
44 accommodation for the analysis of other pertinent elements for air toxics and source attribution  
45 work. This will not conflict with the TSP Pb FRM field sampler since the extraction and  
46 analytical portion of the FRM can be separated from the sample collection method. It may be

1 appropriate to constrain evaluation of the high-volume TSP sampler filter extraction process to  
2 Pb, since most air agencies would presumably use the PM<sub>10</sub> FRM with Teflon filters for other  
3 metals analysis. Teflon filters from a PM<sub>10</sub> FRM are more suitable for trace metal analysis than  
4 the quartz or glass fiber media needed for TSP samplers because of fewer contamination issues.  
5 Teflon filters can also be used for XRF analysis, a cost effective approach for analysis of  
6 multiple elements.

7  
8 4. *Inter-laboratory testing of the method will be done to assess between-laboratory variability*  
9 *(CV) at the 95% confidence interval. What are the Panel's views on a reasonable level on*  
10 *inter-laboratory variability?*  
11

12 The Subcommittee is generally comfortable with the comprehensiveness of the planned  
13 inter-laboratory testing. A full array of laboratory and extraction method comparisons will be  
14 performed using spiked and archived sample filter strips. The results will be analyzed to  
15 distinguish the components of variance attributable to intra-laboratory precision and inter-  
16 laboratory bias. The Subcommittee believes that the existing Federal Reference Method for  
17 extraction and analysis should be added to the experimental design to support quantitative  
18 comparisons between new and historical data.

19  
20 The Subcommittee urges the Agency to consider decoupling the tests of extraction and  
21 analysis, as is recommended by EPA's methods development and validation guidance (USEPA,  
22 1992) cited in the white paper. Extraction and analysis could be distinguished by collecting  
23 different laboratories' extracts for analysis by a single operator on a single instrument, and  
24 sending extracts prepared by a single operator to different laboratories for analysis. The  
25 procedure-resolved results would allow future consideration of alternative method combinations.  
26

27 On the specific question of "a reasonable level of inter-laboratory variability", the  
28 theoretical implications of target bias and precision values are discussed in the individual  
29 comments by Dr. Warren White. The Subcommittee does not recommend a specific level, but  
30 rather recommends identifying and taking into consideration the data quality objectives of the  
31 overall measurement.  
32  
33

34 **References:**  
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40

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- 2 Filter Material. In *Compendium of Methods for the Determination of Inorganic Compounds in*
- 3 *Ambient Air*, EPA/625/R-96/010a, Cincinnati, OH.
- 4
- 5 USEPA. 1999b. Compendium Method IO-3.5, Determination of Metals in Ambient Particulate Matter
- 6 Using Inductively Coupled Plasma/Mass Spectrometry (ICP/MS). In *Compendium of Methods for the*
- 7 *Determination of Inorganic Compounds in Ambient Air*, EPA/625/R-96/010a, Cincinnati, OH.
- 8
- 9 USEPA, 2007. Method 6020A, Inductively Coupled Plasma-Mass Spectroscopy. In *Test*
- 10 *Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846)*, Washington, DC.

**Enclosure C**

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3 **Compendium of Individual CASAC AAMMS Comments on EPA’s White Paper, *Approach***  
4 ***for the Development of a New Federal Reference Method (FRM) for Lead in Total Suspended***  
5 ***Particulates (Pb-TSP)***  
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9 **Comments from Mr. George A. Allen..... 14**  
10 **Comments from Dr. Judith Chow ..... 16**  
11 **Comments from Mr. Bart Croes ..... 20**  
12 **Comments from Dr. Kenneth Demerjian ..... 22**  
13 **Comments from Dr. Delbert J. Eatough..... 23**  
14 **Comments from Mr. Dirk Felton ..... 27**  
15 **Comments from Dr. Philip Hopke ..... 30**  
16 **Comments from Dr. Jay Turner..... 31**  
17 **Comments from Dr. Warren White ..... 34**  
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1 **Comments from Mr. George A. Allen**

2  
3 General background

4  
5 This charge to the AAMMS does not include the sample collection method for the Pb  
6 FRM -- that remains the Hi-Volume sampler with quartz or glass-fiber filters at this time. The  
7 issues discussed here are related to analysis of these filters for Pb and related issues, in the  
8 context of revising the Pb FRM's analytical method to better suit the new and much (10 times)  
9 lower PB NAAQS that is now in effect. As EPA notes, this large drop in the NAAQS requires  
10 revision of the analytical method to insure that data of high quality can be reported at these much  
11 lower concentration loadings on the FRM Hi-Vol filter. These lower loadings require assessment  
12 of both the filter extraction process and the analysis method used for the Pb FRM. Analytical  
13 methods have also changed dramatically since the Pb FRM was last revised; this process allows  
14 the FRM to be updated to take advantage of these newer technologies.

15  
16 It is important to note that for these components of the Pb FRM, there are likely to be  
17 FEM methods approved that may be more practical for routine use. Still, it is important to have a  
18 robust and well characterized FRM in place even though analysis of Pb from Hi-Vol filters by  
19 any reasonable method with sufficient sensitivity is probably much more robust than the  
20 uncertainties inherent in the existing Pb FRM Hi-Vol sampling method. This process updates the  
21 "back end" of the method; I strongly encourage EPA to continue development of a "larger  
22 particle Lower-Vol" Pb FRM sampler that can provide accurate and reproducible samples to  
23 better harmonize the improvements in the Pb-FRM filter analysis being discussed here.

24  
25 *Charge Question 1. "What are the panel's views on the two extraction method options of heated*  
26 *ultrasonic and graphitic hot block with nitric/hydrochloric acid for the extraction of Pb from*  
27 *TSP?"*

28  
29 Either extraction method should meet the needs of a revised Pb FRM, and both of these  
30 methods are currently approved by EPA as FEM methods for Pb extraction off a Hi-Vol filter.  
31 Assuming their performance is similar across the expected lower range of Pb filter loadings, I  
32 would recommend using the simpler method, which in this case appears to be the graphitic hot  
33 block with nitric acid, Method EQL-0710-192. It is worth noting here that a graphitic hot block  
34 may not be necessary; aluminum has been shown to work well and is a simpler approach. While  
35 the other method (sonication and both acids, EQL-0510-191) may be needed for extraction of  
36 other metals, it is not needed for Pb, and this is a Pb FRM, not an FRM intended for wider use.  
37 Sonication adds complexity to the method especially if "trace" analysis protocols are used;  
38 quartz fiber filters produces a "filter mush" that requires an extra step to remove the filter  
39 material from the liquid, usually with a centrifuge. Glass fiber filters may also need this  
40 treatment after sonication.

1 *Charge Question 2. “What are the panel’s views on ICP-MS as the analysis method for Pb-*  
2 *TSP?”*

3  
4 For the Pb-FRM, ICP-MS is clearly the preferred analysis technique. It is a highly  
5 sensitive and specific method for Pb; there are no other obvious candidate methods.

6  
7 *Charge Question 3. “What are the panel’s views on the approach described for evaluating and*  
8 *testing the method prior to proposal as a new FRM for Pb-TSP?”*

9  
10 The described approach is rigorous. The description of the “archived” field (real  
11 samples?) filters needs to be clarified -- where are the samples from, what are the loadings, etc.  
12 This use of real samples for assessing extraction, especially at lower Pb loadings, is an important  
13 part of the evaluation since dry loading combined with a large amount of other material may  
14 effect the extraction process. The information in Table 1 (dry NIST SRMs) needs clarification.  
15 How will the dry SRM be applied to the filter? What does the “minimum weight” column mean?  
16

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

28  
29 *Charge Question 4. “Inter-laboratory testing of the method will be done to assess between*  
30 *laboratory variability (CV) at the 95% confidence interval. What are the panel’s views on a*  
31 *reasonable level of inter-laboratory variability?”*

32  
33 Inter-laboratory method testing is an important component of the FRM assessment, since  
34 it will better reflect the real-world performance of the method -- which is usually somewhat  
35 degraded from ideal testing conditions. For an acceptable level of inter-lab variability that  
36 includes variability from filter extractions, a starting point for this value might be the recovery  
37 range noted in the white paper: “The SRMs are expected to be recovered within 80 to 120% of  
38 the certified value per method 6020A”. If initial test results show a tighter recovery range, then  
39 the inter-lab criteria could be tightened. I would expect much of the inter-lab variability to be  
40 from the extraction process, since a well-controlled ICP-MS analysis for Pb should have  
41 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.

*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 [HNO<sub>3</sub>]/2.23 M hydrochloric acid [HCl]) and graphite hot block (with 3.5 % HNO<sub>3</sub> [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. However, the extraction method should be performance-based (e.g., Ashley et al., 1999; Oehme and Lund, 1979) and not limited to the two most commonly used extraction methods defined in the white paper. For example, Moreira et al. (2005) showed that the microwave and the heating block digestion methods performed equally well for lead.

The procedure for the heated ultrasonic HNO<sub>3</sub>/HCl method is more cumbersome and requires a centrifuge to complete the extraction. This method adds 15.0 ± 0.15 ml of the HNO<sub>3</sub>/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; HNO<sub>3</sub> 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 HNO<sub>3</sub> (1:19 v/v) from concentrated HNO<sub>3</sub> (67 – 70%) to each extraction vessel, ensuring that the filter strip is covered with HNO<sub>3</sub> 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 *Question 2: What are the panel's views on ICP-MS as the analysis method for Pb-TSP?*

2  
3 As stated in the white paper, Pb can be analyzed by ICP-MS, just as it can be analyzed by  
4 atomic absorption spectrometry (AAS) with a graphite furnace and ICP-atomic emission  
5 spectroscopy (ICP-AES) once it is in solution. It can be accurately quantified to several orders of  
6 magnitude below the necessary working range. The ICP-MS should support a method detection  
7 limit (MDL) of 0.0075  $\mu\text{g}/\text{m}^3$ . The instrument will be well within its capabilities, resulting in  
8 accurate and precise results.

9  
10 The analysis method for Pb should be performance-based. As long as the MDL,  
11 precision ( $\pm 15\%$  at 90% confidence interval), and accuracy ( $\pm 5\%$ ) are within the EPA's specified  
12 levels, other analytical methods (e.g., AAS with graphite furnace, ICP-AES, X-ray fluorescence  
13 [XRF], or proton-induced X-ray emission [PIXE]) should be available as options (e.g., Harper et  
14 al., 2004; Margui et al., 2005). Unless the state or local agency is already set up for ICP-MS, it  
15 will be costly to initially identify, procure, and set-up for acid digestion ( $\sim \$5,000 - 10,000$ ; e.g.,  
16 hot block, flow hood) and ICP-MS ( $\sim \$200,000$ ). An advantage of ICP-MS is the ability to  
17 quantify different isotopic abundances for Pb, which may be related to their sources (Moreira et  
18 al., 2005; Oehme and Lund, 1979; Huggins, 2002; Herner et al., 2006).

19  
20 *Question 3: What are the panel's views on the approach described for evaluating and testing the*  
21 *method prior to proposal as a new FRM for Pb-TSP?*

22  
23 The white paper states the proposed approach for determining method performance (i.e.,  
24 analysis of standard reference materials [SRMs], verification of filters spiked with a known  
25 concentration of NIST traceable Pb salts solution, examination of interference and filter matrix  
26 effects, determination of MDL, and intra-laboratory method performance [e.g., assess bias within  
27  $\pm 10\%$  and precision within  $\pm 15\%$ , evaluation of glass and quartz-fiber filter matrices, analysis of  
28 spiked filter strips, SRMs, and real-world samples, tests for small variations in extraction  
29 temperature and time, and evaluation of extract storage stability]).

30  
31 Additional tests need to be planned and conducted to ensure 100% extraction efficiency.  
32 Extraction of spiked-samples with NIST traceable Pb salt or SRMs does not necessarily verify  
33 the extent of a complex matrix of ambient or source samples.

34  
35 *Question 4: Inter-laboratory testing of the method will be done to assess between-laboratory*  
36 *variability (CV) at the 95% confidence interval. What are the panel's views on a reasonable*  
37 *level of inter-laboratory variability?*

38  
39 Inter-laboratory testing as listed in the white paper (e.g., method performance assessment  
40 of the four participating laboratories, analysis of spiked filter samples and actual filter samples)  
41 is adequate. It would be worthwhile to examine previously published composition for Pb  
42 analyses. It would also be helpful to specify the concentration range representing the measured  
43 and calibrated concentration range. The total number of samples to be performed for each type of

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

3  
4 In addition to the calculation of coefficient of variation (CV) at the 95% confidence  
5 interval, equivalence and comparability should be established for the inter-laboratory comparison  
6 as defined in Mathai et al. (1990). The U.S. EPA criteria for equivalence between Federal  
7 Equivalent Methods (FEM) and FRM for PM<sub>2.5</sub> mass concentration, such as: 1) linear regression  
8 slope of  $1 \pm 0.05$ ; 2) linear regression intercept of  $0 \pm 1 \mu\text{g}/\text{m}^3$ ; and 3) linear regression  
9 correlation coefficient ( $r$ ) of  $\geq 0.97$  can be modified and adapted for “equivalence.” The  
10 following criteria can be considered for “comparability” within the stated precision: 1) the slope  
11 (by either ordinary least squares [OLS] or effective variance [EF] weighting) equals unity within  
12 three standard errors, or average ratios ( $y/x$ ) equal unity within one standard deviation; 2) the  
13 intercept does not significantly differ from zero within three standard errors; and 3) the  
14 correlation coefficient exceeds 0.9 (Berkson, 1950; Kendall, 1951; Madansky, 1959). This is a  
15 less demanding definition than equivalence because it considers the reported precisions of the  
16 two measurements being compared; these may be larger than the requirements for an FEM used  
17 to determine compliance, but still sufficient to discern concentration differences (Watson and  
18 Chow, 2002).

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17  
18

1 **Comments from Mr. Bart Croes**

2  
3 Staff should be commended for taking a systematic approach towards implementation of  
4 the revised National Ambient Air Quality Standard (NAAQS) for lead (Pb) in total suspended  
5 particulates (TSP). I appreciate the opportunity to comment during several stages of the process,  
6 and agree with the general approach taken by U.S. EPA toward extraction and analysis as  
7 described in the white paper. My comments reflect input from California Air Resources Board  
8 (ARB) staff responsible for implementing U.S. EPA monitoring requirements and using the data  
9 in source apportionment and health studies.

10  
11 **Charge Questions:**

12  
13 *1. What are the panel's views on the two extraction method options of heated ultrasonic and*  
14 *graphitic hot block with nitric/hydrochloric acid for the extraction of Pb from TSP?*

15  
16 Both methods are acceptable for extraction of Pb from TSP for NAAQS compliance  
17 purposes. Since SLT agencies are already extracting Pb as part of source apportionment and air  
18 toxics monitoring networks, and want to conserve resources, this flexibility is desirable. Pb is  
19 easy to extract, but it would be desirable to have performance standards for extraction efficiency  
20 in order to demonstrate equivalency for data from other existing networks.

21  
22 *2. What are the panel's views on ICP-MS as the analysis method for Pb-TSP?*

23  
24 ICP-MS is preferred as the FRM, but other analytical methods besides should be allowed.  
25 The ARB air toxics network (Xontech 924, low volume sampler TSP, Teflon filter) uses ICP-MS  
26 for toxic metals, including Pb, because of high accuracy and precision across many species (in a  
27 single scan) over the entire ambient concentration range.

28  
29 The Flame Atomic Absorption Spectroscopy (FAAS) method is used for the existing high  
30 volume sampler TSP-Pb network by many SLT agencies, and also has good precision and  
31 accuracy. The FAAS method should be retained as an FEM. ARB's high volume sampler TSP-  
32 Pb network uses Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) and has a  
33  $1.0 \text{ ng/m}^3$  ( $0.0010 \text{ } \mu\text{g/m}^3$ ) limit of detection (LOD), far below the new NAAQS of  $0.15$   
34  $\mu\text{g/m}^3$ . A cursory look at the last few months of data from two FRM sites (Calexico and  
35 Tijuana) showed all results to be well above this LOD. The GFAAS method should be retained  
36 as an FEM.

37  
38 *3. What are the panel's views on the approach described for evaluating and testing the method*  
39 *prior to proposal as a new FRM for Pb-TSP?*

40  
41 With the inclusion of the AAS methods discussed above, the approach described for  
42 evaluating and testing the proposed analytical method for a Pb-TSP FRM appears adequate,  
43 especially the range of spiked and ambient samples and number of proposed facilities (four) for  
44 the inter-laboratory comparison. The criteria that each laboratory will achieve bias (accuracy)  
45  $\leq 10\%$  and precision  $\leq 15\%$  for the spiked filter strips seems loose and could be tightened.

1 Typically, the ARB laboratory sees  $\leq 5\%$  bias and  $\leq 5\%$  precision for metals analyses, but perhaps  
2  $\leq 10\%$  for both is a more realistic expectation.  
3

4 *4. Inter-laboratory testing of the method will be done to assess between-laboratory variability*  
5 *(CV) at the 95% confidence interval. What are the panel's views on a reasonable level of inter-*  
6 *laboratory variability?*  
7

8 An inter-laboratory bias (accuracy)  $\leq 10\%$  and precision  $\leq 15\%$  for the group of  
9 measurements that make up a 3-month average is a reasonable expectation. The inter-laboratory  
10 comparison should be weighted toward the ambient samples and spiked samples that are near the  
11 level of the NAAQS.  
12  
13  
14

1 **Comments from Dr. Kenneth Demerjian**

2  
3 *Charge question 1. What are the panel's views on the two extraction method options of heated*  
4 *ultrasonic and graphitic hot block with nitric/hydrochloric acid for the extraction of Pb from*  
5 *TSP?*  
6

7 The ideal approach would be to develop performance based standards (quantification of  
8 extraction efficiency) from which to quantify acceptable extraction procedures. The design of an  
9 intercomparison study which would consider a wide-range of real-world samples (i.e. spanning  
10 filter loading and particle composition) to evaluate these techniques will result in substantial  
11 additional work for EPA. Although many versions of the traditional extraction approach using  
12 heated ultrasonic water bath with nitric/hydrochloric acids have been used successfully, they do  
13 not represent the current state-of-art (e.g. microwave digestion). If the agency or states view the  
14 Pb measurement approach as an opportunity to consider the measurement of other PM metals the  
15 newer digestion technologies may be of even greater interest.  
16

17 *Charge question 2. What are the panel's views on ICP-MS as the analysis method for Pb-TSP?*  
18

19 The ICP-MS is the state-of-art measurement method of choice.  
20

21 *Charge question 3. What are the panel's views on the approach described for evaluating and*  
22 *testing the method prior to proposal as a new FRM for Pb-TSP?*  
23

24 The subject white paper provides an acceptable description and adequate guidance  
25 regarding the development of a new FRM for Pb-TSP and QA/QC requirements.  
26

27 *Charge question 4. Inter-laboratory testing of the method will be done to assess between*  
28 *laboratory variability (CV) at the 95% confidence interval. What are the panel's views on a*  
29 *reasonable level of inter-laboratory variability?*  
30

31 The proposed inter-laboratory testing procedures as outlined are adequate to judge the  
32 performance and acceptability of individual laboratories. Differences in laboratory performance  
33 may likely reside from sampling handling and preparation (i.e. extraction). An assessment of the  
34 typical variability in extraction efficiencies may be the determining factor in what should be  
35 viewed as to reasonable level of inter-laboratory variability.  
36  
37

## Comments from Dr. Delbert J. Eatough

Individual response to Charge Questions for the Clean Air Scientific Advisory Committee's (CASAC) Ambient Air Monitoring & Methods Subcommittee Peer Review on the Approach for the Development of a New Federal Reference Method (FRM) for Lead (Pb) in Total Suspended Particulates (TSP).

Prepared in connection with the AAMMS committee consensus response to EPA in connection with the September 15, 2010 AAMMS call.

*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 <sub>3</sub>	15 mL, 1 M HNO <sub>3</sub> , 2 M HCl	20 mL, 1:19 v/v HNO <sub>3</sub>
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. This method does, however add an additional step to remove the fibers produced. As pointed out by others, all of the techniques are a little dated. Using a more current technique, such as microwave digestion would be preferable. 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 reports.

Likewise, there are no studies from any given laboratory which allow comparisons of the three techniques. EPA is planning a detailed laboratory study as part of the protocol moving

1 forward. This will be a valuable step and should do much to better define important elements  
2 which should be part of the EPA inter-laboratory evaluation and testing program to follow.  
3

4 Finally, I would like to suggest that all three methods, plus microwave extraction, and not  
5 just the two outlined in the white paper should be evaluated on an equal footing. This will  
6 provide a tie to previous analyses and give an indication as to whether a change from the older  
7 analytical scheme is needed with respect to the extraction method.  
8

9 *2. What are the panel's views on ICP-MS as the analysis method for Pb-TSP?*  
10

11 The analytical techniques used for the determination of Pb in the various extract solutions  
12 to be analyzed, as outlined in charge question 1, is required by EPA to have a MDL for Pb of 5%  
13 of the NAAQS (0.15 µg/m<sup>3</sup>), or 0.008 µg/m<sup>3</sup>. As recently summarized by C 33 avender (EPA,  
14 OAQPS) in a presentation at the March 2, 2009 National Air Quality Conference in Addison,  
15 TX, expected MDLs for Pb in TSP and PM<sub>10</sub> methods are:  
16

Estimated MDL: (µg/m <sup>3</sup> )	Sample Analysis Methods
0.002 to 0.00005 <sup>a,c</sup>	Graphite Furnace Atomic Absorption (GFAA)
0.0007 <sup>b</sup>	Energy-dispersive X-Ray Fluorescence (EDXRF)
0.00006 <sup>c</sup>	Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
0.0003 <sup>c</sup>	Inductively Coupled Plasma Atomic Emission spectrometry (ICP-AES/OES)

<sup>a</sup> Estimated MDL retrieved from AQS  
<sup>b</sup> 40 CRF Part 50, Appendix Q  
<sup>c</sup> 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

17  
18  
19 Each of the methods listed above are capable of given data within the required MDL.  
20 While ICPMS has the anticipated lowest MDL in the Table, this extra level of lower detection is  
21 not needed for the purposes of the NAAQS for Pb as currently outlined. While evaluating the  
22 ICP-MS method as an alternate method for data analysis would be warranted, I see no reason to  
23 dump the long standing GFAA method for which we have decades of experience. Moving ahead  
24 with both methods in the evaluation proposed by EPA would seem warranted. The comparison  
25 of the two methods will enhance our understanding of both precision and accuracy in the  
26 determination of Pb under the current standard. Since both methods will use the various extract  
27 solutions outlined in charge question 1, there is no practical impediment to this approach.  
28

29 I would like to make a few final points in regards to the above Table. All of the  
30 techniques, except for EDXRF analysis are ideally suited for analysis of solutions, such as those  
31 produced by the procedures highlighted under charge question 1. However, the procedures  
32 required to produce those solutions are laborious, expensive and prone to sample contamination  
33 introduction. The solution extraction approach is required under the current FRM technique for  
34 Pb in TSP. But making an effort to move any from this requirement would be highly desirable.

1 EPA has put in place the possibilities for both low volume TSP samplers or the acceptance of a  
2 PM<sub>10</sub> value for Pb measurements in the future in the 40 CFR 50 document. These were both  
3 directions the AAMMS urged EPA to move in the past and I encourage EPA to actively  
4 incorporate evaluation of these methods into some phases of the development of FRMs for Pb. If  
5 such a path is not taken, then comparison data which would allow the incorporation of either a  
6 low volume TSP sampler or a PM<sub>10</sub> metric in the future will not be obtained and moving one of  
7 these directions will not be possible. Either technique would allow the use of EDXRF (or  
8 equivalent methods) for the direct analysis of collected samples without an extraction step. This  
9 would be highly desirable.

10  
11 *3. What are the panel's views on the approach described for evaluating and testing the method*  
12 *prior to proposal as a new FRM for Pb-TSP?*

13  
14 As outlined in the charge questions and in the white paper, the approach which EPA will  
15 take to validate any new methods for analysis of TSP Pb is based on the guidance documents  
16 and references provided with the charge questions. Particular weight is given to information  
17 contained in Validation and Peer Review of U.S. Environmental Protection Agency Chemical  
18 Methods of Analysis, prepared for The EPA Forum on Environmental Measurements (FEM);  
19 FEM Document Number 2005-01, October 14, 2005. The approach to be used includes the  
20 analysis of Standard Reference Materials (SRMs) and NIST-traceable Pb salt solutions;  
21 assessment of method detection limits (MDLs), bias, precision; and inter-laboratory testing to  
22 assess between laboratory variability. The approach is reasonable, well thought out and based on  
23 solid guidance to EPA. I urge EPA to keep in focus the point that the lowest MDL is not the  
24 prime factor which should be considered in making a decision. As long as any analytical  
25 technique has a MDL within the requirements of the standard, it should be evaluated on an equal  
26 footing with the methods with the lowest MDL. There are three important modifications I would  
27 suggest to the approach outlined in the white paper:

- 28  
29 (1). Include in the single laboratory evaluation of the four extraction methods outlined  
30 in 1. above to better inform the process and set the protocols as EPA moves into  
31 multilaboratory evaluations.  
32  
33 (2). Include a minimum of both ICP-MS and GFAA in both the single laboratory  
34 study and multi-laboratory evaluations so that there is a solid basis for either  
35 retaining the GFAA method in the FRM (along with ACP-MS if adopted) or  
36 switching to only the ICP-MS method. I urge this evaluation because of the  
37 legacy in both data and laboratory experience with the current analytical method.  
38  
39 (3). Include comparison measurements with both a low flow TSP sampler and a PM<sub>10</sub>  
40 sampler to develop a data set which would allow EPA to consider moving away  
41 from the high volume TSP sampling procedure in the future. I particularly urge  
42 EPA to include the PM<sub>10</sub> measurements and direct analysis of the collected filter  
43 material to allow the Pb program to become more consistent with sampling for the  
44 PM standard in the future.  
45

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

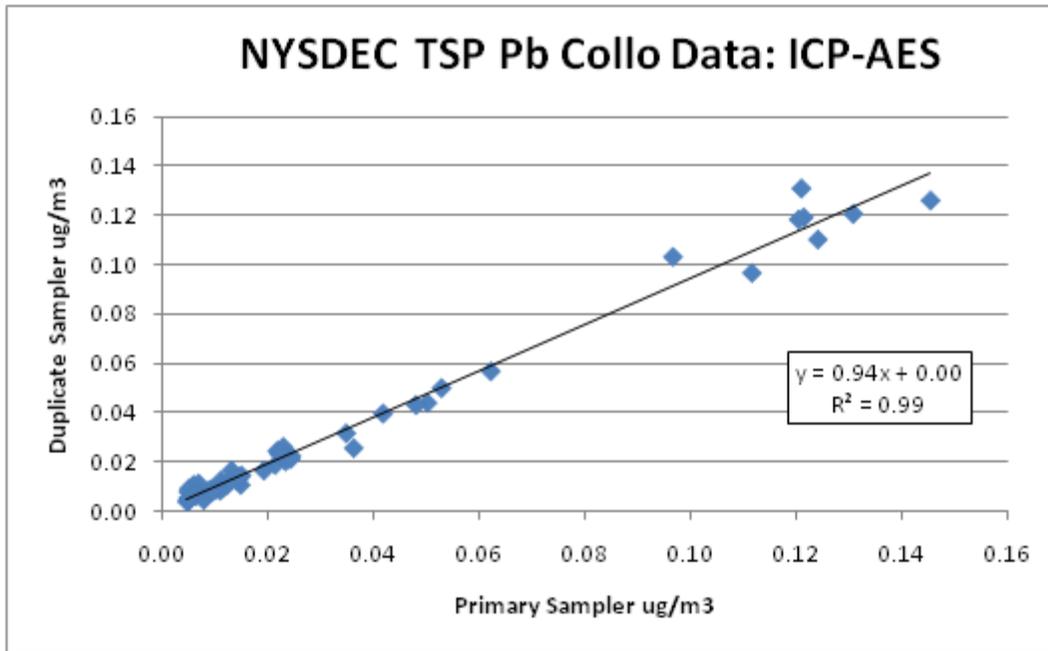
4  
5 I concur with the points in the consensus report.

6  
7

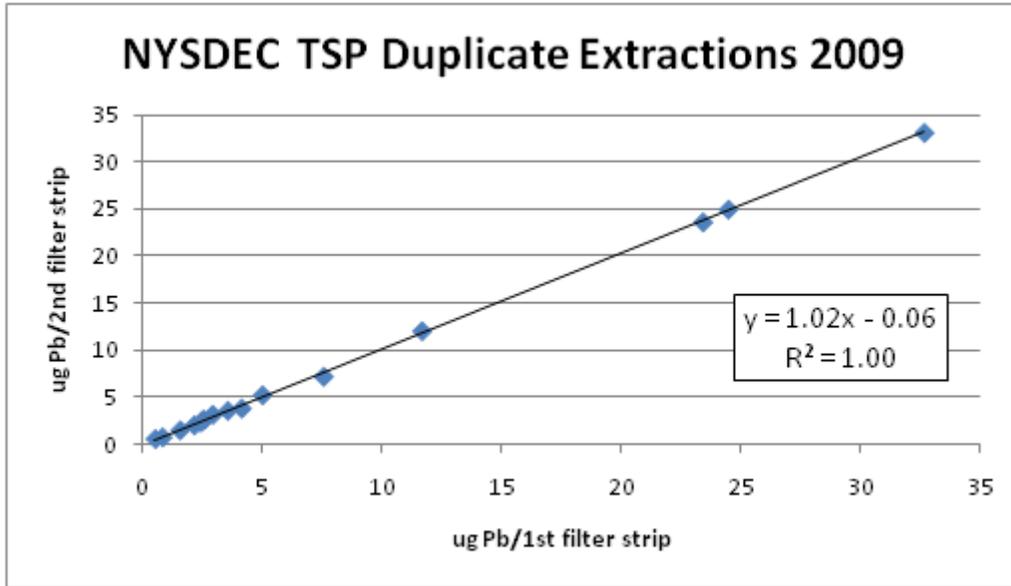
## Comments from Mr. Dirk Felton

### 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.

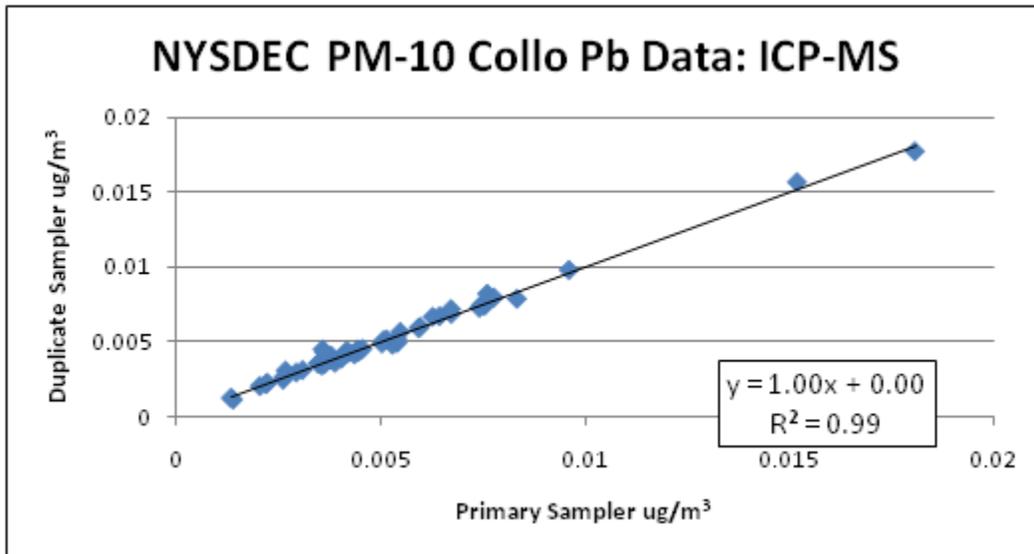


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ICPMS is used by most monitoring agencies in the NATTS program for the analysis of low-volume PM-10 filters for toxics metals including Pb. The data for this program is used for trends determinations and risk assessments so data accuracy is important 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.



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14  
15  
16  
17

1 **Response to Charge Questions**

2  
3 *1. What are the panel's views on the two extraction method options of heated ultrasonic and*  
4 *graphitic hot block with nitric/hydrochloric acid for the extraction of Pb from TSP?*

5  
6 Either extraction method is acceptable for NAAQS Pb monitoring. Monitoring Agencies  
7 are likely to prefer one method over another because it is either cost effective or because it is  
8 better suited for the analyses of other elements.  
9

10 Since Pb is relatively easy to extract, it would be preferable to have a range of acceptable  
11 extraction parameters such as acid types and concentrations, temperatures, heating methods and  
12 filtration included in the FRM. Performance standards for extraction efficiency could be  
13 included to ensure that the method selected by specific laboratories is adequate for compliance  
14 data. This approach would not only make the samples collected for Pb NAAQS monitoring  
15 useful for other programs but will also make the samples collected for other programs such as air  
16 toxics eligible for use in comparison to the Pb NAAQS.  
17

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

19  
20 The method is acceptable but is more accurate than is necessary for high volume TSP  
21 filter analysis. The advantage of making this method a FRM is that it is also suitable for use with  
22 low volume PM-10 filters. The FAAS method is adequate for high volume sample analysis and  
23 is performed in-house by many State and Local monitoring agencies. The FAAS method should  
24 be retained as an FEM but limited to use for high volume samples.  
25

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

28  
29 The approach looks adequate though some of the evaluation criteria are not very tight.  
30 Recoveries, inter-method precisions and bias at high concentrations should be better than the  
31 criteria set forth in the white paper. The criteria should be tightest at the level of the NAAQS.  
32

33 The sampled filters should also be selected to look for real world interferences. The  
34 white paper mentions that filters will be selected to cover a range of Pb but they should also  
35 cover a range of other factors such as heavy crustal or EC loadings that may potentially interfere  
36 with the analysis results.  
37

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

41  
42 The comparisons between labs should include criteria that indicate performance at low  
43 concentrations, high concentrations and of course at the level of the NAAQS. The evaluation  
44 should also emphasize the performance for real world samples.  
45  
46

1 **Comments from Dr. Philip Hopke**

2  
3  
4 *1. What are the panel's views on the two extraction method options of heated ultrasonic and*  
5 *graphitic hot block with nitric/hydrochloric acid for the extraction of Pb from TSP?*

6  
7 The methods proposed appear to be adequate for extracting lead from TSP samples, but  
8 they have failed to evaluate modern extraction techniques. There is no discussion of microwave  
9 digestion where you can automate multiple samples. There are systems that can run up to 40  
10 samples at a time with monitoring of the temperature of each extraction cell to ensure uniform  
11 extraction. Thus, the Agency has missed an opportunity to permit efficient, uniform extraction  
12 that would make the analyses faster, more uniform and simpler to run in large numbers.

13  
14 *2. What are the panel's views on ICP-MS as the analysis method for Pb-TSP?*

15  
16 ICP-MS is an appropriate method.

## Comments from Dr. Peter McMurry

1  
2  
3  
4 *1. What are the panel's views on the two extraction method options of heated ultrasonic and*  
5 *graphitic hot block with nitric/hydrochloric acid for the extraction of Pb from TSP?*  
6

7 I am not an expert on methods used for extracting Lead (Pb), so I will not to comment on  
8 them.  
9

10 *2. What are the panel's views on ICP-MS as the analysis method for Pb-TSP?*  
11

12 Again, I have no particular expertise on analytical methods used to determine Lead (Pb)  
13 concentrations, so I will not comment on the choice of ICP-MS as the analysis method for the  
14 FRM. My only concern about this is that if state or local agencies use another method that  
15 produces equivalent results, then perhaps it should also be allowed.  
16

17 *3. What are the panel's views on the approach described for evaluating and testing the method*  
18 *prior to proposal as a new FRM for Pb-TSP?*  
19

20 My primary concern is that the standard involves the analysis of samples collected with a  
21 TSP sampler. There must be a reason that TSP samplers are used rather than, for example, PM10.  
22 Are TSP samplers also used for other types of sampling? It would seem that mandating TSP as  
23 well as PM10 sampling would impose unnecessary burdens on state and local agencies. Also,  
24 TSP samples are less well characterized than PM10 samples.  
25

26 Other AAMM members have had more experience than I at method evaluation. I defer to  
27 their judgement on this topic.  
28

29 *4. Inter-laboratory testing of the method will be done to assess between-laboratory variability*  
30 *(CV) at the 95% confidence interval. What are the panel's views on a reasonable level of inter-*  
31 *laboratory variability?*  
32

33 It would appear that the interlaboratory testing plan is based on well-established  
34 paradigms.  
35

36 What procedures will be employed to ensure that a given laboratory continues to analyze  
37 samples accurately over time, after the initial intercomparison is complete?  
38  
39

1 **Comments from Dr. Jay Turner**

2  
3  
4 It is appropriate that the Agency revise the FRM for Pb-TSP to provide for suitable  
5 sample analyses to determine compliance with the Pb NAAQS revisions promulgated in  
6 November 2008. Advice has been solicited concerning the extraction and analytical methods,  
7 method validation and testing, and target for inter-laboratory variability.  
8

9 I commend the EPA for the thoughtful approach that is being taken to the revisions,  
10 including the proposed methods evaluation study.  
11

12 **Charge Questions and Responses**

13  
14 *1. What are the panel's views on the two extraction method options of heated ultrasonic and*  
15 *graphitic hot block with nitric/hydrochloric acid for the extraction of Pb from TSP?*  
16

17 The two methods (EQL-0510-191 and EQL-710-192) are reasonable candidate methods.  
18 They are consistent with current laboratory equipment and practices. Our group's recent  
19 experience with graphite hot block sample digestions for air toxics PM10 metals (including but  
20 not limited to Pb) has been very positive.  
21

22 I am comfortable with more than one extraction method being included in the FRM. My  
23 key concern is that clear equivalency criteria be developed so that additional, commonly-used  
24 extraction protocols can be designated as FEM methods. It would be beneficial if EPA included  
25 certain additional extraction methods in the proposed evaluation study and made the FEM  
26 designations, rather than placing this burden on state/local agencies. For example, Pb is a target  
27 analyte for the National Air Toxics Trends Station (NATTS) network PM10 metals  
28 measurements. Given that several state/local agencies are already performing these analyses, it  
29 might be advantageous if the same extraction method could be used for the Pb-TSP analysis.  
30

31 On a technical note, the extraction description in EQL-710-192 concludes with the step  
32 "Shake the extract vigorously for 5 seconds (with the filter strip in the extraction vessel) and let  
33 settle for at least an hour. The sample is now ready for analysis." What are the provisions for  
34 storing the sample(s) for some length of time between extraction and analysis? Also, does the  
35 one hour of settling time guarantee that no filtration of the extract is required? A filtration step is  
36 included in EPA Compendium Method IO-3.1 (Selection, Preparation, and Extraction of Filter  
37 Material), the metals extraction SOP posted under the air toxics section of the EPA AMTIC web  
38 site (<http://www.epa.gov/ttnamti1/files/ambient/airtox/metalsop.pdf>), and the Technical  
39 Assistance Document for the National Air Toxics Trends Station Program (Revision 2, April  
40 2009; <http://www.epa.gov/ttn/amtic/files/ambient/inorganic/mthd-3-5.pdf>).  
41

42 What are the plans for the initial demonstration of performance for each analytical  
43 laboratory? While the candidate methods will be evaluated using the Text Matrix appended to  
44 the White Paper, would there be advantages to having each analytical laboratory perform tests

1 with SRM or some other standardized samples as part of an initial demonstration of  
2 performance? This is not addressed in the candidate SOPs.

3  
4 *2. What are the panel's views on ICP-MS as the analysis method for Pb-TSP?*

5  
6 ICP-MS is appropriate as the reference method. It has suitable sensitivity and minimal  
7 issues with interferences. In addition to contract laboratories, many state/local agencies are  
8 already performing ICP-MS analysis for air toxics PM10 metals (see e.g. Table 8 in National Air  
9 Toxics Trends Stations Quality assurance Annual Report, Calendar Year 2007;  
10 <http://www.epa.gov/ttnamt1/files/ambient/airtox/NATTS2007QAAnnualReport.pdf>). Again,  
11 there might be advantages to harmonization with the NATTS method which is EPA  
12 Compendium Method IO-3.5 (Determination of Metals in Ambient Particulate Matter Using  
13 Inductively Couple Plasma/Mass Spectrometry). The EPA should consider including GFAAS in  
14 the proposed evaluation study, possibly leading to designation as an FEM directly by the Agency.  
15 Also, FAAS should be included in the evaluation study to provide connection to historical  
16 analysis methods.

17  
18 I encourage the designation of a single analytical method as the FRM, specifically a  
19 method that has sufficiently high sensitivity to be suitable should the Pb NAAQS concentration  
20 threshold be revised downward at a later time. In this case, any additional qualifying methods  
21 for the current standard could be designated as FEM.

22  
23 *3. What are the panel's views on the approach described for evaluating and testing the method*  
24 *prior to proposal as a new FRM for Pb-TSP?*

25  
26 The approach is sound although the test criteria ideally would be framed within the  
27 context of a DQO, but there is no evidence that this has been done. Tests and criteria have been  
28 defined in the Test Matrix appended to the White Paper. I have some concerns about the broad  
29 range for the SRM recoveries (80-120%). While this recovery range is a commonly used  
30 criterion, should it be tighter for NAAQS compliance measurements? Also, should recovery  
31 tests be performed at even higher nominal mass loadings? The NAAQS is based on a three-  
32 month rolling average. For 1-in-6 day sampling this is nominally 15 samples and thus a few very  
33 high concentration samples could lead to a violation and it would be important to have accurate  
34 measurements at high concentrations since the NAAQS is an arithmetic average.

35  
36 *4. Inter-laboratory testing of the method will be done to assess between-laboratory variability*  
37 *(CV) at the 95% confidence interval. What are the panel's views on a reasonable level of inter-*  
38 *laboratory variability?*

39  
40 The target performance for inter-laboratory variability should take into consideration the  
41 overall measurement quality objectives and the performance achieved by the method(s) from the  
42 intra-laboratory method performance evaluation.

## 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 high-volume (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 high-volume 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 high-volume filter will be sectioned into eight strips; four pairs of adjacent strips will be distributed to four different laboratories. Each laboratory will analyze each extract in triplicate and report the individual results. The resulting data set will support the analysis of variance techniques with which Long et al. resolved observed variations into components attributable to within-laboratory and between-laboratory standard deviations.

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 HNO<sub>3</sub> procedure and the other with the ultrasonic HNO<sub>3</sub> 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. The experimental design could 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.

If more than four laboratories or two extraction methods might be compared, this would require some reconfiguration of the present design. It is also worth noting that the inter-laboratory discussion (pp. 27-28) in the EPA methods development and validation guidance (USEPA, 1992), cited by the white paper, explicitly calls for decoupling the tests of the extraction and determinative procedures:

*When validating a sample preparation method, the participating laboratories should only perform the sample preparation procedure. The collected samples should then be sent to one laboratory for analysis. The analysis should be done by a single operator on a single instrument in a single batch to minimize analytical variability inherent to the determinative method. Conversely, if a determinative method is to be validated, the developer should have a single operator perform all of the sample preparation*

1           *operations in order to minimize operator and laboratory variability inherent to the*  
2           *sample preparative procedures. The sample extracts should then be split and sent to the*  
3           *laboratories participating in the validation study for the analytical determination.*  
4

5           On the charge question of “a reasonable level of inter-laboratory variability”, we can note  
6 that Long et al. judged that two observations by different laboratories using the previous FRM  
7 would not differ by more than 28% of the concentration level more than 5% of the time due to  
8 chance alone. Alternatively, if 10% bias and 15% precision are tolerated for each lab, then  
9 differences of  $50\% = 2.77 \times (10\%^2 + 15\%^2)^{1/2}$  could be expected 5% of the time. [The factor 2.77  
10 is the two-sided 5% critical value (1.96) for the normal distribution, multiplied by the square root  
11 of two to account for the independent uncertainties in two observations.] For comparisons  
12 between n-sample averages, differences of  $2.77 \times (10\%^2 + 15\%^2/n)^{1/2}$  could be expected 5% of the  
13 time. Averaging 16 (three months of one-day-in-six sampling) observations, for example, would  
14 thus reduce the 5% confidence level difference from 50% to 30%.

15  
16           Whether these are “reasonable” levels of variability requires a consideration of data  
17 quality objectives (USEPA, 2006). Given the epistemic uncertainties in our exposure and risk  
18 assessments for lead, an acceptable level of uncertainty for the indicator cannot be derived from  
19 scientific principles alone.

20  
21  
22 USEPA, 1992. Development and Validation of SW-846 Methods Phase 2: Formal Validation. In  
23 *Guidance for the Methods Development and Methods Validation for the RCRA Program*,  
24 Washington, DC.

25  
26 USEPA, 2006. Guidance on Systematic Planning Using the Data Quality Objectives Process.  
27 EPA/240/B-06/001, Washington, DC. Available at: [http://www.epa.gov/quality/qs-docs/g4-](http://www.epa.gov/quality/qs-docs/g4-final.pdf)  
28 [final.pdf](http://www.epa.gov/quality/qs-docs/g4-final.pdf)  
29  
30

1 **Comments from Dr. Yousheng Zheng**

2  
3  
4 *Charge Question 1: What are the panel's views on the two extraction method options of heated*  
5 *ultrasonic and graphitic hot block with nitric/hydrochloric acid for the extraction of Pb from*  
6 *TSP?*  
7

8 EPA has presented two options for lead extraction from TSP filters – Option 1: heated  
9 ultrasonic nitric and hydrochloric acid filter extraction, and Option 2: heated nitric acid hot block  
10 digestion. I don't have experience with these two specific extraction procedures. However, based  
11 on my past experience with acid digestion of TSP samples, the mixture of nitric acid and  
12 hydrochloric acid provides more aggressive and thorough extraction of metals than nitric acid  
13 alone. More aggressive extraction may or may not be important for lead. It certainly makes  
14 difference for extracting some other metals. With ICP-MS, multiple metal analyses will be easier  
15 than the current FRM using FAAS. Multiple metal analyses will provide more useful information  
16 for source identification and apportionment. With the ease and value of having multiple metals  
17 analyses, it is anticipated that more agencies would analyze multiple metals beyond lead.  
18 Therefore, a procedure that has stronger digestion and extraction power for not only lead, but  
19 also other metals is beneficial.  
20

21 In addition to hydrochloric acid, Option 1 uses a slightly higher nitric acid concentration  
22 than Option 2 (64.4 mL of concentrated nitric acid in 1000 mL vs. 50 mL in 1000 mL). Option 1  
23 also uses ultrasonic waves to provide agitation and to aid extraction.  
24

25 Overall, Option 1 seems to be a stronger method than Option 2. Unless Option 1 is more  
26 susceptible to interference due to presence of hydrochloric acid or chlorides, I would favor  
27 Option 1. As part of EPA's further evaluation of the two candidate methods before final selection  
28 of the FRM, I would suggest that EPA address vulnerability between the two methods in terms  
29 of potential interference in the two methods, i.e., does the presence of hydrochloric acid make  
30 the subsequent ICP-MS analysis more susceptible to interference in the context of a typical  
31 ambient TSP samples as the matrix? As stated in Section 7.2 of SW-846 Method 6020A, "many  
32 more molecular-ion interferences are observed when hydrochloric and sulfuric acids are used".  
33 This question may have been investigated and answered, but not included in the materials  
34 provided for this subcommittee review.  
35

36 *Charge Question 2: What are the panel's views on ICP-MS as the analysis method for Pb-TSP?*  
37

38 EPA has cited the advantages of using ICP-MS over the current FRM analytic method  
39 (FAAS). I agree that ICP-MS should be a significantly better method than FAAS. My only  
40 comments are:  
41

- 42 1. Potential interferences (including isobaric elemental interferences, physical and  
43 chemical interferences, and interferences that may be caused by introduction of  
44 hydrochloric acid as discussed above;) should be addressed as part of EPA's  
45 evaluation.

- 1           2. If possible, EPA should consider some secondary objectives to leverage and  
2 maximize the benefits of conducting the evaluation. These secondary evaluations may  
3 include:  
4           a. Analyzing other elements in addition to Pb. If the results are favorable, they  
5 can be used to support monitoring agencies' effort to analyze multiple  
6 elements at a small incremental cost and acquire valuable data for other  
7 programs such as air toxics studies, source apportionment, etc.  
8           b. Analyzing samples using the current FRM (i.e., FAAS) and XRF method in  
9 parallel to the evaluation of the candidate ICP-MS methods so that  
10 comparisons can be made. A comparison with FAAS may help understand the  
11 past monitoring data and bridge the past and future data. A comparison with  
12 XRF may be useful because a large body of data has been and can be  
13 generated by XRF.  
14           3. The candidate FRM methods are designed for analyzing TSP filters collected by high  
15 volume samplers. With a large number of PM10 samplers in operations, it would be  
16 desirable to evaluate suitability of applying the candidate ICP-MS methods to the  
17 PM10 filters collected by more widely used PM10 samplers. If the new ICP-MS  
18 based FRM is also suitable for analyzing the PM10 filters collected by common  
19 PM10 samplers, it will make it easier for monitoring agencies to analyze these filters  
20 for Pb and other metals, not necessarily for lead NAAQS attainment determination  
21 but for other air programs.  
22

23 *Charge Question 3: What are the panel's views on the approach described for evaluating and*  
24 *testing the method prior to proposal as a new FRM for Pb-TSP?*  
25

26           The proposed approach seems to be comprehensive. I don't have specific comments at  
27 this time.  
28

29 *Charge Question 4: Inter-laboratory testing of the method will be done to assess between-*  
30 *laboratory variability (CV) at the 95% confidence interval. What are the panel's views on a*  
31 *reasonable level of inter-laboratory variability?*  
32

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