UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

MEMORANDUM

SUBJECT: Draft Federal Reference Method (FRM) and Federal Equivalent Method (FEM) Criteria for Lead in PM10 (Pb-PM10)

FROM: Joann Rice, OAQPS/AQAD/AAMG

TO: Lead NAAQS Review Docket (OAR-2006-0735)

The Environmental Protection Agency (the Agency) is in the process of reviewing the National Ambient Air Quality Standard (NAAQS) for Lead (Pb). As part of that review, the Agency is considering options that would rely on Pb in PM_{10} monitoring data for attainment determinations. As such, we are considering proposing a new Federal Reference Method (FRM) for Pb in PM_{10} (Pb-PM_{10}). The agency is also considering revising the existing Federal Equivalent Method (FEM) criteria to include provisions specific for Pb-PM_{10} sampling and to reflect potential revision to the NAAQS level for Pb. The purpose of this memorandum is to provide a basis for consultation with the Clean Air Scientific Advisory Committee (CASAC) Ambient Air Monitoring & Methods (AAMM) Subcommittee on March 25, 2008.

New FRM for Pb-PM_{10}

An FRM for Pb-PM_{10} would have two components – the sampler (i.e., the device that collects the sample) and the analysis method (the device that analyses the sample for Pb content). We are considering basing the Pb-PM_{10} sampler on the recently promulgated, low-volume PM_{10C} FRM sampler (Appendix O to Part 50) for Pb-PM_{10}. The low-volume PM_{10C} sampler meets more demanding performance criteria (Appendix L to Part 50) than conventional PM_{10} samplers and will be operated at local conditions. Also, the low-volume PM_{10C} sampler can be equipped with sequential sampling capabilities or the ability to collect multiple samples between operator visits. This is desirable if the sampling frequency is increased to accommodate a potential change to a monthly averaging time for the Pb NAAQS. Use of a low-volume sampler for the Pb-PM_{10} FRM also provides network efficiencies and consistencies with the $PM_{2.5}$, PM_{10}, and $PM_{10-2.5}$ networks, which also make use of low-volume samplers to collect PM at local conditions.

We are considering using the X-Ray Fluorescence (XRF) analysis technique as the analysis method for the Pb-PM_{10} FRM. The XRF analysis method has acceptable precision, bias, and method detection limits (MDLs) when coupled with the low-volume PM_{10} sampler. The XRF analysis method also has several advantages which make it desirable. XRF does not require sample preparation or extraction with acids prior to analysis. It is a non-destructive method; therefore, the sample can be archived for future analysis or re-analysis if needed. XRF analysis is a cost-effective approach (commercial costs of about $50-$70 per analysis) that can be used to

simultaneously analyze for many additional metals such as arsenic, antimony, and iron which may be useful in source apportionment. XRF is also the method used for characterization of elements in EPA's urban and rural $PM_{2.5}$ speciation monitoring networks, and will likely also be used for EPA's $PM_{10-2.5}$ coarse speciation monitoring network.

Attachment 1 contains the draft regulatory text for the Pb-PM_{10} FRM.

Revised Federal Equivalent Method (FEM)

There are several other analysis methods commonly used which are also expected to meet the necessary precision, bias, and MDLs necessary to be used in the Pb surveillance monitoring network [e.g., graphite furnace atomic absorption (GFAA), and inductively coupled plasma mass spectrometry (ICP/MS)]. Furthermore, advances in continuous Pb monitoring methods are being made which may one day lead to an acceptable continuous Pb monitor. These methods should be made available as FEMs. Section 53.33 of 40 CFR Part 53, Subpart C describes the current FEM demonstration requirements. Several of these requirements would need to be revised to be consistent with a potentially lowered Pb NAAQS and for the potential addition of a Pb-PM_{10} FRM. The following paragraphs describe the aspects of the FEM criteria that we are considering revising. Attachment 2 contains draft regulatory text for potential revisions to the Pb FEM criteria.

FEM Testing Concentrations. The current FEM requirements state that the ambient Pb concentration range at which the FEM comparability testing must be conducted to be valid is 0.5 to 4.0 $\mu g/m^3$. Currently there are few locations in the United States where FEM testing can be conducted with assurance that the ambient concentrations during the time of the testing would exceed 0.5 $\mu g/m^3$. In addition, the Agency is considering lowering the Pb NAAQS level. As such, we are proposing to revise the Pb concentration requirements for candidate FEM testing to a range of the range of 30% of the NAAQS and 250% of the NAAQS in $\mu g/m^3$.

Precision, Accuracy, and Method Detection Limit. The current FEM requirements state that the maximum precision and accuracy for candidate analytical methods must be 15% and 5% respectively. No changes are proposed to be made to these requirements. The current FEM does not have a requirement for a maximum MDL. In order to ensure that candidate analytical methods have adequate sensitivity or MDLs, we are proposing to add a requirement that the MDL must be equal to or less than $1/10^{th}$ the level of Pb NAAQS.

Table 1 summarizes the estimated MDLs for several analysis methods which should be considered as FEM analysis methods for Pb-PM_{10}. The estimated MDLs are based on published instrument detection limits which typically take into account only instrument signal-to-noise ratios. It is important to note that the MDLs in Table 1 are estimates and these values will vary as a function of the specific instrument used, detector age, instrument signal-to-noise level, and therefore, MDLs should be determined periodically for each specific instrument.

Table 1. Summary of Candidate Analysis Method Detection Limits for a Pb-PM_{10} FRM or FEM		
Analysis Method	**Estimated Method Detection Limits**	**Estimated Method Detection Limit in Air ($\mu g/m^3$)**
Atomic Absorption (AA)	15 µg/L [a]	0.01[c]
X-Ray Fluorescence (XRF)	1.5 ng/cm^2 [b]	0.001[d]
Graphite Furnace Atomic Absorption (GFAA)	0.05 µg/L [a]	0.00004[c]
Inductively Coupled Plasma/Mass Spectrometry (ICP/MS)	0.08 µg/L [b]	0.00006[c]

[a] Taken from the Perkin Elmer Guide to Atomic Spectroscopy Techniques and Applications [1]
[b] One-sigma detection limit taken from the Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air; IO-3.3 [2]
[c] Based on 46.2-mm filter extraction volume of 0.020 L and sample volume of 24 m^3 of air.
[d] Based on 46.2-mm filter area of 11.86 cm^2 and sample volume of 24 m^3 of air.

Audit Concentrations. The existing FEM requirements require that audit samples be analyzed at levels equal to 100, 300, and 750 µg per spiked filter strip (equivalent to 0.5, 1.5, and 3.75 $\mu g/m^3$ of sampled air). We are proposing to revise the levels of the audit concentrations to 30%, 100% and 250% of the Pb NAAQS.

Sample Filter Types. The existing FEM requirements are based on the high-volume TSP sampler, and as such, refers to ¾ x 8-inch glass fiber strips. In order to also accommodate the use of low-volume sample filters, we are proposing to add references to 46.2-mm PTFE sample filters.

Quality Assurance (QA)

Modifications will need to be made to the QA requirements for Pb in 40 CFR Part 58 Appendix A paragraph 3.3.4 in order to accommodate Pb-PM_{10} monitoring. Paragraph 3.3.4 specifies requirements for annual flow rate audits and Pb strip audits. Other QA requirements for TSP samplers are intended to be applicable to Pb-TSP samplers. As part of the overall Pb NAAQS review, it is appropriate to revise these requirements to consolidate all the QA requirements for Pb monitoring in paragraph 3.3.4.

In general, we suggest applying the current QA requirements for PM_{10} to the Pb-PM_{10} sampler. However, in some cases Pb-TSP methods have different QA requirements than PM_{10} low volume methods. Therefore, edits may be needed to clarify when requirements apply Pb-PM_{10} or Pb-TSP in order to avoid confusion between the two methods.

The following paragraphs discuss the potential QA changes.

Collocated sampling requirement. The collocation requirement for TSP (paragraph 3.3.1) are intended to apply to TSP samplers used for Pb-TSP monitoring. These requirements are the same for PM_{10} (paragraph 3.3.1), as such, no changes are needed to accommodate low-volume Pb-PM_{10}. However, it is appropriate to clarify that this requirement also applies to Pb-TSP monitoring by adding a reference to this requirement in paragraph 3.3.4.

Flow rate verification requirement. The sampler flow rate verifications requirement (paragraph 3.3.2) for low volume PM_{10} and TSP are at different intervals. While this appears appropriate and no change is needed, it is appropriate to clarify that this requirement also applies to Pb-TSP monitoring by adding a reference to this requirement in paragraph 3.3.4.

Semi-annual flow rate audit. Paragraph 3.3.4.1 has an error in the text that suggests an annual flow rate audit for Pb, but then includes reference in the text for semi-annual audits. This error should be corrected in the proposal. Also, references to the Pb reference method would need to be changed to include the potential Pb-PM_{10} FRM.

Pb Filter Audits. Paragraph 3.3.4.2 discusses the audit procedures for the lead analysis method. This section assumes the use of a high volume TSP sampler, and will need to be edited to account for the potential Pb-PM_{10} FRM. In addition, the audit concentration ranges may not be appropriate if the NAAQS is lowered. It is appropriate to lower the audit ranges for Pb-TSP from 0.5 to 1.5 to 0.05 to 0.4 ug/m^3 for the low concentration and from 3.0 to 5.0 to 0.5 to 2.0 ug/m^3 for the higher concentration standard.

Performance Evaluation Program. Unlike the $PM_{2.5}$ and $PM_{10-2.5}$ Performance Evaluation Program (PEP), Pb does not have an independent estimate of the overall sampling and analysis bias. It may be appropriate to require one PEP-like audit at one site within each PQAO (primary quality assurance organization) once per year. In addition, for each quarter, one collocated sample from one site within each PQAO should be sent to a national independent laboratory for analysis. The combination of the PEP value and independent collocation will provide enough data to provide a reasonable assessment of overall bias and data comparability.

References

1. Guide to Atomic Spectroscopy Techniques and Applications: AA, GFAA, ICP, ICP-MS; PerkinElmer instruments, Norwalk, CT; 2000 (www.perkinelmer.com)

2. Inorganic Compendium Method IO-3.3; Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy; U.S. Environmental Protection Agency, Cincinnati, OH 45268. EPA/625/R-96/010a. June 1999.

Attachment 1
Draft FRM Regulatory Text

Appendix Q to Part 50 – Reference Method for the Determination of Lead in Particulate Matter as PM_{10} Collected From Ambient Air - Proposed

This Federal Reference Method (FRM) draws heavily from the specific analytical protocols used by the U.S. EPA.

1. A*pplicability and Principle*

1.1 This method provides for the measurement of the lead (Pb) concentration in particulate matter less than 10 micrometers (PM_{10}) in ambient air. PM_{10} is collected on a 46.2 mm diameter polytetrafluoroethylene (PTFE) filter for 24-hours using active sampling at local conditions with a low-volume air sampler. The low-volume sampler has an average flow rate of 16.7 liters per minute (Lpm) and total sampled volume of 24-cubic meters (m^3) of air. The analysis is performed on each individual 24-hour sample. For the purpose of this method, PM_{10} is defined as particulate matter having an aerodynamic diameter in the nominal range of 10 micrometers (10 μm) or less.

1.2 For this reference method, PM_{10} shall be collected with the PM_{10c} federal reference method (FRM) sampler as described in Appendix O to Part 50 using the same sample period and measurement procedures. This sampling method will use the performance requirements specified in Appendix L of Part 50. The concentration of Pb in the atmosphere is determined in the total volume of air sampled and expressed in micrograms per cubic meter ($\mu g/m^3$) at local temperature and pressure conditions.

1.3 The FRM will serve as the basis for approving Federal Equivalent Methods (FEMs) as specified in 40 CFR Part 53 (Reference and Equivalent Methods).

1.4 An electrically powered air sampler for PM_{10c} draws ambient air at a constant volumetric flow rate into a specially shaped inlet and through an inertial particle size separator, where the suspended particulate matter in the PM_{10} size range is separated for collection on a PTFE filter over the specified sampling period. The lead content of the PM_{10c} sample is analyzed by energy-dispersive X-ray fluorescence spectrometry (EDXRF). Energy-dispersive X-ray fluorescence spectrometry provides a means for identification of an element by measurement of its characteristic X-ray emission energy. The method allows for quantification of the element by measuring the emitted characteristic line intensity and then relating this intensity to the elemental concentration. The number or intensity of X-rays produced at a given energy provides a measure of the amount of the element present by comparisons with calibration standards. The X-rays are detected and the spectral signals are acquired and processed with a personal computer. EDXRF is commonly used as a non-destructive method for quantifying trace elements in PM. An EPA method for the EDXRF analysis of ambient particulate matter is described in reference 1 of section 8. A detailed explanation of quantitative X-ray spectrometry is described in references 2 and 3.

1.5 Quality assurance (QA) procedures for the collection of monitoring data are contained in Part 58, Appendix A.

2. *PM_{10c} Lead Measurement Range and Method Detection Limit.* The values given below are typical of the method capabilities. Absolute values will vary for individual situations depending on the instrument, detector age, and operating conditions used. Data are typically reported in ng/m^3 for ambient air samples; however, for this reference method, data will be reported in $\mu g/m^3$ at local temperature and pressure conditions.

2.1 *EDXRF Measurement Range.* The typical ambient air measurement range is 0.001 to 30 µg Pb/m^3, assuming an upper range calibration standard of about 60 µg Pb per square centimeter (cm^2), a filter deposit area of 11.86 cm^2, and an air volume of 24-m^3. The top range of the EDXRF instrument is much greater than what is stated here. The top measurement range of quantification is defined by the level of the high concentration calibration standard used and can be increased to expand the measurement range as needed.

2.2 *Method Detection Limit (MDL).* A typical one-sigma estimate of the method detection limit (MDL) is about 2 ng Pb/cm^2 or 0.001 µg Pb/m^3, assuming a filter size of 46.2-mm (filter deposit area of 11.86 cm^2) and a sample air volume of 24-m^3. The MDL is an estimate of the lowest amount of lead that can be detected by the analytical instrument. The one-sigma detection limit for Pb is calculated the average overall uncertainty or propagated error for Pb, determined from measurements on a series of blank filters. The sources of random error which are considered are calibration uncertainty; system stability; peak and background counting statistics; uncertainty in attenuation corrections; uncertainty in peak overlap corrections; and uncertainty in flow rate, but the dominating source is by far peak and background counting statistics. Laboratories are to estimate the MDLs using 40 CFR Part 136, Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit." (Reference 4).

3. *Factors Affecting Bias and Precision of Lead Determination by EDXRF*

3.1 *Filter Deposit*. Too much deposit material can be problematic because XRF analysis and data processing programs for aerosol samples are designed specifically for a thin film or thin layer of material to be analyzed. The X-ray spectra are subject to distortion if unusually heavy deposits are analyzed. This is the result of internal absorption of both primary and secondary X-rays within the sample. The optimum filter loading is about 150 $\mu g/cm^2$ or 1.6 mg/filter for a 46.2-mm filter. Too little deposit material can also be problematic due to low counting statistics and signal noise. The particle mass deposit should minimally be 15 $\mu g/cm^2$. A properly collected sample will have a uniform deposit over the entire collection area. Sample heterogeneity can lead to very large systematic errors. Samples with physical deformities (including a visually non-uniform deposit area) should not be quantitatively analyzed.

3.2 *Spectral Interferences and Spectral Overlap.* Spectral interference occurs when the entirety of the analyte spectral lines of two species are nearly 100% overlapped. There are only a few cases where this may occur and they are instrument specific: Si/Rb, Si/Ta, S/Mo, S/Tl, Al/Br, Al/Tm. These interferences are determined during instrument calibration and automatically corrected for by the XRF instrument software. No spectral interference is expected for Pb, but this interference does occur for other elements and should be addressed when multi-elemental analysis is performed. There can be instances when lines partially overlap the Pb spectral lines, but with the energy resolution of modern detectors, these overlaps are typically de-convoluted using standard spectral de-convolution software. An EDXRF protocol for Pb must define which Pb lines are used for quantification and where spectral overlaps occur. Some of the overlaps may

be very small and some severe. A de-convolution protocol must be available to separate all the lines which overlap with Pb.

3.3 *Particle Size Effects and Attenuation Correction Factors.* X-ray attenuation is dependent on the X-ray energy, mass sample loading, composition, and particle size. In some cases, the excitation and fluorescent X-rays are attenuated as they pass through the sample. In order to relate the measured intensity of the X-rays to the thin-film calibration standards used, the magnitude of the any attenuation present must be corrected for. The effect is especially significant and more complex for PM_{10} measurements, especially for the lighter elements that may also be measured. An average attenuation and uncertainty for each coarse particle element is based on a broad range of elements and is a one-time calculation that gives an attenuation factor for use in all subsequent particle analyses. See reference 5, 6, and 7 of section 8 for more discussion on addressing this issue. Essentially no attenuation corrections are necessary for Pb in PM10: both the incoming excitation X-rays used for analyzing lead and the fluoresced Pb X-rays are sufficiently energetic that for particles in this size range and for normal filter loadings, the Pb x-ray yield is not significantly impacted by attenuation. However, this issue must be addressed when doing multi-element analyses.

4. *Precision*

4.1 Measurement system precision is assessed according to the procedures set forth in Appendix A to part 58. Measurement precision is assessed from collocated sampling and analysis. The goal for acceptable measurement uncertainty, as precision, is defined as an upper 90 percent confidence limit for the coefficient of variation (CV) of 15 percent.

5. *Bias*

5.1 Measurement system bias for monitoring data is assessed according to the procedures set forth in Appendix A of part 58. The bias is assessed through an audit using spiked filters. The goal for measurement bias is defined as an upper 95 percent confidence limit for the absolute bias of 10 percent.

6. *Measurement of PTFE Filters by EDXRF*

6.2 *Sampling*

6.2.1 *Low-Volume PM_{10c} Sampler.* The PM_{10c} sampler shall be of like manufacturer, design and configuration and calibrated as described in Part 50, Appendix L.

6.2.2 *PTFE Filters and Filter Acceptance Testing.* The PTFE filters used for PM_{10c} sample collection shall meet the specifications provided in Part 50, Appendix L. The following proposed requirements are similar to those currently specified for the acceptance of $PM_{2.5}$ filters that are tested for trace elements by EDXRF. For large batches of filters (greater than 500 filters) randomly select 50 filters from a given batch. For small batches (less than 500 filters) a lesser number of filters may be taken. Analyze each filter separately and calculate the average lead concentration in ng/cm^2. Ninety percent, or 45 of the 50 filters, must have an average lead concentration that is less than 4.8 ng Pb/cm^2 (approximately 2 times the estimated one-sigma detection limit for Pb by EDXRF).

6.3 *Analysis.* The four main categories of random and systematic error encountered in X-ray fluorescence analysis include errors from sample collection, the X-ray source, the counting process, and inter-element effects. These errors are addressed through the calibration process and mathematical corrections in the instrument software.

6.3.1 ED*XRF Analysis Instrument*. An energy-dispersive XRF system is used. Energy-dispersive XRF systems are available from a number of commercial vendors including Thermo (www.thermo.com) and PANalytical (www.panalytical.com).[1] The analysis is performed at room temperature in either vacuum or in a helium atmosphere. The specific details of the corrections and calibration algorithms are typically included in commercial analytical instrument software routines for automated spectral acquisition and processing and vary by manufacturer. It is important for the analyst to understand the correction procedures and algorithms of the particular system used, to ensure that the necessary corrections are applied.

6.3.2 *Thin film standards*. Thin film standards are used for calibration because they most closely resemble the layer of particles on a filter. Thin films standards are typically deposited on Nuclepore substrates. The preparation of thin film standards is discussed in reference 6, and 9. Thin film standards are commercially available from MicroMatter Inc. (Arlington, WA).[1]

6.3.3 *Filter Preparation*. Filters used for sample collection are 46.2-mm PTFE filters with a pore size of 2 microns and filter deposit area 11.86 cm^2. Filters scheduled for XRF analysis are removed from cold storage and allowed to reach room temperature. All filter samples received for analysis are checked for any holes, tears, or a non-uniform deposit which would prevent quantitative analysis. A properly collected sample will have a uniform deposit over the entire collection area. Samples with physical deformities are not quantitatively analyzable. The filters are carefully removed with tweezers from the Petri dish and securely placed into the instrument-specific sampler holder for analysis. No other preparation of the samples is required.

6.3.4 *Calibration*. In general, calibration determines each element's sensitivity, i.e., its response in x-ray counts/sec to each $\mu g/cm^2$ of a standard and an interference coefficient for each element that causes interference with another one (See section 3.2 above). The sensitivity can be determined by a linear plot of count rate versus concentration ($\mu g/cm^2$) in which the slope is the instrument's sensitivity for that element. A more precise way, which requires fewer standards, is to fit sensitivity versus atomic number. Calibration is a complex task in the operation of an XRF system. Two major functions accomplished by calibration are the production of reference spectra which are used for fitting and the determination of the elemental sensitivities. Included in the reference spectra (referred to as "shapes") are background-subtracted peak shapes of the elements to be analyzed, as well as peak shapes for interfering element energies and spectral backgrounds. Pure element thin film standards are used for the element peak shapes and clean filter blanks from the same lot as unknowns are used for the background. The analysis of PM filter deposits is based on the assumption that the thickness of the deposit is small with respect to the characteristic lead X-ray transmission thickness. Therefore, the concentration of lead in a sample is determined by first calibrating the spectrometer with thin film standards to determine sensitivity factors and then analyzing the unknown samples under identical excitation conditions as used to determine the calibration factors. Calibration is performed only when significant repairs occur or when a change in fluorescers, X-ray tubes, or detector is made. Calibration

[1] The mention of commercial products does not imply endorsement by the U.S. Environmental Protection Agency.

establishes the elemental sensitivity factors and the magnitude of interference or overlap coefficients. See reference 8 for more detailed discussion of calibration and analysis of shapes standards for background correction, coarse particle absorption corrections, and spectral overlap.

6.3.4.1 *Spectral Peak Fitting.* The EPA uses a library of pure element peak shapes (shape standards) to extract the elemental background-free peak areas from an unknown spectrum. It is also possible to fit spectra using peak stripping or analytically defined functions such as modified Gaussian functions. The EPA shape standards are generated from pure, mono-elemental thin film standards. The shape standards are acquired for sufficiently long times to provide a large number of counts in the peaks of interest. It is not necessary for the concentration of the standard to be known. A slight contaminant in the region of interest in a shape standard can have a significant and serious effect on the ability of the least squares fitting algorithm to fit the shapes to the unknown spectrum. It is these elemental shapes that are fitted to the peaks in an unknown sample during spectral processing by the analyzer. In addition to this library of elemental shapes there is also a background shape spectrum for the filter type used as discussed below in section 6.3.4.2 of this section.

6.3.4.2 *Background Measurement and Correction.* A background spectrum generated by the filter itself must be subtracted from the X-ray spectrum prior to extracting peak areas. The background shape standards which are used for background fitting are created at the time of calibration. About 20-30 clean blank filters are kept in a sealed container and are used exclusively for background measurement and correction. The spectra acquired on individual blank filters are added together to produce a single spectrum for each of the secondary targets or fluorescers used in the analysis of lead. Individual blank filter spectra which show contamination are excluded from the summed spectra. The summed spectra are fitted to the appropriate background during spectral processing. Background correction is automatically included during spectral processing of each sample.

7. *Calculation.*

7.1 The PM_{10} lead concentration in the atmosphere ($\mu g/m^3$) is calculated using the following equation:

$$M_{Pb} = \frac{C_{Pb} \times A}{V_{LC}}$$

where,

$\boldsymbol{M_{Pb}}$ is the mass per unit volume for lead in $\mu g/m^3$;
$\boldsymbol{C_{Pb}}$ is the mass per unit area for lead in $\mu g/cm^2$ as provided by the XRF instrument software;
$\boldsymbol{A}$ is the filter deposit area in cm^2;
$\boldsymbol{V_{LC}}$ is the total volume of air sampled by the PM_{10c} sampler in actual volume units measured at local conditions of temperature and pressure, as provided by the sampler in m^3.

8. *References*

1. Inorganic Compendium Method IO-3.3; Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy; U.S. Environmental Protection Agency, Cincinnati, OH 45268. EPA/625/R-96/010a. June 1999.

2. Jenkins, R., Gould, R.W., and Gedcke, D. Quantitative X-ray Spectrometry: Second Edition. Marcel Dekker, Inc., New York, NY. 1995.

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4. Code of Federal Regulations (CFR) 40, Part 136, Appendix B; Definition and Procedure for the Determination of the Method Detection Limit – Revision 1.11

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7. Drane, E.A, Rickel, D.G., and Courtney, W.J., "Computer Code for Analysis X-Ray Fluorescence Spectra of Airborne Particulate Matter," in *Advances in X-Ray Analysis*, J.R. Rhodes, Ed., Plenum Publishing Corporation, New York, NY, p. 23 (1980).

8. Analysis of Energy-Dispersive X-ray Spectra of ambient Aerosols with Shapes Optimization, Guidance Document; TR-WDE-06-02; prepared under contract EP-D-05-065 for the U.S. Environmental Protection Agency, National Exposure Research Laboratory. March 2006.

9. Billiet, J., Dams, R., and Hoste, J. (1980) Multielement Thin Film Standards for XRF Analysis, X-Ray Spectrometry, 9(4): 206-211.

Attachment 2
Draft FEM Criteria Regulatory Text

40 Part 53 AMBIENT AIR MONITORING REFERENCE AND EQUIVALENT METHODS

Subpart C: Procedures for Determining Comparability between Candidate Methods and Reference Methods

Subpart 53.33 - Proposed Revisions to the Test Procedure for Methods for Lead (Pb)

(a) *Comparability.* Comparability is shown for Pb methods when the differences between:

(1) Measurements made by a candidate method, and

(2) Measurements made by the reference method on simultaneously collected Pb samples (or the same sample, if applicable), are less than or equal to the values specified in table C–3 of this subpart.

(b) *Test measurements.* Test measurements may be made at any number of test sites. Augmentation of pollutant concentrations is not permitted, hence an appropriate test site or sites must be selected to provide Pb concentrations in the specified range.

(c) *Collocated samplers.* The ambient air intake points of all the candidate and reference method collocated samplers shall be positioned at the same height above the ground level, and between 2 meters (1 meter for samplers with flow rates less than 200 liters per minute (L/min)) and 4 meters apart. The samplers shall be oriented in a manner that will minimize spatial and wind directional effects on sample collection.

(d) *Sample collection.* Collect simultaneous 24-hour samples (filters) of Pb at the test site or sites with both the reference and candidate methods until at least 10 filter pairs have been obtained. A candidate method which employs a sampler and sample collection procedure that are identical to the sampler and sample collection procedure specified in the reference method, but uses a different analytical procedure, may be tested by analyzing common samples. The common samples shall be collected according to the sample collection procedure specified by the reference method and each shall be divided for respective analysis in accordance with the analytical procedures of the candidate method and the reference method.

(e) *Audit samples.* Three audit samples must be obtained from the address given in § 53.4(a). For Pb in TSP collected by the high-volume sampling method, the audit samples are ¾ x 8-inch glass fiber strips containing known amounts of Pb in micrograms per strip (µg/strip) equivalent to the following nominal percentages of the National Ambient Air Quality Standard (NAAQS): 30%, 100 %, and 250%. For Pb in PM_{10} collected by the low-volume sampling method, the audit samples are 46.2-mm polytetrafluorethylene (PTFE) filters containing known amounts of Pb in micrograms per filter (µg/filter) equivalent to the same percentages of the NAAQS: 30%, 100%, and 250%. The true amount of Pb, in total µg/strip (for TSP) or total µg/filter (for PM_{10}), will be provided with each audit sample.

(f) *Filter analysis.*

(1) For both the reference method samples and the audit samples, analyze each filter or filter extract three times in accordance with the reference method analytical procedure. The analysis of replicates should not be performed sequentially, i.e., a single sample should not be analyzed three times in sequence. Calculate the indicated Pb concentrations for the reference method samples in micrograms per cubic meter ($\mu g/m^3$) for each analysis of each filter. Calculate the indicated total Pb amount for the audit samples in µg/strip for each analysis of each strip or µg/filter for each analysis of each audit filter. Label these test results as R_{1A}, R_{1B}, R_{1C}, R_{2A}, R_{2B}, * * *, Q_{1A}, Q_{1B}, Q_{1C}, * * *, where R denotes results from the reference method samples; Q

denotes results from the audit samples; 1, 2, 3 indicate the filter number, and A, B, C indicate the first, second, and third analysis of each filter, respectively.

(2) For the candidate method samples, analyze each sample filter or filter extract three times and calculate, in accordance with the candidate method, the indicated Pb concentration in µg/m3 for each analysis of each filter. Label these test results as C_{1A}, C_{1B}, C_{2C}, * * *, where C denotes results from the candidate method. For candidate methods which provide a direct measurement of Pb concentrations without a separable procedure, $C_{1A}=C_{1B}=C_{1C}$, $C_{2A}=C_{2B}=C_{2C}$, etc.

(g) *Average Pb concentration.* For the reference method, calculate the average Pb concentration for each filter by averaging the concentrations calculated from the three analyses using equation 1 of this section:

Equation 1

$$R_{iave} = \frac{\left(R_{iA} + R_{iB} + R_{iC}\right)}{3}$$

Where, i is the filter number.

(h) *Accuracy.*

(1)(i) For the audit samples, calculate the average Pb concentration for each strip or filter by averaging the concentrations calculated from the three analyses using equation 2 of this section:

Equation 2

$$Q_{iave} = \frac{\left(Q_{iA} + Q_{iB} + Q_{iC}\right)}{3}$$

Where, i is audit sample number.

(ii) Calculate the percent difference (Dq) between the indicated Pb concentration for each audit sample and the true Pb concentration (Tq) using equation 3 of this section:

Equation 3

$$D_{qi} = \frac{Q_{iave} - T_{qi}}{T_{qi}} \times 100$$

(2) If any difference value (D_{qi}) exceeds ±5 percent, the accuracy of the reference method analytical procedure is out-of-control. Corrective action must be taken to determine the source of the error(s) (e.g., calibration standard discrepancies, extraction problems, etc.) and the reference method and audit sample determinations must be repeated according to paragraph (f) of this section, or the entire test procedure (starting with paragraph (d) of this section) must be repeated.

(i) *Acceptable filter pairs.* Disregard all filter pairs for which the Pb concentration, as determined in paragraph (g) of this section by the average of the three reference method determinations, falls outside the range of 30% to 250% of the Pb NAAQS level in µg/m^3 for Pb in both TSP and PM_{10}. All remaining filter pairs must be subjected to the tests for precision and comparability in paragraphs (j) and (k) of this section. At least five filter pairs must be within the specified concentration range for the tests to be valid.

(j) *Test for precision.*

(1) Calculate the precision (P) of the analysis (in percent) for each filter and for each method, as the maximum minus the minimum divided by the average of the three concentration values, using equation 4 or equation 5 of this section:

Equation 4

$$P_{Ri} = \frac{R_{i\,\max} - R_{i\,\min}}{R_{iave}} \times 100$$

or

Equation 5

$$P_{Ci} = \frac{C_{i\,\max} - C_{i\,\min}}{C_{iave}} \times 100$$

where, i indicates the filter number.

(2) If any reference method precision value (P_{Ri}) exceeds 15 percent, the precision of the reference method analytical procedure is out-of-control. Corrective action must be taken to determine the source(s) of imprecision, and the reference method determinations must be repeated according to paragraph (f) of this section, or the entire test procedure (starting with paragraph (d) of this section) must be repeated.

(3) If any candidate method precision value (P_{Ci}) exceeds 15 percent, the candidate method fails the precision test.

(4) The candidate method passes this test if all precision values (i.e., all P_{Ri}'s and all P_{Ci}'s) are less than 15 percent.

(k) Test for comparability. (1) For each filter or analytical sample pair, calculate all nine possible percent differences (D) between the reference and candidate methods, using all nine possible combinations of the three determinations (A, B, and C) for each method using equation 6 of this section:

Equation 6

$$D_{in} = \frac{C_{ij} - R_{jk}}{R_{jk}} \times 100$$

where, i is the filter number, and n numbers from 1 to 9 for the nine possible difference combinations for the three determinations for each method (j = A, B, C, candidate; k = A, B, C, reference).

(2) If none of the percent differences (D) exceeds ±20 percent, the candidate method passes the test for comparability.

(3) If one or more of the percent differences (D) exceed ±20 percent, the candidate method fails the test for comparability.

(4) The candidate method must pass both the precision test (paragraph (j) of this section) and the comparability test (paragraph (k) of this section) to qualify for designation as an equivalent method.

(l) *Method Detection Limit (MDL).*

(1) Calculate the estimated MDL using the guidance provided in 40 CFR, Part 136 Appendix B. It is essential that all sample processing steps of the analytical method be included

in the determination of the method detection limit. Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with the final results in $\mu g/m^3$. The MDL must be equal to, or less than $1/10^{th}$ the level of the Pb NAAQS.

Table C–3 to Subpart C of Part 53—Test Specifications for Pb in TSP and Pb in PM_{10} Methods

Concentration range equivalent to percentage of NAAQS in $\mu g/m^3$	30% to 250%
Minimum number of 24-hr measurements	5
Maximum precision	15%
Maximum analytical accuracy	±5%
Maximum difference, percent of reference method	±20 %
Estimated Method Detection Limit (MDL), $\mu g/m^3$	NAAQS level/10