

the annual fourth maximum have also been truncated to the third decimal place.

### 3. Design Values for Primary and Secondary Ambient Air Quality Standards for Ozone

The air quality design value at a monitoring site is defined as that concentration that when reduced to the level of the standard ensures that the site meets the standard. For a concentration-based standard, the air quality design value is simply the standard-related test statistic. Thus, for the primary and secondary standards, the 3-year average annual fourth-highest daily maximum 8-hour average O<sub>3</sub> concentration is also the air quality design value for the site.

[73 FR 16511, Mar. 27, 2008]

#### 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 an acceptable (see section 6.1.2) 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. Gravimetric mass analysis of PM<sub>10c</sub> filters is not required for Pb analysis. 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 for measurement of 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). This FRM specifically applies to the analysis of Pb in PM<sub>10</sub> filters collected with the PM<sub>10c</sub> sampler. If these filters are analyzed for elements other than Pb, then refer to the guidance provided in the EPA Inorganic Compendium Method IO-3.3 (Reference 1 of section 8) for multi-element analysis.

1.4 The PM<sub>10c</sub> air sampler 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<sub>10</sub> size range is separated for collection on a PTFE filter over the specified sampling period. The Pb content of the PM<sub>10</sub> 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 intensity of X-rays emitted at the characteristic photon energy 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. A detailed explanation of quantitative X-ray spectrometry is described in references 2, 3 and 4.

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

2. *PM<sub>10</sub>Pb Measurement Range and 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 ng/m<sup>3</sup> for ambient air samples; however, for this reference method, data will be reported in μg/m<sup>3</sup> at local temperature and pressure conditions.

2.1 *EDXRF Pb Measurement Range.* The typical ambient air measurement range is 0.001 to 30 μg Pb/m<sup>3</sup>, assuming an upper range calibration standard of about 60 μg Pb per square centimeter (cm<sup>2</sup>), a filter deposit area of 11.86 cm<sup>2</sup>, and an air volume of 24 m<sup>3</sup>. 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 *Detection Limit (DL).* A typical estimate of the one-sigma detection limit (DL) is about 2 ng Pb/cm<sup>2</sup> or 0.001 μg Pb/m<sup>3</sup>, assuming a filter size of 46.2 mm (filter deposit

area of 11.86 cm<sup>2</sup>) and a sample air volume of 24 m<sup>3</sup>. The DL is an estimate of the lowest amount of Pb that can be reliably distinguished from a blank filter. 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 from the filter lot(s) in use. Detection limits must be determined for each filter lot in use. If a new filter lot is used, then a new DL must be determined. The sources of random error which are considered are calibration uncertainty; system stability; peak and background counting statistics; uncertainty in attenuation corrections; and uncertainty in peak overlap corrections, but the dominating source by far is peak and background counting statistics. At a minimum, laboratories are to determine annual estimates of the DL using the guidance provided in Reference 5.

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

3.1 *Filter Deposit.* 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; however, this is not an issue for Pb due to the energetic X-rays used to fluoresce Pb and the energetic characteristic X-rays emitted by Pb. The optimum mass filter loading for multi-elemental EDXRF analysis is about 100 µg/cm<sup>2</sup> or 1.2 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 µg/cm<sup>2</sup>. The maximum PM<sub>10</sub> filter loading or upper concentration limit of mass expected to be collected by the PM<sub>10c</sub> sampler is 200 µg/m<sup>3</sup> (Appendix O to Part 50, Section 3.2). This equates to a mass loading of about 400 µg/cm<sup>2</sup> and is the maximum expected loading for PM<sub>10c</sub> filters. This maximum loading is acceptable for the analysis of Pb and other high-Z elements with very energetic characteristic X-rays. A properly collected sample will have a uniform deposit over the entire collection area. Samples with physical deformities (including a visually non-uniform deposit area) should not be quantitatively analyzed. Tests on the uniformity of particle deposition on PM<sub>10c</sub> filters showed that the non-uniformity of the filter deposit represents a small fraction of the overall uncertainty in ambient Pb concentration measurement. The analysis beam of the XRF analyzer does not cover the entire filter collection area. The minimum allowable beam size is 10 mm.

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. The presence of arsenic (As) is a problematic interference for EDXRF systems which use the Pb L<sub>α</sub> line exclusively to quantify the Pb con-

centration. This is because the Pb L<sub>α</sub> line and the As K<sub>α</sub> lines severely overlap. The use of multiple Pb lines, including the L<sub>β</sub> and/or the L<sub>γ</sub> lines for quantification must be used to reduce the uncertainty in the Pb determination in the presence of As. 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. 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 any attenuation present must be corrected for. See references 6, 7, and 8 for more discussion on 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.

### 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 20 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 15 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 PM<sub>10</sub> 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 filter lots (greater than 500 filters) randomly select 20 filters from a given lot. For small lots (less than 500 filters) a lesser number of filters may be taken. Analyze each blank filter separately and calculate the average lead concentration in ng/cm<sup>2</sup>. Ninety percent, or 18 of the 20 filters, must have an average lead concentration that is less than 4.8 ng Pb/cm<sup>2</sup>.

**6.1.2.1 Filter Blanks.** Field blank filters shall be collected along with routine samples. Field blank filters will be collected that are transported to the sampling site and placed in the sampler for the duration of sampling without sampling. Laboratory blank filters from each filter lot used shall be analyzed with each batch of routine sample filters analyzed. Laboratory blank filters are used in background subtraction as discussed below in Section 6.2.4.

**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. Spectral processing methods are well established and most commercial analyzers have software that can implement the most common approaches (references 9-11) to background subtraction, peak overlap correction, counting and deadtime corrections.

**6.2.1 EDXRF Analysis Instrument.** An energy-dispersive XRF system is used. Energy-dispersive XRF systems are available from a number of commercial vendors. Examples include Thermo ([www.thermo.com](http://www.thermo.com)), Spectro (<http://www.spectro.com>), Xenometrix (<http://www.xenometrix.com>) and PANalytical (<http://www.panalytical.com>).<sup>1</sup> 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 films standards are typically deposited on Nuclepore substrates. The

preparation of thin film standards is discussed in reference 8, and 10. The NIST SRM 2783 (Air Particulate on Filter Media) is currently available on polycarbonate filters and contains a certified concentration for Pb. Thin film standards at 15 and 50 µg/cm<sup>2</sup> 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>. Cold storage is not a requirement for filters analyzed for Pb; however, if filters scheduled for XRF analysis were stored cold, they must be allowed to reach room temperature prior to analysis. All filter samples received for analysis are checked for any holes, tears, or a non-uniform deposit which would prevent quantitative analysis. 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 from contamination prior to analysis. Filters must be kept covered when not being analyzed. No other preparation of filter 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 µg/cm<sup>2</sup> 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 (µg/cm<sup>2</sup>) 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 interfering elements) and spectral backgrounds. Pure element thin film standards are used for the element peak shapes and clean filter blanks from the same lot as routine filter samples are used for the background. The analysis of Pb in PM filter deposits is based on the assumption that the thickness of the deposit is small with respect to the characteristic Pb 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 the sensitivity factor for Pb and then analyzing the unknown samples under identical excitation conditions as used to determine the calibration. Calibration shall be

<sup>1</sup>These are examples of available systems and is not an all inclusive list. The mention of commercial products does not imply endorsement by the U.S. Environmental Protection Agency.

performed annually or when significant repairs or changes occur (e.g., a change in fluorescers, X-ray tubes, or detector). 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 peak 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. Background spectra must be obtained for each filter lot used for sample collection. The background shape standards which are used for background fitting are created at the time of calibration. If a new lot of filters is used, new background spectra must be obtained. A minimum of 20 clean blank filters from each filter lot 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 atypical 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 *PM<sub>10</sub> Pb concentrations.* The PM<sub>10</sub> Pb concentration in the atmosphere (µg/m<sup>3</sup>) 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 µg/m<sup>3</sup>;

$C_{Pb}$  is the mass per unit area for lead in µg/cm<sup>2</sup> as measured by XRF;

$A$  is the filter deposit area in cm<sup>2</sup>;

$V_{LC}$  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 m<sup>3</sup>.

#### 7.2 PM<sub>10</sub> Pb Uncertainty Calculations.

The principal contributors to total uncertainty of XRF values include: field sampling; filter deposit area; XRF calibration; attenuation or loss of the x-ray signals due to the other components of the particulate sample; and determination of the Pb X-ray emission peak area by curve fitting. See reference 12 for a detailed discussion of how uncertainties are similarly calculated for the PM<sub>2.5</sub> Chemical Speciation program.

The model for calculating total uncertainty is:

$$\delta_{tot} = (\delta_f^2 + \delta_a^2 + \delta_c^2 + \delta_v^2)^{1/2}$$

Where,

$\delta_f$  = fitting uncertainty (XRF-specific, from 2 to 100+%)

$\delta_a$  = attenuation uncertainty (XRF-specific, insignificant for Pb)

$\delta_c$  = calibration uncertainty (combined lab uncertainty, assumed as 5%)

$\delta_v$  = volume/deposition size uncertainty (combined field uncertainty, assumed as 5%)

#### 8. References

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## APPENDIX R TO PART 50—INTERPRETATION OF THE NATIONAL AMBIENT AIR QUALITY STANDARDS FOR LEAD

### 1. General.

(a) This appendix explains the data handling conventions and computations necessary for determining when the primary and secondary national ambient air quality standards (NAAQS) for lead (Pb) specified in § 50.16 are met. The NAAQS indicator for Pb is defined as: lead and its compounds, measured as elemental lead in total suspended particulate (Pb-TSP), sampled and analyzed by a Federal reference method (FRM) based on appendix G to this part or by a Federal equivalent method (FEM) designated in accordance with part 53 of this chapter. Although Pb-TSP is the lead NAAQS indicator, surrogate Pb-TSP concentrations shall also be used for NAAQS comparisons; specifically, valid surrogate Pb-TSP data are concentration data for lead and its compounds, measured as elemental lead, in particles with an aerodynamic size of 10 microns or less (Pb-PM<sub>10</sub>), sampled and analyzed by an

FRM based on appendix Q to this part or by an FEM designated in accordance with part 53 of this chapter. Surrogate Pb-TSP data (*i.e.*, Pb-PM<sub>10</sub> data), however, can only be used to show that the Pb NAAQS were violated (*i.e.*, not met); they can not be used to demonstrate that the Pb NAAQS were met. Pb-PM<sub>10</sub> data used as surrogate Pb-TSP data shall be processed at face value; that is, without any transformation or scaling. Data handling and computation procedures to be used in making comparisons between reported and/or surrogate Pb-TSP concentrations and the level of the Pb NAAQS are specified in the following sections.

(b) Whether to exclude, retain, or make adjustments to the data affected by exceptional events, including natural events, is determined by the requirements and process deadlines specified in §§ 50.1, 50.14, and 51.930 of this chapter.

(c) The terms used in this appendix are defined as follows:

*Annual monitoring network plan* refers to the plan required by section 58.10 of this chapter.

*Creditable samples* are samples that are given credit for data completeness. They include valid samples collected on required sampling days and valid “make-up” samples taken for missed or invalidated samples on required sampling days.

*Daily values* for Pb refer to the 24-hour mean concentrations of Pb (Pb-TSP or Pb-PM<sub>10</sub>), measured from midnight to midnight (local standard time), that are used in NAAQS computations.

*Design value* is the site-level metric (*i.e.*, statistic) that is compared to the NAAQS level to determine compliance; the design value for the Pb NAAQS is selected according to the procedures in this appendix from among the valid three-month Pb-TSP and surrogate Pb-TSP (Pb-PM<sub>10</sub>) arithmetic mean concentration for the 36-month period consisting of the most recent 3-year calendar period plus two previous months (*i.e.*, 36 3-month periods) using the last month of each 3-month period as the period of report.

*Extra samples* are non-creditable samples. They are daily values that do not occur on scheduled sampling days and that can not be used as “make-up samples” for missed or invalidated scheduled samples. Extra samples are used in mean calculations. For purposes of determining whether a sample must be treated as a make-up sample or an extra sample, Pb-TSP and Pb-PM<sub>10</sub> data collected before January 1, 2009 will be treated with an assumed scheduled sampling frequency of every sixth day.

*Make-up samples* are samples taken to replace missed or invalidated required scheduled samples. Make-ups can be made by either the primary or collocated (same size fraction) instruments; to be considered a