



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
RESEARCH TRIANGLE PARK, NC 27711

JUN 15 2008

MEMORANDUM

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

**FROM:** Joann Rice, OAQPS/AQAD/AAMG *JRC For*

**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<sub>10</sub> monitoring data for attainment determinations. As such, we proposed a new Federal Reference Method (FRM) for Pb in PM<sub>10</sub> (Pb-PM<sub>10</sub>) on May 20, 2008 (73 FR 29184). The purpose of this memorandum is to provide a basis for a peer review to be conducted with the Clean Air Scientific Advisory Committee (CASAC) Ambient Air Monitoring & Methods (AAMM) Subcommittee on July 14, 2008.

An FRM for Pb-PM<sub>10</sub> 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 proposed basing the Pb-PM<sub>10</sub> sampler on the recently promulgated, low-volume PM<sub>10C</sub> FRM sampler (Appendix O to Part 50) for Pb-PM<sub>10</sub>. The low-volume PM<sub>10C</sub> sampler meets more demanding performance criteria (Appendix L to Part 50) than conventional PM<sub>10</sub> samplers and will be operated at local conditions. Also, the low-volume PM<sub>10C</sub> 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<sub>10</sub> FRM also provides network efficiencies and consistencies with the PM<sub>2.5</sub>, PM<sub>10</sub>, and PM<sub>10-2.5</sub> networks, which also make use of low-volume samplers to collect PM at local conditions.

We proposed the X-Ray Fluorescence (XRF) analysis technique as the analysis method for the Pb-PM<sub>10</sub> FRM. The XRF analysis method is expected to have acceptable precision, bias, and method detection limits (MDLs) when coupled with the low-volume PM<sub>10</sub> 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<sub>2.5</sub> speciation monitoring networks, and will likely also be used for EPA's PM<sub>10-2.5</sub> coarse speciation monitoring network. Attachment 1 contains the proposed regulatory text for the Pb-PM<sub>10</sub> FRM.

**Attachment 1**  
**Proposed FRM Regulatory Text**

**Appendix Q to Part 50 – Reference Method for the Determination of Lead in Particulate Matter as PM<sub>10</sub> Collected From Ambient Air**

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

*1. Applicability and Principle*

1.1 This method provides for the measurement of the lead (Pb) concentration in particulate matter that is 10 micrometers or less (PM<sub>10</sub>) in ambient air. PM<sub>10</sub> 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<sup>3</sup>) of air. The analysis of Pb in PM<sub>10</sub> is performed on each individual 24-hour sample. For the purpose of this method, PM<sub>10</sub> 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<sub>10</sub> shall be collected with the PM<sub>10c</sub> federal reference method (FRM) sampler as described in Appendix O to Part 50 using the same sample period, measurement procedures, and requirements specified in Appendix L of Part 50. The PM<sub>10c</sub> sampler is also being used to for measurement PM<sub>10-2.5</sub> mass by difference and as such, the PM<sub>10c</sub> sampler must also meet all of the performance requirements specified for PM<sub>2.5</sub> in Appendix L. The concentration of Pb in the atmosphere is determined in the total volume of air sampled and expressed in micrograms per cubic meter (μg/m<sup>3</sup>) 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 in section 2.1 and 2.2 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  $\text{ng}/\text{m}^3$  for ambient air samples; however, for this reference method, data will be reported in  $\mu\text{g}/\text{m}^3$  at local temperature and pressure conditions.

2.1 *EDXRF Measurement Range*. The typical ambient air measurement range is 0.001 to 30  $\mu\text{g Pb}/\text{m}^3$ , assuming an upper range calibration standard of about 60  $\mu\text{g Pb}$  per square centimeter ( $\text{cm}^2$ ), a filter deposit area of 11.86  $\text{cm}^2$ , and an air volume of 24- $\text{m}^3$ . 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 1.5  $\text{ng Pb}/\text{cm}^2$  or 0.001  $\mu\text{g Pb}/\text{m}^3$ , assuming a filter size of 46.2-mm (filter deposit area of 11.86  $\text{cm}^2$ ) and a sample air volume of 24- $\text{m}^3$ . 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 as the average overall uncertainty or propagated error for Pb, determined from measurements on a series of blank filters. The sources of random error that 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 results from internal absorption of both primary and secondary X-rays within the sample. The optimum filter loading is about  $150 \mu\text{g}/\text{cm}^2$  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 about  $15 \mu\text{g}/\text{cm}^2$ . 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. Interferences need to be addressed when multi-elemental analysis is performed. The presence of arsenic (As) is a problematic interference for EDXRF systems which use the Pb  $L_{\alpha}$  line exclusively to quantify the Pb concentration. This is because the Pb  $L_{\alpha}$  line and the As  $K_{\alpha}$  lines severely overlap. However, if the instrument software is able to use multiple Pb lines, including the  $L_{\beta}$  and/or the  $L_{\gamma}$  lines for quantification, then the uncertainty in the Pb determination in the presence of As can be significantly reduced. There can be instances when lines partially overlap the Pb spectral lines, but with the energy resolution of most detectors, these overlaps are typically de-convoluted using standard spectral de-convolution software provided by the instrument vendor. 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 used 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<sub>10</sub> 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 mineral compositions and is a one-time calculation that gives an attenuation factor for use in all subsequent particle analyses. See references 6, 7, and 8 of section 8 for more discussion on addressing this issue. Essentially no attenuation corrections are necessary for Pb in PM<sub>10</sub>: 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 method 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*

### *6.1 Sampling*

6.1.1 *Low-Volume PM<sub>10c</sub> Sampler.* The low-volume PM<sub>10c</sub> sampler shall be used for sample collection and operated in accordance with the performance specifications described in Part 50, Appendix L.

6.1.2 *PTFE Filters and Filter Acceptance Testing.* The PTFE filters used for PM<sub>10c</sub> sample collection shall meet the specifications provided in Part 50, Appendix L. The following requirements are similar to those currently specified for the acceptance of PM<sub>2.5</sub> 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<sup>2</sup>. Ninety percent, or 45 of the 50 filters, must have an average lead concentration that is less than 4.8 ng Pb/cm<sup>2</sup>.

6.2 *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.



6.2.1 *EDXRF Analysis Instrument.* An energy-dispersive XRF system is used. Energy-dispersive XRF systems are available from commercial vendors including Thermo ([www.thermo.com](http://www.thermo.com)) and PANalytical ([www.panalytical.com](http://www.panalytical.com)). Note the mention of commercial products does not imply endorsement by the U.S. Environmental Protection Agency. 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.

6.2.2 *Thin film standards.* Thin film standards are used for calibration because they most closely resemble the layer of particles on a filter. Thin film 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).

6.2.3 *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<sup>2</sup>. Filters are typically archived in cold storage prior to analysis. Filters that are scheduled for XRF analysis are removed from storage and allowed to reach room temperature if stored cold. 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. Care must be taken to protect filters to avoid contamination prior to analysis. Filters must be kept covered when not being analyzed. No other preparation of the samples is required.

6.2.4 *Calibration.* In general, calibration determines each element's sensitivity, i.e., its response in X-ray counts/sec to each  $\mu\text{g}/\text{cm}^2$  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 ( $\mu\text{g}/\text{cm}^2$ ) 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 Pb 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 establishes the elemental sensitivity factors and the magnitude of interference or overlap coefficients. See reference 7 for more detailed discussion of calibration and analysis of shapes standards for background correction, coarse particle absorption corrections, and spectral overlap.

6.2.4.1 *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 6.2.4.2 of this section.

6.2.4.2 *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<sub>10</sub> lead concentration in the atmosphere ( $\mu\text{g}/\text{m}^3$ ) is calculated using the following equation:

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

where,

$M_{Pb}$  is the mass per unit volume for lead in  $\mu\text{g}/\text{m}^3$ ;

$C_{Pb}$  is the mass per unit area for lead in  $\mu\text{g}/\text{cm}^2$  as provided by the XRF instrument software;

$A$  is the filter deposit area in  $\text{cm}^2$ ;

$V_{LC}$  is the total volume of air sampled by the PM<sub>10c</sub> sampler in actual volume units measured at local conditions of temperature and pressure, as provided by the sampler in  $\text{m}^3$ .

## 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.
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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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