

**List of Subjects in 33 CFR Part 165**

Harbors, Marine safety, Navigation (water), Reporting and record keeping requirements, Security measures, Waterways.

For the reasons discussed in the preamble, the Coast Guard proposes to amend 33 CFR part 165 as follows:

**PART 165—REGULATED NAVIGATION AREAS AND LIMITED ACCESS AREAS**

■ 1. The authority citation for part 165 continues to read as follows:

**Authority:** 33 U.S.C. 1226, 1231; 46 U.S.C. Chapters 701, 3306, 3707; 50 U.S.C. 191, 195; 33 CFR 1.05–1, 6.04–1, 6.04–6, and 160.5; Pub. L. 107–295, 116 Stat. 2064; Department of Homeland Security Delegation No. 0170.1

■ 2. In § 165.1332, amend the table in paragraph (a)(1) by:  
 a. Revising the entries for “City of Renton Fireworks,” “Bainbridge Island Fireworks,” and “Port Townsend Sunrise Rotary”; and  
 b. Adding entries for “Tacoma Freedom Fair,” “Brewster 4th of July,” “Port Ludlow Fireworks,” “Boston Harbor 4th of July,” and “Everett 4th of July.”

Harbor 4th of July,” and “Everett 4th of July.”

The revisions and additions read as follows:

**§ 165.1332 Safety Zones; Annual Fireworks Displays within the Captain of the Port Puget Sound Zone.**

- (a) \* \* \*
- (1) \* \* \*

Event name	Event location	Latitude	Longitude
* * * * *	* * * * *	* * * * *	* * * * *
City of Renton Fireworks	Renton, Lake Washington	47° 30.386' N	122° 12.502' W
Bainbridge Island Fireworks	Eagle Harbor	47° 37.142' N	122° 30.397' W
Port Townsend Sunrise Rotary	Port Townsend	47° 08.413' N	122° 45.531' W
Tacoma Freedom Fair	Commencement Bay	47° 17.103' N	122° 28.410' W
Brewster 4th of July	Brewster	48° 05.362' N	119° 47.147' W
Port Ludlow Fireworks	Port Ludlow	47° 55.161' N	122° 41.157' W
Boston Harbor 4th of July	Boston Harbor	47° 08.626' N	122° 54.149' W
Everett 4th of July	Port Gardner	48° 00.672' N	122° 13.391' W

\* \* \* \* \*

Dated: January 14, 2013.

**S. J. Ferguson,**

*Captain, U.S. Coast Guard, Captain of the Port, Puget Sound.*

[FR Doc. 2013–02432 Filed 2–4–13; 8:45 am]

**BILLING CODE 9110–04–P**

**ENVIRONMENTAL PROTECTION AGENCY**

**40 CFR Parts 50**

[EPA–HQ–OAR–2012–0210; FRL–9775–6]

RIN 2060–AP89

**Method for the Determination of Lead in Total Suspended Particulate Matter**

**AGENCY:** Environmental Protection Agency (EPA).

**ACTION:** Proposed rule.

**SUMMARY:** Data used for comparison with the lead (Pb) national ambient air quality standards (NAAQS), must be collected using either a Federal Reference Method (FRM) or a Federal Equivalent Method (FEM) as defined in the Code of Federal Regulations (CFR). The EPA is proposing to establish a new FRM for measuring Pb in total suspended particulate matter (TSP) collected from ambient air. The

proposed method is intended for use by analytical laboratories performing the analysis of Pb in TSP to support data collection for the Pb NAAQS. The EPA is also proposing to make the existing FRM for Pb a new FEM, and retain currently designated FEMs. This proposed action avoids any disruption to existing Pb monitoring networks and data collection and would also not affect the FRM for TSP sample collection (High-Volume Method).

**DATES:** Comments must be received on or before March 7, 2013

**ADDRESSES:** Submit your comments, identified by Docket ID No. EPA–HQ–OAR–2012–0210 by one of the following methods:

- *www.regulations.gov:* Follow the on-line instructions for submitting comments.
- *Email:* a-and-r-docket@epamail.epa.gov
- *Fax:* (202) 566–9744
- *Mail:* Federal Reference Method for Lead in Total Suspended Particulate Matter, U.S. Environmental Protection Agency, EPA Docket Center (EPA/DC), Air and Radiation Docket and Information Center, MC 2822T, 1200 Pennsylvania Ave. NW., Washington, DC 20460.
- *Hand Delivery:* EPA Docket Center, Room 3334 in the EPA West Building, located at 1301 Constitution Ave. NW.,

Washington, DC 20460. The Docket is open to the public on all federal government work days from 8:30a.m. to 4:30p.m. Such deliveries are only accepted during the Docket’s normal hours of operation, and special arrangements should be made for deliveries of boxed information.

**Instructions:** Direct your comments to Docket ID No. EPA–HQ–OAR–2012–0210. The EPA’s policy is that all comments received will be included in the public docket without change and may be made available online at *www.regulations.gov*, including any personal information provided, unless the comment includes information claimed to be Confidential Business Information (CBI) or other information whose disclosure is restricted by statute. Do not submit information that you consider to be CBI or otherwise protected through *www.regulations.gov* or email. The *www.regulations.gov* Web site is an “anonymous access” system, which means the EPA will not know your identity or contact information unless you provide it in the body of your comment. If you send an email comment directly to the EPA without going through *www.regulations.gov*, your email address will be automatically captured and included as part of the comment that is placed in the public docket and made available on the

Internet. If you submit an electronic comment, the EPA recommends that you include your name and other contact information in the body of your comment and with any disk or CD-ROM you submit. If the EPA cannot read your comment due to technical difficulties and cannot contact you for clarification, the EPA may not be able to consider your comment. Electronic files should avoid the use of special characters, any form of encryption, and be free of any defects or viruses. For additional information about the EPA's public docket, visit the EPA Docket Center homepage at <http://www.epa.gov/epahome/dockets.htm>. All documents in the docket are listed in the <http://www.regulations.gov> index. Although listed in the index, some information is not publicly available, e.g., CBI or other information whose disclosure is restricted by statute. Certain other material, such as copyrighted material, is not placed on the Internet and will be publicly available only in hard copy form. Publicly available docket materials are available either electronically at [www.regulations.gov](http://www.regulations.gov) or in hard copy at the Air Docket, EPA/DC, EPA West, Room 3334, 1301 Constitution Avenue NW., Washington, DC. The Docket Facility and the Public Reading Room are open from 8:30 a.m. to 4:30 p.m., Monday through Friday, excluding legal holidays. The telephone number for the Public Reading Room is (202) 566-1744, and the telephone number for the Air Docket is (202) 566-1742.

**FOR FURTHER INFORMATION CONTACT:** Ms. Joann Rice, Office of Air Quality Planning and Standards, Air Quality Assessment Division, Ambient Air Monitoring Group (C304-06), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711; telephone number: (919) 541-3372; fax number: (919) 541-1903; email address: [rice.joann@epa.gov](mailto:rice.joann@epa.gov).

**SUPPLEMENTARY INFORMATION:**

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**I. Background**

*A. Purpose of the New Reference Method*

On November 12, 2008, the EPA substantially strengthened the National Ambient Air Quality Standard for Lead (73 FR 66964). The EPA revised the level of the primary (health-based) standard from 1.5 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ) of Pb to 0.15  $\mu\text{g}/\text{m}^3$  of Pb measured in TSP and revised the secondary (welfare-based) standard to be identical in all respects to the primary standard. The current Pb in TSP FRM is based on Flame Atomic Absorption Spectroscopy (FAAS) as specified in 40 CFR part 50, Appendix G. The FRM in Appendix G was originally promulgated in 1978 when FAAS was widely used and considered the best available method to support Pb NAAQS data collection at a level of 1.5  $\mu\text{g}/\text{m}^3$ . A new Pb in TSP FRM is needed to: (1) Take advantage of improved extraction methods that are now available with improved precision, sample throughput, and extraction efficiency; (2) address advances in measurement technology that have occurred since promulgation of the original FRM; and (3) address the improved measurement sensitivity (detection limits) needed in response to the tightened Pb NAAQS.

The reference method for Pb in TSP includes two parts, the analysis method for Pb in TSP as specified in Appendix G and the reference method for high-volume sampling of TSP as specified in 40 CFR 50, Appendix B. The proposed FRM will become a replacement for the analytical method in Appendix G. The EPA is proposing a new FRM for the analysis of Pb in TSP based on Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The FRM would serve as the definitive method for routinely analyzing Pb for comparison to the NAAQS and also serve as the standard of comparison for determining equivalence of candidate FEMs. The method is proposed as a new Appendix G to 40 CFR part 50. The FRM that was promulgated in 1978 as Appendix G would become an approved FEM and the currently designated FEMs would be

retained. The EPA believes this is appropriate because the new FRM is based on two methods that were tested and approved as FEMs (EQL-0510-191 and EQL-0710-192) to ensure comparability with the existing FRM. The proposed approach permits continued use of the old FRM (as an FEM) and the existing FEMs. This avoids any disruption to state and local air monitoring agencies using these methods for Pb monitoring. The reference method for high volume sampling of TSP will continue to be performed in accordance with the FRM described in Appendix B, and, therefore, is not included as part of this proposed FRM.

With the much tightened NAAQS in 2008 and the need for increased measurement sensitivity, an improved measurement technology has become available to better meet the needs of the current NAAQS. The FAAS FRM is less frequently used in the Pb ambient monitoring network (about 10 percent of the sites reported Pb in TSP data to the EPA's Air Quality System in 2012 using the FRM) and ICP-based methods have increased in popularity. The FAAS method is mainly used as the reference method for testing and designation of candidate FEMs for Pb in accordance with 40 CFR 53.33. With the lowered Pb concentration testing range in Part 53 and new requirement for a Method Detection Limit (MDL) of 0.0075  $\mu\text{g}/\text{m}^3$  (described below), the FAAS method sensitivity and availability of laboratories with FAAS capability have created some challenges for comparability testing of new FEMs.

In 2008, the EPA also revised the performance-based requirements for Pb FEMs in Part 53. The performance requirements were revised to be consistent with the revised Pb NAAQS level. Specifically, the Pb concentration range at which the FEM comparability testing is conducted was lowered to a range of 0.045 to 0.375  $\mu\text{g}/\text{m}^3$  and the requirement for a minimum method detection limit was established at 0.0075  $\mu\text{g}/\text{m}^3$ . The detection limit of the proposed FRM is more than adequate to meet the reduced testing range and detection limit requirements. The proposed FRM's average detection limit for Pb-spiked filters is estimated at 0.00009  $\mu\text{g}/\text{m}^3$ , which is well below the requirement of 0.0075  $\mu\text{g}/\text{m}^3$ .

*B. Rationale for Selection of the New Reference Method*

The proposed FRM is based on two recently approved FEMs for extracting Pb from glass fiber filters for subsequent analysis by ICP-MS: (1) Method EQL-0510-191 which uses a heated ( $80 \pm 5^\circ$

C) ultrasonic water bath with 1.03M nitric (HNO<sub>3</sub>)/2.23M hydrochloric (HCl) acids, and (2) Method EQL-0710-192 which uses a heated (95 ± 5° C) graphite block (hot block) with 3.5 percent volume/volume (v/v) HNO<sub>3</sub>. In selecting the proposed methodology, the EPA's primary considerations were: methods that have already been tested and approved against the FAAS FRM (current Appendix G); use of equipment that is commonly used; a method that is practical (use of a single vessel for the entire extraction process and storage); and a method with improved sensitivity and throughput to increase efficiency and cost effectiveness over the current FRM. ICP-MS was chosen as the analytical technique because it has much improved sensitivity, selectivity, linear range, and is much more readily available than FAAS in laboratories today.

The proposed FRM uses methods from two existing FEMs that have been proven comparable to FAAS and, therefore, retains consistency with the legacy FRM (Rice 2013). The proposed FRM is only intended for the analysis of Pb in TSP and allows for the use of glass fiber, quartz, or Teflon® filters. HNO<sub>3</sub> alone is sufficient for the extraction of Pb; however, the ultrasonic extraction method includes HCl to allow monitoring agencies some flexibility for future needs that may include the extraction of other metals. HCl is needed to aid the extraction of other metals that are not easily brought into solution with HNO<sub>3</sub> alone. The proposed FRM was evaluated for the extraction of Pb only. If the proposed FRM is used for metals other than Pb, the user must evaluate the FRM's applicability before use. The heated block extraction method uses only HNO<sub>3</sub> and must also be evaluated by the user before use to extract metals other than Pb.

The approach and key specifications of the method were submitted for peer review to the Clean Air Scientific Advisory Committee (CASAC) Ambient Air Monitoring and Methods Subcommittee. Public meetings were held to discuss the method and related monitoring issues on September 15, 2010. Comments on the proposed method and approach were provided in writing in a letter dated November 30, 2010 (EPA-CASAC-11-002),<sup>1</sup>

<sup>1</sup> CASAC's final report on the Approach for the Development of a New Federal Reference Method (FRM) for Lead in Total Suspended Particulates (Pb-TSP) can be found at: [http://yosemite.epa.gov/sab/sabproduct.nsf/DA39026E54BAF46E8525781D00606633/\\$File/EPA-CASAC-11-002-unsigned.pdf](http://yosemite.epa.gov/sab/sabproduct.nsf/DA39026E54BAF46E8525781D00606633/$File/EPA-CASAC-11-002-unsigned.pdf)

forwarded by CASAC to the Administrator.

The CASAC was supportive of the ICP-MS analytical method and found the approach to be appropriate with superior sensitivity and specificity for Pb. The CASAC recommended a strategy, using a performance-based FRM, to provide flexibility for use of non-FRM or FEM measurement methods and recommended that a third extraction method (microwave) be added to the FRM for its greater sample throughput and potential for reduced sample-to-sample variability. The CASAC viewed the comprehensiveness of the FRM test plan to be appropriate, and recommended that the EPA consider separating the extraction methods from the analytical methods so that any of the proposed FRM extraction methods can be used with any of the proposed FRM analytical measurement methods.

The federal reference and equivalence testing method for Pb in 40 CFR 53.33 serves as the performance-based method approach for the FEM approval process. Candidate methods are tested using the performance specifications of part 40 CFR part 53 for acceptance and approval as equivalent methods. Users also have the flexibility to test and submit additional extraction and analysis methods for review and approval as equivalent methods. The EPA believes that microwave extraction is a viable option and is already available as an approved FEM<sup>2</sup>. The ultrasonic and hot block approaches are sufficient for the extraction of Pb and provide high sample throughput, low consumable costs, and lower equipment costs while minimizing the risk of cross contamination and sample loss. In addition, the EPA believes that the existing FEMs<sup>3</sup> currently provide a wide variety of extraction and analytical methods and the EPA strongly encourages monitoring agencies to consider adopting one of the already approved FEMs in lieu of submitting new FEM applications. The proposed FRM has two extraction methods (heated ultrasonic and hot block) and one analytical method (ICP-MS). The proposed FRM allows for the use of either of the two extraction methods specified with the ICP-MS analytical method. The method also allows for the use of glass fiber, Teflon®, or quartz filter media for the collection of Pb in TSP.

<sup>2</sup> FEM EQL-0400-0140 (65 FR 26603, May 8, 2000)

<sup>3</sup> The list of current FEMs is located at: <http://epa.gov/ttn/amtic/files/ambient/criteria/reference-equivalent-methods-list.pdf>

## II. Summary of Method

The proposed FRM uses the ambient air sample collection procedures of the high-volume TSP method (40 CFR part 50, Appendix B) and the analytical procedure for the measurement of Pb based on ICP-MS. Two extraction methods are proposed: one using heated ultrasonic and one using heated block digestion. The proposed extraction methods and ICP-MS analysis method have been tested and found acceptable for extraction of Pb from glass fiber, Teflon®, or quartz filter media (Rice 2013). The proposed method will replace the existing FRM specified in 40 CFR part 50, Appendix G. Although the existing FRM in Appendix G is adequate, the proposed FRM offers advantages over the current FRM by providing improved sensitivity or detection limits, precision, sample throughput, and extraction efficiency.

## III. Statutory and Executive Order Reviews

### A. Executive Order 12866: Regulatory Planning and Review and Executive Order 13563: Improving Regulation and Regulatory Review

This action is not a "significant regulatory action" under the terms of Executive Order 12866 (58 FR 51735, October 4, 1993) and is, therefore, not subject to review under Executive Orders 12866 and 13563 (76 FR 3821, January 21, 2011).

### B. Paperwork Reduction Act

This action does not impose an information collection burden under the provisions of the *Paperwork Reduction Act*, 44 U.S.C. 3501 *et seq.* Burden is defined at 5 CFR 1320.3(b). The proposed rule is for a new FRM for Pb in TSP, and to designate the existing FRM as an FEM, and does not add any information collection requirements beyond those imposed by the existing Pb monitoring requirements.

### C. Regulatory Flexibility Act

The Regulatory Flexibility Act (RFA) generally requires an agency to prepare a regulatory flexibility analysis of any rule subject to notice and comment rulemaking requirements under the Administrative Procedure Act or any other statute unless the agency certifies that the rule will not have a significant economic impact on a substantial number of small entities. Small entities include small businesses, small organizations, and small governmental jurisdictions.

For purposes of assessing the impacts of this proposed rule on small entities, small entity is defined as (1) a small

business as defined by the Small Business Administration's (SBA) regulations at 13 CFR 121.201; (2) a small governmental jurisdiction that is a government of a city, county, town, school district or special district with a population of less than 50,000; and (3) a small organization that is any not-for-profit enterprise which is independently owned and operated and is not dominant in its field.

After considering the economic impacts of this proposed rule on small entities, I certify that this action will not have a significant economic impact on a substantial number of small entities. This proposed rule will not impose any additional monitoring requirements beyond those specified in the current regulations, nor will it require any changes in approved monitoring methods. As such, it will not impose any requirements on small entities. The EPA continues to be interested in the potential impacts of the proposed rule on small entities and welcomes comments on issues related to such impacts.

#### *D. Unfunded Mandates Reform Act*

This action contains no federal mandates under the provisions of Title II of the Unfunded Mandates Reform Act of 1995 (UMRA), 2 U.S.C. 1531–1538 for state, local, or tribal governments or the private sector. This action imposes no enforceable duty on any state, local or tribal governments or the private sector. Therefore, this action is not subject to the requirements of sections 202 or 205 of the UMRA. This action is also not subject to the requirements of section 203 of UMRA because it contains no regulatory requirements that might significantly or uniquely affect small governments. This action proposes to establish a new FRM for state and local air monitoring agencies to use as one of the approved methods for measurement of Pb in TSP and to designate the existing FRM as an FEM. It does not create any additional monitoring requirements or require changes in approved monitoring methods.

#### *E. Executive Order 13132: Federalism*

This action does not have federalism implications. It will not have substantial direct effects on the states, on the relationship between the national government and the states, or on the distribution of power and responsibilities among the various levels of government, as specified in Executive Order 13132. This action proposes to establish a new FRM for state and local air monitoring agencies to use as one of the approved methods

for measurement of Pb in TSP and to designate the existing FRM as an FEM. This action does not create any new monitoring requirements or require any changes in approved monitoring methods. Thus, Executive Order 13132 does not apply to this action. In the spirit of Executive Order 13132, and consistent with the EPA policy to promote communications between the EPA and state and local governments, the EPA specifically solicits comment on this proposed rule from state and local officials.

#### *F. Executive Order 13175: Consultation and Coordination With Indian Tribal Governments*

This action does not have tribal implications, as specified in Executive Order 13175 (65 FR 67249, November 9, 2000). This proposed rule imposes no requirements on tribal governments. This action proposes to establish a new FRM for state and local air monitoring agencies to use as one of the approved methods for measurement of Pb in TSP and to designate the existing FRM as an FEM. This action does not create any new monitoring requirements nor require any changes in approved monitoring methods. Thus, Executive Order 13175 does not apply to this action. In the spirit of Executive order 13175, the EPA specifically solicits additional comment on this proposed action from tribal officials.

#### *G. Executive Order 13045: Protection of Children From Environmental Health and Safety Risks*

The EPA interprets EO 13045 (62 F.R. 19885, April 23, 1997) as applying only to those regulatory actions that concern health or safety risks, such that the analysis required under section 5–501 of the EO has the potential to influence the regulation. This action is not subject to EO 13045 because it does not establish an environmental standard intended to mitigate health or safety risks.

#### *H. Executive Order 13211: Actions Concerning Regulations That Significantly Affect Energy Supply, Distribution, or Use*

This action is not subject to Executive Order 13211 (66 FR 28355 (May 22, 2001)), because it is not a significant regulatory action under Executive Order 12866.

#### *I. National Technology Transfer and Advancement Act*

Section 12(d) of the National Technology Transfer and Advancement Act of 1995 (“NTTAA”), Public Law 104–113 (15 U.S.C. 272 note) directs the EPA to use voluntary consensus

standards in its regulatory activities unless to do so would be inconsistent with applicable law or otherwise impractical. Voluntary consensus standards are technical standards (e.g., materials specifications, test methods, sampling procedures, and business practices) that are developed or adopted by voluntary consensus standards bodies. NTTAA directs the EPA to provide Congress, through OMB, explanations when the agency decides not to use available and applicable voluntary consensus standards.

The proposed rule involves environmental monitoring and measurement consistent with the Agency's Performance Based Measurement System (PBMS). The PBMS approach is intended to be more flexible and cost-effective for the regulated community; it is also intended to encourage innovation in analytical technology and improved data quality. Specifically, this proposed rule would establish a new FRM for Pb in TSP measurements. The EPA used voluntary consensus standards in the preparation of this FRM. The FRM is the benchmark against which all ambient monitoring methods are compared. The FRM is not a voluntary consensus standard.

The FEM equivalency criteria contained in 40 CFR part 53 constitutes performance criteria. Therefore, the EPA is not precluding the use of any method, whether it constitutes a voluntary consensus standard or not, as long as it meets the specified performance criteria in 40 CFR part 53 and is approved by the EPA pursuant to those regulations.

The EPA welcomes comments on this aspect of the proposed rulemaking and, specifically, invites the public to identify potentially-applicable voluntary consensus standards and to explain why such standards should be used in this regulation.

#### *J. Executive Order 12898: Federal Actions To Address Environmental Justice in Minority Populations and Low-Income Populations*

Executive Order (EO) 12898 (59 FR 7629 (Feb. 16, 1994)) establishes federal executive policy on environmental justice. Its main provision directs federal agencies, to the greatest extent practicable and permitted by law, to make environmental justice part of their mission by identifying and addressing, as appropriate, disproportionately high and adverse human health or environmental effects of their programs, policies, and activities on minority populations and low-income populations in the United States.

The EPA has determined that this proposed rule will not have

disproportionately high and adverse human health or environmental effects on minority or low-income populations because it does not affect the level of protection provided to human health or the environment. This action proposes to establish a new FRM for state and local air monitoring agencies to use as one of the approved methods for measurement of Pb in TSP and to designate the existing FRM as an FEM.

#### List of Subjects in 40 CFR Part 50

Environmental protection, Air pollution control, and Lead.

Dated: January 25, 2013.

**Lisa P. Jackson,**  
Administrator.

For reasons stated in the preamble, title 40, chapter I of the Code of Federal Regulations proposes to amend as set forth in the following.

#### PART 50—NATIONAL PRIMARY AND SECONDARY AMBIENT AIR QUALITY STANDARDS

■ 1. The authority citation for part 50 continues to read as follows:

**Authority:** 42 U.S.C. 7401, et seq.

■ 2. Appendix G to part 50 is revised to read as follows:

#### Appendix G to Part 50—Reference Method for the Determination of Lead in Total Suspended Particulate Matter

##### 1.0 Scope and applicability

Based on review of the air quality criteria and national ambient air quality standards (NAAQS) for lead (Pb) completed in 2008, the EPA made revisions to the primary and secondary NAAQS for Pb to protect public health and welfare. The EPA revised the level from 1.5  $\mu\text{g}/\text{m}^3$  to 0.15  $\mu\text{g}/\text{m}^3$  while retaining the current indicator of Pb in total suspended particulate matter (Pb-TSP).

Pb-TSP is collected for 24 hours on a TSP filter as described in Appendix B of part 50, the Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method). This method is for the determination of Pb from TSP filters by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using a heated ultrasonic bath with nitric and hydrochloric acid or a heated block (hot block) digester with nitric acid for filter extraction.

This method is based on the EPA's Office of Solid Waste (SW-846) Method 6020A—Inductively Coupled Plasma Mass Spectrometry.<sup>1</sup> Wording in certain sections of this method is paraphrased or taken directly from Method 6020A.

1.1 ICP-MS is applicable for the sub- $\mu\text{g}/\text{mL}$  (ppb) determination of Pb in a wide variety of matrices. The method sensitivity is more than adequate for determining Pb at concentrations equal to, or less than, 5 percent of the level of the Pb NAAQS (0.15  $\mu\text{g}/\text{m}^3$ ) for Pb-TSP. Results reported for monitoring or compliance purposes are

calculated in  $\mu\text{g}/\text{m}^3$  at local conditions (LC). This procedure describes a method for the acid extraction of Pb in particulate matter collected on glass fiber, quartz, or Teflon® filters and measurement of the extracted Pb using ICP-MS.

1.2 Due to variations in the isotopic abundance of Pb, the value for total Pb must be based on the sum of the signal intensities for isotopic masses, 206, 207, and 208. Most instrument software packages are able to sum the primary isotope signal intensities automatically.

1.3 ICP-MS requires the use of an internal standard. <sup>115</sup>In (Indium), <sup>165</sup>Ho (Holmium), and <sup>209</sup>Bi (Bismuth) are recommended internal standards for the determination of Pb.

1.4 Use of this method is restricted to use by, or under supervision of, properly trained and experienced personnel. Requirements include training and experience in inorganic sample preparation, including acid extraction, and also knowledge in the recognition and in the correction of spectral, chemical and physical interference in ICP-MS.

##### 2.0 Summary of method

2.1 This method describes the acid extraction of Pb in particulate matter collected on glass fiber, quartz, or Teflon® ambient air filters with subsequent measurement of Pb by ICP-MS. Estimates of the Method Detection Limit (MDL) or sensitivity of the method are provided in Tables 1, 3 and 5 and determined using either blank filters or Pb-spiked filters or strips analyzed in accordance with the guidance provided in 40 CFR part 136, Appendix B—Determination and procedures for the Determination of the Method Detection Limit—Revision 1.1. The analytical range of the method is 0.00024  $\mu\text{g}/\text{m}^3$  to 0.60  $\mu\text{g}/\text{m}^3$ , and based on the low and high calibration curve standards and a nominal filter sample volume of 2000  $\text{m}^3$ .

2.2 This method includes two extraction methods. In the first method, a solution of HNO<sub>3</sub> and HCl is added to the filter strips in plastic digestion tubes and the tubes are placed in a heated ultrasonic bath for one hour to facilitate the extraction of Pb. Following ultrasonication, the samples are brought to a final volume of 40 mL, vortex mixed or shaken vigorously, and centrifuged prior to aliquots being taken for ICP-MS analysis. In the second method, a solution of dilute HNO<sub>3</sub> is added to the filter strips in plastic digestion tubes and the tubes placed into the heated block digester. The filter strip is completely covered by the solution. The tubes are covered with polypropylene watch glasses and refluxed. After reflux, the samples are diluted to a final volume of 50 mL with reagent water and mixed before analysis.

2.3 Calibration standards and check standards are prepared to matrix match the acid composition of the samples. ICP-MS analysis is then performed. With this method, the samples are first aspirated and the aerosol thus created is transported by a flow of argon gas into the plasma torch. The ions produced (e.g., Pb<sup>+</sup>) in the plasma are extracted via a differentially-pumped vacuum interface and are separated on the

basis of their mass-to-charge ratio. The ions are quantified by a channel electron multiplier or a Faraday detector and the signal collected is processed by the instrument's software. Interferences must be assessed and corrected for, if present.

##### 3.0 Definitions

Pb—Elemental or ionic lead  
HNO<sub>3</sub>—Nitric acid  
HCl—Hydrochloric acid  
ICP-MS—Inductively Coupled Plasma Mass Spectrometer  
MDL—Method detection limit  
RSD—Relative standard deviation  
RPD—Relative percent difference  
CB—Calibration Blank  
CAL—Calibration Standard  
ICB—Initial calibration blank  
CCB—Continuing calibration blank  
ICV—Initial calibration verification  
CCV—Continuing calibration verification  
LLCV—Lower Level Calibration Verification, serves as the lower level ICV and lower level CCV  
RB—Reagent blank  
RBS—Reagent blank spike  
MSDS—Material Safety Data Sheet  
NIST—National Institute of Standards and Technology

D.I. water—Deionized water  
SRM—NIST Standard Reference Material  
CRM—Certified Reference Material  
EPA—Environmental Protection Agency  
v/v—volume to volume ratio

##### 4.0 Interferences

4.1 Reagents, glassware, plasticware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. If reagent blanks, filter blanks, or quality control blanks yield results above the detection limit, the source of contamination must be identified. All containers and reagents used in the processing of the samples must be checked for contamination prior to sample extraction and analysis. Reagents shall be diluted to match the final concentration of the extracts and analyzed for Pb. Labware shall be rinsed with dilute acid solution and the solution analyzed. Once a reagent or labware article (such as extraction tubes) from a manufacturer has been successfully screened, additional screening is not required unless contamination is suspected.

4.2 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z) as the species of interest. There are no species found in ambient air that will result in isobaric interference with the three Pb isotopes (206, 207, and 208) being measured. Polyatomic interferences occur when two or more elements combine to form an ion with the same mass-to-charge ratio as the isotope being measured. Pb is not subject to interference from common polyatomic ions and no correction is required.

4.3 The distribution of Pb isotopes is not constant. The analysis of total Pb should be based on the summation of signal intensities for the isotopic masses 206, 207, and 208. In most cases, the instrument software can perform the summation automatically.

4.4 Physical interferences are associated with the sample nebulization and transport

processes as well as with ion-transmission efficiencies. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers of the ICP-MS. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. These interferences are compensated for by use of internal standards. Sample dilution will reduce the effects of high levels of dissolved salts, but calibration standards must be prepared in the extraction medium and diluted accordingly.

4.5 Memory interferences are related to sample transport and result when there is carryover from one sample to the next. Sample carryover can result from sample deposition on the sample and skimmer cones and from incomplete rinsing of the sample solution from the plasma torch and the spray chamber between samples. These memory effects are dependent upon both the analyte being measured and sample matrix and can be minimized through the use of suitable rinse times.

#### 5.0 Health and safety cautions

5.1 The toxicity or carcinogenicity of reagents used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Each laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in the chemical analysis. Specifically, concentrated nitric acid presents various hazards and is moderately toxic and extremely irritating to skin and mucus membranes. Use this reagent in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

5.2 Concentrated  $\text{HNO}_3$  and  $\text{HCl}$  are moderately toxic and extremely irritating to the skin. Use these reagents in a fume hood, and if eye and skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents. The component of this procedure requiring the greatest care is  $\text{HNO}_3$ .  $\text{HNO}_3$  is a strong, corrosive, oxidizing agent that requires protection of the eyes, skin, and clothing. Items to be worn during use of this reagent include:

1. Safety goggles (or safety glasses with side shields),
2. Acid resistant rubber gloves, and
3. A protective garment such as a laboratory apron.  $\text{HNO}_3$  spilled on clothing will destroy the fabric; contact with the skin underneath will result in a burn.

It is also essential that an eye wash fountain or eye wash bottle be available during performance of this method. An eye wash bottle has a spout that covers the eye. If acid or any other corrosive gets into the eye, the water in this bottle is squirted onto the eye to wash out the harmful material. Eye

washing should be performed with large amounts of water immediately after exposure. Medical help should be sought immediately after washing. If either acid, but especially  $\text{HNO}_3$ , is spilled onto the skin, wash immediately with large amounts of water. Medical attention is not required unless the burn appears to be significant. Even after washing and drying,  $\text{HNO}_3$  may leave the skin slightly brown in color; this will heal and fade with time.

5.3 Pb salts and Pb solutions are toxic. Great care must be taken to ensure that samples and standards are handled properly; wash hands thoroughly after handling.

5.4 Care must be taken when using the ultrasonic bath and heated block digester as they are capable of causing mild burns. Users should refer to the safety guidance provided by the manufacturer of their specific equipment.

5.5 Analytical plasma sources emit radio frequency radiation in addition to intense ultra violet (UV) radiation. Suitable precautions should be taken to protect personnel from such hazards. The inductively coupled plasma should only be viewed with proper eye protection from UV emissions.

#### 6.0 Equipment

6.1 Thermo Scientific X-Series ICP-MS or equivalent. The system must be capable of providing resolution better or equal to 1.0 atomic mass unit (amu) at 10 percent peak height. The system must have a mass range from at least 7 to 240 amu that allows for the application of the internal standard technique. For the measurement of Pb, an instrument with a collision or reaction cell is not required.

#### 6.2 Ultrasonic extraction equipment

6.2.1 Heated ultrasonic bath capable of maintaining a temperature of  $80^\circ\text{C}$ ; VWR Model 750HT, 240W, or equivalent. Ultrasonic bath must meet the following performance criteria:

1. Cut a strip of aluminum foil almost the width of the tank and double the depth.
2. Turn the ultrasonic bath on and lower the foil into the bath vertically until almost touching the bottom of the tank and hold for 10 seconds.
3. Remove the foil from the tank and observe the distribution of perforations and small pin prick holes. The indentations should be fine and evenly distributed. The even distribution of indentations indicates the ultrasonic bath is acceptable for use.

6.2.2 Laboratory centrifuge, Beckman GS-6, or equivalent.

6.2.3 Vortex mixer, VWR Signature Digital Vortex Mixer, VWR Catalog No. 14005-824, or equivalent.

#### 6.3 Heated block extraction equipment

6.3.1 Heated block digester, SCP Science DigiPrep Model MS, No. 010-500-205 block digester capable of maintaining a temperature of  $95^\circ\text{C}$ , or equivalent.

#### 6.4 Materials and Supplies

- Argon gas supply, 99.99 percent purity or better. National Welders Microbulk, or equivalent.
- Plastic digestion tubes with threaded caps for extraction and storage, SCP Science DigiTUBE® Item No. 010-500-063, or equivalent.

- Disposable polypropylene ribbed watch glasses (for heated block extraction), SCP Science Item No. 010-500-081, or equivalent.

- Pipette, Rainin EDP2, 100  $\mu\text{L}$ ,  $\pm 1$  percent accuracy,  $\leq 1$  percent RSD (precision), with disposable tips, or equivalent.

- Pipette, Rainin EDP2, 1000  $\mu\text{L}$ ,  $\pm 1$  percent accuracy,  $\leq 1$  percent RSD (precision), with disposable tips, or equivalent.

- Pipette, Rainin EDP2, 1-10 mL,  $\pm 1$  percent accuracy,  $\leq 1$  percent RSD (precision), with disposable tips, or equivalent.

- Pipette, Thermo Lab Systems, 5 mL,  $\pm 1$  percent accuracy,  $\leq 1$  percent RSD (precision), with disposable tips, or equivalent.

- Plastic tweezer, VWR Catalog No. 89026-420, or equivalent.

- Laboratory marker.

- Ceramic knife, Kyocera LK-25, and non-metal ruler or other suitable cutting tools for making straight cuts for accurately measured strips.

- Blank labels or labeling tape, VWR Catalog No. 36425-045, or equivalent.

- Graduated cylinder, 1 L, VWR 89000-260, or equivalent.

- Volumetric flask, Class A, 1 L, VWR Catalog No. 89025-778, or equivalent.

- Millipore Element deionized water system, or equivalent, capable of generating water with a resistivity of  $\geq 17.9 \text{ M}\Omega\text{-cm}$ .

- Disposable syringes, 10-mL, with 0.45 micron filters (must be Pb-free).

- Plastic or Teflon® wash bottles.

- Glassware, Class A—volumetric flasks, pipettes, and graduated cylinders.

- Glass fiber, quartz, or Teflon® filters from the same filter manufacturer and lot used for sample collection for use in the determination of the MDL and for laboratory blanks.

#### 7.0 Reagents and standards

7.1 Reagent—or trace metals-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

7.2 Concentrated nitric acid, 67-70 percent, SCP Science Catalog No. 250-037-177, or equivalent.

7.3 Concentrated hydrochloric acid (for the ultrasonic extraction method), 33-36 percent, SCP Science Catalog No. 250-037-175, or equivalent.

7.4 Deionized water—All references to deionized water in the method refer to deionized water with a resistivity  $\geq 17.9 \text{ M}\Omega\text{-cm}$ .

7.5 Standard stock solutions may be commercially purchased for each element or as a multi-element mix. Internal standards may be purchased as a mixed multi-element solution. The manufacturer's expiration date and storage conditions must be adhered to.

7.5.1 Lead standard, 1000  $\mu\text{g/mL}$ , NIST traceable, commercially available with certificate of analysis. High Purity Standards Catalog No. 100028-1, or equivalent.

7.5.2 Indium (In) standard, 1000  $\mu\text{g/mL}$ , NIST traceable, commercially available with certificate of analysis. High Purity Standards Catalog No. 100024-1, or equivalent.

7.5.3 Bismuth (Bi) standard, 1000  $\mu\text{g/mL}$ , NIST traceable, commercially available with

certificate of analysis. High Purity Standards Catalog No. 100006–1, or equivalent.

7.5.4 Holmium (Ho) standard, 1000 µg/mL, NIST traceable, commercially available with certificate of analysis. High Purity Standards Catalog No. 100023–1, or equivalent.

7.5.5 Second source lead standard, 1000 µg/mL, NIST traceable, commercially available with certificate of analysis. Must be from a different vendor or lot than the standard described in 7.5.1. Inorganic Ventures Catalog No. CGPB–1, or equivalent.

7.5.6 Standard Reference Materials, NIST SRM 2583<sup>2</sup>, 2586<sup>3</sup>, 2587<sup>4</sup> or 1648<sup>5</sup>, or equivalent.

**Note:** The In, Bi, and Ho internal standards may also be purchased as 10 µg/mL standards. Calibration standards are prepared by diluting stock standards to the appropriate levels in the same acid concentrations as in the final sample volume. The typical range for calibration standards is 0.001 to 2.00 µg/mL. At a minimum, the curve must contain a blank and five Pb containing calibration standards. The calibration standards are stored at ambient laboratory temperature. Calibration standards must be prepared weekly and verified against a freshly prepared ICV using a NIST-traceable source different from the calibration standards.

7.6 Internal standards may be added to the test solution or by on-line addition. The nominal concentration for an internal standard is 0.010 µg/mL (10 ppb). Bismuth (Bi) or holmium (Ho) are the preferred internal standards for Pb but indium (In) may be used in the event the sample contains bismuth and high recoveries are observed.

7.7 Three laboratory blank solutions are required for analysis: (1) The calibration blank is used in the construction of the calibration curve and as a periodic check of system cleanliness (ICB and CCB); (2) the reagent blank (RB) is carried through the extraction process to assess possible contamination; and (3) the rinse blank is run between samples to clean the sample introduction system. If RBs or laboratory blanks yield results above the detection limit, the source of contamination must be identified. Screening of labware and reagents is addressed in Section 4.1.

7.7.1 The calibration blank is prepared in the same acid matrix as the calibration standards and samples and contains all internal standards used in the analysis.

7.7.2 The RB contains all reagents used in the extraction and is carried through the extraction procedure at the same time as the samples.

7.7.3 The rinse blank is a solution of 1–2 percent HNO<sub>3</sub> (v/v) in reagent grade water. A sufficient volume should be prepared to flush the system between all standards and samples analyzed.

7.7.4 The EPA currently provides glass fiber, quartz, and Teflon® filters to air monitoring agencies as requested annually. As part of the procurement process, these filters are tested for acceptance by the EPA. The current acceptance criteria for glass fiber and quartz filters is 15 µg per filter or 0.0075 µg/m<sup>3</sup> using a nominal sample volume of 2000 m<sup>3</sup> and 4.8 ng/cm<sup>2</sup> or 0.0024 µg/m<sup>3</sup> for Teflon® filters using a nominal sample volume of 24 m<sup>3</sup>. Acceptance test results for filters obtained by the EPA are typically well below the criterion specified and also below the recently revised Pb method performance detection limit of 0.0075 µg/m<sup>3</sup>; therefore, blank subtraction should not be done.

7.7.5 If filters are not provided by the EPA for sample collection and analysis, filter lot blanks should be analyzed for Pb content. For large filter lots (≤500 filters) randomly select 20 to 30 filters from the lot and analyze the filter or filter strips for Pb. For smaller filter lots a lesser number of filters can be analyzed. Glass, quartz and Teflon® filters must not have levels of Pb above the criteria specified in section 7.7.4 and, therefore, blank correction should not be performed. If acceptance testing shows levels of Pb above the criteria in Section 7.7.4, corrective action must be taken to reduce the levels before proceeding.

7.8 The Initial Calibration Verification (ICV), Lower Level Calibration Verification (LLCV), and Continuing Calibration Verification (CCV) solutions are prepared from a different Pb source than the calibration curve standards and at a concentration that is either at or below the midpoint on the calibration curve, but within the calibration range. Both are prepared in the same acid matrix as the calibration standards. Note that the same solution may be used for both the ICV and CCV. The ICV/CCV and LLCV solutions must be prepared fresh daily.

7.9 Tuning Solution. Prepare a tuning solution according to the instrument manufacturer's recommendations. This solution will be used to verify the mass calibration and resolution of the instrument.

8.0 Quality Control (QC)

8.1 Standard QC practices shall be employed to assess the validity of the data generated. Included are: MDL, RB, duplicate samples, spiked samples, serial dilutions, ICV, CCV, LLCV, ICB, CCB, and SRMs/CRMs.

8.2 MDLs must be calculated in accordance with 40 CFR part 136, appendix

B. RBs with low-level standard spikes can be used to estimate the MDL. The low-level standard spike is added to at least seven individual filter strips and then carried through the entire extraction procedure. This will result in at least 7 individual samples to be used for the MDL. The recommended range for spiking the strips is 2–5 times the estimated MDL.

8.3 For each batch of samples, one RB and one reagent blank spike (RBS) spiked at the same level as the sample spike (see Section 8.6) must be prepared and carried throughout the entire process. The results of the RB must be below 0.001 µg/mL. The recovery for the RBS must be within ± 20 percent of the expected value. If the RB yields a result above 0.001 µg/mL, the source of contamination must be identified and the extraction and analysis repeated. Reagents and labware must be suspected as sources of contamination. Screening of reagents and labware is addressed in Section 4.1.

8.4 Any samples that exceed the highest calibration standard must be diluted and rerun so that the concentration falls within the curve. The minimum dilution will be 1 to 5 with matrix matched acid solution.

8.5 The internal standard response must be monitored during the analysis. If the internal standard response falls below 70 percent or rises above 120 percent of expected due to possible matrix effects, the sample must be diluted and reanalyzed. The minimum dilution will be 1 to 5 with matrix matched acid solution. If the first dilution does not correct the problem, additional dilutions must be run until the internal standard falls within the specified range.

8.6 For every batch of samples prepared, there must be one duplicate and one spike sample prepared. The spike added is to be at a level that falls within the calibration curve, normally the midpoint of the curve. The initial plus duplicate sample must yield a relative percent difference ≤ 20 percent. The spike must be within ± 20 percent of the expected value.

8.7 For each batch of samples, one extract must be diluted five-fold and analyzed. The corrected dilution result must be within ±10 percent of the undiluted result. The sample chosen for the serial dilution shall have a concentration at or above 10X the lowest standard in the curve to ensure the diluted value falls within the curve. If the serial dilution fails, chemical or physical interference should be suspected.

8.8 ICB, ICV, LLCV, CCB and CCV samples are to be run as shown in the following table.

Sample	Frequency	Performance specification
ICB .....	Prior to first sample .....	Less than 0.001 µg/mL.
ICV .....	Prior to first sample .....	Within 90 to 110 percent of the expected value.
LLCV .....	Daily, before first sample and after last sample .....	±10 percent of the expected value.
CCB .....	After every 10 extracted samples .....	Less than 0.001 µg/mL.
CCV .....	After every 10 extracted samples .....	Within 90–110 percent of the expected value.

If any of these QC samples fails to meet specifications, the source of the unacceptable performance must be determined, the

problem corrected, and any samples not bracketed by passing QC samples must be reanalyzed.

8.9 For each batch of samples, one certified reference material (CRM) must be combined with a blank filter strip and carried



through the entire extraction procedure. The result must be within  $\pm 10$  percent of the expected value.

8.10 For each run, a LLCV must be analyzed. The LLCV must be prepared at a concentration not more than three times the lowest calibration standard and at a concentration not used in the calibration curve. The LLCV is used to assess performance at the low end of the curve. If the LLCV fails ( $\pm 10$  percent of the expected value) the run must be terminated, the problem corrected, the instrument recalibrated, and the analysis repeated.

8.11 Pipettes used for volumetric transfer must have the calibration checked at least once every 6 months and pass  $\pm 1$  percent accuracy and  $\leq 1$  percent RSD (precision) based on five replicate readings. The pipettes must be checked weekly for accuracy with a single replicate. Any pipette that does not meet  $\pm 1$  percent accuracy on the weekly check must be removed from service, repaired, and pass a full calibration check before use.

8.12 Samples with physical deformities are not quantitatively analyzable. The analyst should visually check filters prior to proceeding with preparation for holes, tears, or non-uniform deposit which would prevent representative sampling. Document any deformities and qualify the data with flags appropriately. Care must be taken to protect filters from contamination. Filters must be kept covered prior to sample preparation.

#### 9.0 ICP-MS Calibration

Follow the instrument manufacturer's instructions for the routine maintenance, cleaning, and ignition procedures for the specific ICP-MS instrument being used.

9.1 Ignite the plasma and wait for at least one half hour for the instrument to warm up before beginning any pre-analysis steps.

9.2 For the Thermo X-Series with Xt cones, aspirate a 10 ng/mL tuning solution containing In, Bi, and Ce(Cerium). Monitor the intensities of In, Bi, Ce, and CeO (Cerium oxide) and adjust the instrument settings to achieve the highest In and Bi counts while minimizing the CeO/Ce oxide ratio. For other instruments, follow the manufacturer's recommended practice. Tune to meet the instrument manufacturer's specifications. After tuning, place the sample aspiration probe into a 2 percent HNO<sub>3</sub> rinse solution for at least 5 minutes to flush the system.

9.3 Aspirate a 5 ng/mL solution containing Co, In, and Bi to perform a daily instrument stability check. Run 10 replicates of the solution. The percent RSD for the replicates must be less than 3 percent at all masses. If the percent RSD is greater than 3 percent, the sample introduction system, pump tubing, and tune should be examined, and the analysis repeated. Place the sample aspiration probe into a 2 percent HNO<sub>3</sub> rinse solution for at least 5 minutes to flush the system.

9.4 Load the calibration standards in the autosampler and analyze using the same method parameters that will be used to analyze samples. The curve must include one blank and at least 5 Pb-containing calibration standards. The correlation coefficient must be at least 0.998 for the curve to be accepted. The lowest standard must recover  $\pm 15$

percent of the expected value and the remaining standards must recover  $\pm 10$  percent of the expected value to be accepted.

9.5 Immediately after the calibration curve is completed, analyze an ICV and an ICB. The ICV must be prepared from a different source of Pb than the calibration standards. The ICV must recover 90–110 percent of the expected value for the run to continue. The ICB must be less than 0.001  $\mu\text{g/mL}$ . If either the ICV or the ICB fails, the run must be terminated, the problem identified and corrected, and the analysis re-started.

9.6 A LLCV, CCV and a CCB must be run after the ICV and ICB. A CCV and CCB must be run at a frequency of not less than every 10 extracted samples. A typical analytical run sequence would be: Calibration blank, Calibration standards, ICV, ICB, LLCV, CCV, CCB, Extracts 1–10, CCV, CCB, Extracts 11–20, CCV, CCB, Extracts 21–30, CCV, CCB, LLCV, CCV, CCB. Extracts are any field sample or QC samples that have been carried through the extraction process. The CCV solution is prepared from a different source than the calibration standards and may be the same as the ICV solution. The LLCV must be within  $\pm 10$  percent of expected value. The CCV value must be within  $\pm 10$  percent of expected for the run to continue. The CCB must be less than 0.001  $\mu\text{g/mL}$ . If either the CCV, LLCV, or CCB fails, the run must be terminated, the problem identified and corrected, and the analysis re-started from the last passing CCV/LLCV/CCB set.

9.7 A LLCV, CCV, and CCB set must be run at the end of the analysis. The LLCV must be within  $\pm 30$  percent of expected value. If either the CCV, LLCV, or CCB fails, the run must be terminated, the problem identified and corrected, and the analysis re-started from the last passing CCV/LLCV/CCB set.

#### 10.0 Heated Ultrasonic Filter Strip Extraction

All plasticware (e.g., Nalgene) and glassware used in the extraction procedures is soaked in 1 percent HNO<sub>3</sub> (v/v) for at least 24 hours and rinsed with reagent water prior to use. All mechanical pipettes used must be calibrated to  $\pm 1$  percent accuracy and  $\leq 1$  percent RSD at a minimum of once every 6 months.

##### 10.1 Sample Preparation—Heated Ultrasonic Bath

10.1.1 Extraction solution (1.03M HNO<sub>3</sub> + 2.23M HCl). Prepare by adding 500 mL of deionized water to a 1000 mL flask, adding 64.4 mL of concentrated HNO<sub>3</sub> and 182 mL of concentrated HCl, shaking to mix, allowing solution to cool, diluting to volume with reagent water, and inverting several times to mix. Extraction solution must be prepared at least weekly.

10.1.2 Use a ceramic knife and non-metal ruler, or other cutting device that will not contaminate the filter with Pb. Cut a  $\frac{3}{4}$  inch X 8 inch strip from the glass fiber or quartz filter by cutting a strip from the edge of the filter where it has been folded along the 10 inch side at least 1 inch from the right or left side to avoid the un-sampled area covered by the filter holder. The filters must be carefully handled to avoid dislodging deposits.

10.1.3 Using plastic tweezers, roll the filter strip up in a coil and place the rolled

strip in the bottom of a labeled 50 mL extraction tube. In a fume hood, add 15.00  $\pm$  0.15 mL of the extraction solution (see Section 10.1.1) using a calibrated mechanical pipette. Ensure that the extraction solution completely covers the filter strip.

10.1.4 Loosely cap the 50 mL extraction tube and place it upright in a plastic rack. When all samples have been prepared, place the racks in an uncovered heated ultrasonic water bath that has been preheated to 80  $\pm$  5°C and ensure that the water level in the ultrasonic is above the level of the extraction solution in the tubes but well below the level of the extraction tube caps to avoid contamination. Start the ultrasonic bath and allow the unit to run for 1 hour  $\pm$  5 minutes at 80  $\pm$  5°C.

10.1.5 Remove the rack(s) from the ultrasonic bath and allow the racks to cool.

10.1.6 Add 25.00  $\pm$  0.25 mL of D.I. water with a calibrated mechanical pipette to bring the sample to a final volume of 40.0  $\pm$  0.4 mL. Tightly cap the tubes and vortex mix or shake vigorously. Place the extraction tubes in an appropriate holder and centrifuge for 20 minutes at 2500 revolutions per minute (RPM).

CAUTION—Make sure that the centrifuge holder has a flat bottom to support the flat bottomed extraction tubes.

10.1.7 Pour an aliquot of the solution into an autosampler vial for ICP-MS analysis to avoid the potential for contamination. Do not pipette an aliquot of solution into the autosampler vial.

10.1.8 Decant the extract to a clean tube, cap tightly, and store the sample extract at ambient laboratory temperature. Extracts may be stored for up to six months from the date of extraction.

##### 10.2 47 mm Teflon® Filter Extraction—Heated Ultrasonic Bath

10.2.1 Extraction solution (1.03M HNO<sub>3</sub> + 2.23M HCl). Prepare by adding 500 mL of D.I. water to a 1000mL flask, adding 64.4 mL of concentrated HNO<sub>3</sub> and 182 mL of concentrated HCl, shaking to mix, allowing solution to cool, diluting to volume with reagent water, and inverting several times to mix. Extraction solution must be prepared at least weekly.

10.2.2 Using plastic tweezers, bend the Teflon® filter into a U-shape and insert the filter into a labeled 50 mL extraction tube with the particle loaded side facing the center of the tube. Gently push the filter to the bottom of the extraction tube. In a fume hood, add 25.00  $\pm$  0.15 mL of the extraction solution (see Section 10.2.1) using a calibrated mechanical pipette. Ensure that the extraction solution completely covers the filter.

10.2.3 Loosely cap the 50 mL extraction tube and place it upright in a plastic rack. When all samples have been prepared, place the racks in an uncovered heated ultrasonic water bath that has been preheated to 80  $\pm$  5°C and ensure that the water level in the ultrasonic is above the level of the extraction solution in the tubes but well below the level of the extraction tube caps to avoid contamination. Start the ultrasonic bath and allow the unit to run for 1 hour  $\pm$  5 minutes at 80  $\pm$  5°C.

10.2.4 Remove the rack(s) from the ultrasonic bath and allow the racks to cool.



10.2.5 Add 25.00 ± 0.25 mL of D.I. water with a calibrated mechanical pipette to bring the sample to a final volume of 50.0 ± 0.4 mL. Tightly cap the tubes and vortex mix or shake vigorously. Allow samples to stand for one hour to allow complete diffusion of the extracted Pb. The sample is now ready for analysis.

**Note:** Although Teflon® filters have only been extracted using the ultrasonic extraction procedure in the development of this FRM, Teflon® filters are inert and have very low Pb content. No issues are expected with the extraction of Teflon® filters using the heated block digestion method. However, prior to using Teflon® filters in the heated block extraction method, extraction method performance test using CRMs must be done to confirm performance (see Section 8.9).

11.0 Heated Block Filter Strip Extraction  
All plasticware (e.g., Nalgene) and glassware used in the extraction procedures is soaked in 1 percent HNO<sub>3</sub> for at least 24 hours and rinsed with reagent water prior to use. All mechanical pipettes used must be calibrated to ±1 percent accuracy and ≤ 1 percent RSD at a minimum of once every 6 months.

11.1 Sample Preparation—Heated Block Digestion

11.1.1 Extraction solution (1:19, v/v HNO<sub>3</sub>). Prepare by adding 500 mL of D.I. water to a 1000 mL flask, adding 50 mL of concentrated HNO<sub>3</sub>, shaking to mix, allowing solution to cool, diluting to volume with reagent water, and inverting several times to mix. The extraction solution must be prepared at least weekly.

11.1.2 Use a ceramic knife and non-metal ruler, or other cutting device that will not contaminate the filter with Pb. Cut a 1 inch × 8 inch strip from the glass fiber or quartz filter. Cut a strip from the edge of the filter where it has been folded along the 10 inch side at least 1 inch from the right or left side to avoid the un-sampled area covered by the filter holder. The filters must be carefully handled to avoid dislodging particle deposits.

11.1.3 Using plastic tweezers, roll the filter strip up in a coil and place the rolled strip in the bottom of a labeled 50 mL extraction tube. In a fume hood, add 20.0 ± 0.15 mL of the extraction solution (see Section 11.1.1) using a calibrated mechanical pipette. Ensure that the extraction solution completely covers the filter strip.

11.1.4 Place the extraction tube in the heated block digester and cover with a disposable polyethylene ribbed watch glass. Heat at 95 ± 5 °C for one hour and ensure

that the sample does not evaporate to dryness. For proper heating, adjust the temperature control of the hot block such that an uncovered vessel containing 50 mL of water placed in the center of the hot block can be maintained at a temperature approximately, but no higher than 85 °C. Once the vessel is covered with a ribbed watch glass the temperature of the water will increase to approximately 95 °C.

11.1.5 Remove the rack(s) from the heated block digester and allow the samples to cool.

11.1.6 Bring the samples to a final volume of 50 mL with D.I. water. Tightly cap the tubes and vortex mix or shake vigorously for at least 5 seconds. Set aside (with the filter strip in the tube) for at least 30 minutes to allow the nitric acid trapped in the filter to diffuse into the extraction solution.

11.1.7 Shake thoroughly (with the filter strip in the digestion tube) and let settle for at least one hour. The sample is now ready for analysis.

12.0 Measurement Procedure

12.1 Follow the instrument manufacturer's startup procedures for the ICP-MS.

12.2 Set instrument parameters to the appropriate operating conditions as presented in the instrument manufacturer's operating manual and allow the instrument to warm up for at least 30 minutes.

12.3 Calibrate the instrument per Section 9.0 of this method.

12.4 Verify the instrument is suitable for analysis as defined in Sections 9.2 and 9.3.

12.5 As directed in Section 8.0 of this method, analyze an ICV and ICB immediately after the calibration curve followed by a LLCV, then CCV and CCB. The acceptance requirements for these parameters are presented in Section 8.8.

12.6 Analyze a CCV and a CCB after every 10 extracted samples.

12.7 Analyze a LLCV, CCV and CCB at the end of the analysis.

12.8 A typical sample run will include field samples, field sample duplicates, spiked field sample extracts, serially diluted samples, the set of QC samples listed in Section 8.8 above, and one or more CRMs or SRMs.

12.9 Any samples that exceed the highest standard in the calibration curve must be diluted and reanalyzed so that the diluted concentration falls within the calibration curve.

13.0 Results

13.1 The filter results must be initially reported in µg/mL as analyzed. Any additional dilutions must be accounted for.

The internal standard recoveries must be included in the result calculation; this is done by the ICP-MS software for most commercially-available instruments. Final results should be reported in µg Pb/m<sup>3</sup> to three significant figures as follows:

$$C = ((\mu\text{g Pb/mL} * V_f * A) * D) / V_s$$

Where:

C = Concentration, µg Pb/m<sup>3</sup>

µg Pb/mL = Lead concentration in solution

V<sub>f</sub> = Total extraction solution volume

A = Area correction; ¾" × 8" strip = 5.25 in<sup>2</sup> analyzed, A = 12.0 or 1" × 8" strip = 7 in<sup>2</sup> analyzed, A = 9.0

D = dilution factor (if required)

V<sub>s</sub> = Actual volume of air sampled

The calculation assumes the use of a standard 8 inch × 10 inch TSP filter which has a sampled area of 9 inch × 7 inch (63.0 in<sup>2</sup>) due to the ½ inch filter holder border around the outer edge. The ¾ inch × 8 inch strip has a sampled area of ¾ inch × 7 inch (5.25 in<sup>2</sup>). The 1 inch × 8 inch strip has a sampled area of 1 inch × 7 inch (7.0 in<sup>2</sup>). If filter lot blanks are provided for analysis, refer to Section 7.7.5 of this method for guidance on testing.

14.0 Method Performance

Information in this section is an example of typical performance results achieved by this method. Actual performance must be demonstrated by each individual laboratory and instrument.

14.1 Performance data have been collected to determine MDL for this method. MDLs were determined in accordance with 40 CFR part 136, Appendix B. MDLs were estimated for glass fiber, quartz, and Teflon® filters using seven reagent/filter blank solutions and seven reagent/filter blank solutions spiked with low level Pb at three times the estimated MDL. Tables 1, 3, and 5 shows the MDLs estimated using both the ultrasonic and heated block extraction methods for glass fiber and quartz filters and the ultrasonic method for Teflon® filters. The MDLs are well below the EPA requirement of 5 percent of the current Pb NAAQS or 0.0075 µg/m<sup>3</sup>.

14.2 Extraction method recovery tests with glass fiber and quartz filter strips, and Teflon® filters spiked with NIST SRMs were performed using the ultrasonic/HNO<sub>3</sub> and HCl filter extraction methods and measurement of the dissolved Pb with ICP-MS. Tables 2, 4, and 6 show recoveries obtained with these SRM. The recoveries for all SRMs were ≥ 90 percent at the 95 percent confidence level.

TABLE 1—METHOD DETECTION LIMITS DETERMINED BY ANALYSIS OF REAGENT/GLASS FIBER FILTER BLANKS AND REAGENT/GLASS FIBER FILTER BLANKS SPIKED WITH LOW-LEVEL Pb SOLUTION

	Ultrasonic		Hotblock	
	Blank (µg/m <sup>3</sup> )*	Pb-spiked (µg/m <sup>3</sup> )*	Blank (µg/m <sup>3</sup> )*	Pb-spiked (µg/m <sup>3</sup> )*
n=1 .....	0.0000434	0.0000702	0.000362	0.000533
n=2 .....	0.0000420	0.0000715	0.000400	0.000482
n=3 .....	0.0000439	0.0000611	0.000386	0.000509
n=4 .....	0.0000407	0.0000587	0.000415	0.000427
n=5 .....	0.0000437	0.0000608	0.000414	0.000449
n=6 .....	0.0000437	0.0000607	0.000409	0.000539

TABLE 1—METHOD DETECTION LIMITS DETERMINED BY ANALYSIS OF REAGENT/GLASS FIBER FILTER BLANKS AND REAGENT/GLASS FIBER FILTER BLANKS SPIKED WITH LOW-LEVEL Pb SOLUTION—Continued

	Ultrasonic		Hotblock	
	Blank (µg/m³)*	Pb-spiked (µg/m³)*	Blank (µg/m³)*	Pb-spiked (µg/m³)*
n=7 .....	0.0000403	0.0000616	0.000361	0.000481
Average .....	0.0000425	0.0000635	0.000392	0.000489
Standard .....	0.0000015	0.0000051	0.000023	0.000042
MDL** .....	0.0000047	0.0000161	0.000073	0.000131

\* Assumes 2000 m³ of air sampled.

\*\* MDL is 3.143 times the standard deviation of the results for seven sample replicates analyzed.

TABLE 2—RECOVERIES OF LEAD FROM NIST SRMS SPIKED ONTO GLASS FIBER FILTERS

Extraction method	Recovery, ICP-MS, (percent)			
	NIST 1547 plant	NIST 2709 soil	NIST 2583 dust	NIST 2582 paint
Ultrasonic Bath .....	100±4	98±1	103±8	101±0
Block Digestion .....	92±7	98±3	103±4	94±4

TABLE 3—METHOD DETECTION LIMITS DETERMINED BY ANALYSIS OF REAGENT/QUARTZ FILTER BLANKS AND REAGENT/QUARTZ FILTER BLANKS SPIKED WITH LOW-LEVEL Pb SOLUTION

	Ultrasonic		Hotblock	
	Blank (µg/m³)*	Pb-spiked (µg/m³)*	Blank (µg/m³)*	Pb-spiked (µg/m³)*
n=1 .....	0.000273	0.000533	0.000121	0.000274
n=2 .....	0.000270	0.000552	0.000112	0.000271
n=3 .....	0.000270	0.000534	0.000112	0.000281
n=4 .....	0.000279	0.000684	0.000111	0.000269
n=5 .....	0.000277	0.000532	0.000121	0.000278
n=6 .....	0.000282	0.000532	0.000117	0.000272
n=7 .....	0.000276	0.000552	0.000115	0.000261
Average .....	0.000275	0.000560	0.000116	0.000272
Standard .....	0.000004	0.000055	0.000004	0.000007
MDL** .....	0.000014	0.000174	0.000013	0.000021

\* Assumes 2000 m³ of air sampled.

\*\* MDL is 3.143 times the standard deviation of the results for seven sample replicates analyzed.

TABLE 4—RECOVERIES OF LEAD FROM NIST SRMS SPIKED ONTO QUARTZ FIBER FILTERS

Extraction method	Recovery, ICP-MS, (percent)			
	NIST 1547 plant	NIST 2709 soil	NIST 2583 dust	NIST 2582 paint
Ultrasonic Bath .....	101±6	95±1	91±5	93±1
Block Digestion .....	106±3	104±3	92±6	95±2

TABLE 5—METHOD DETECTION LIMITS DETERMINED BY ANALYSIS OF REAGENT/TEFLON FILTER BLANKS AND REAGENT/TEFLON FILTER BLANKS SPIKED WITH LOW-LEVEL Pb SOLUTION

	Ultrasonic extraction method	
	Blank (µg/m³)*	Pb-spiked (µg/m³)*
n=1 .....	0.000070	0.001775
n=2 .....	0.000039	0.001812
n=3 .....	0.000009	0.001773
n=4 .....	-0.000012	0.001792
n=5 .....	0.000062	0.001712
n=6 .....	-0.000019	0.001767
n=7 .....	0.000033	0.001778
Average .....	0.000026	0.001773
Standard Deviation .....	0.000035	0.000031

TABLE 5—METHOD DETECTION LIMITS DETERMINED BY ANALYSIS OF REAGENT/TEFLON FILTER BLANKS AND REAGENT/TEFLON FILTER BLANKS SPIKED WITH LOW-LEVEL Pb SOLUTION—Continued

	Ultrasonic extraction method	
	Blank ( $\mu\text{g}/\text{m}^3$ )*	Pb-spiked ( $\mu\text{g}/\text{m}^3$ )*
MDL** .....	0.000109	0.000097

\* Assumes 24 m<sup>3</sup> of air sampled.

\*\* MDL is 3.143 times the standard deviation of the results for seven sample replicates analyzed.

TABLE 6—RECOVERIES OF LEAD FROM NIST SRMS SPIKED ONTO TEFLON FILTERS

Extraction method	Recovery, ICP-MS, (percent)			
	NIST 1547 plant	NIST 2709 soil	NIST 2583 dust	NIST 2582 paint
Ultrasonic Bath .....	104±5	93±1	108±11	96±3

### 15.0 Pollution Prevention

15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. The sources of pollution generated with this procedure are waste acid extracts and Pb-containing solutions.

15.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St. NW., Washington, DC 20036, [www.acs.org](http://www.acs.org).

### 16.0 Waste Management

16.1 Laboratory waste management practices must be conducted consistent with all applicable rules and regulations. Laboratories are urged to protect air, water, and land by minimizing all releases from hood and bench operations, complying with the letter and spirit of any sewer and discharge permits and regulations, and by complying with all solid and hazardous waste regulation. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society listed in Section 15.2 of this method.

16.2 Waste HNO<sub>3</sub>, HCl, and solutions containing these reagents and/or Pb must be placed in labeled bottles and delivered to a commercial firm that specializes in removal of hazardous waste.

### 17.0 References

1. Method 6020A—Inductively Coupled Plasma Mass Spectrometry. U.S. Environmental Protection Agency. Revision 1, February 2007.

2. NIST, Certificate of Analysis: Standard Reference Materials 2583, Trace Elements in Indoor Dust, Nominal 90 mg/kg Lead, National Institute of Standards and Technology, Gaithersburg, MD, 1998.

3. NIST, Certificate of Analysis: Standard Reference Materials 2586, Trace Elements in Soil, Nominal 500 mg/Kg Lead, National Institute of Standards and Technology, Gaithersburg, MD, 2008.

4. NIST, Certificate of Analysis: Standard Reference Materials 2587, Trace Elements in Soil Containing Lead from Paint, Nominal 3000 mg/Kg Lead, National Institute of Standards and Technology, Gaithersburg, MD, 2008.

5. NIST, Certificate of Analysis: Standard Reference Materials 1648, Urban Particulate Matter, 0.655 ± 0.033% Lead, National Institute of Standards and Technology, Gaithersburg, MD, 2008.

6. Rice 2013, Results from the Development of a New Federal Reference Method (FRM) for Lead in Total Suspended Particulate (TSP) Matter. Docket # EPA-HQ-OAR-2012-0210.

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## ENVIRONMENTAL PROTECTION AGENCY

### 40 CFR Part 52

[EPA-R06-OAR-2006-0600; FRL-9776-4]

### Approval and Promulgation of Implementation Plans; Texas; Revisions to New Source Review (NSR) State Implementation Plan (SIP); Emergency Orders

**AGENCY:** Environmental Protection Agency (EPA).

**ACTION:** Proposed rule.

**SUMMARY:** EPA is proposing disapproval of revisions to the SIP for the State of Texas that relate to Emergency Orders. This includes portions of SIP revisions that relate to Emergency Orders that were submitted by Texas on August 31, 1993; December 10, 1998; February 1, 2006; and July 17, 2006. EPA is proposing disapproval of these revisions

because these regulations do not meet the requirement of the Clean Air Act (the "Act" or "CAA"), EPA regulations, and applicable policy and guidance. EPA is proposing this action under section 110 and parts C and D of Title I of the Act. EPA is returning the non-air portions of the aforementioned SIP submittals to the State because these provisions cannot be included in the SIP.

**DATES:** Comments must be received on or before March 7, 2013.

**ADDRESSES:** Submit your comments identified by Docket ID No. EPA-R06-OAR-2006-0600 by one of the following methods:

(1) *Federal eRulemaking Portal:* <http://www.regulations.gov>. Follow the on-line instructions for submitting comments.

(2) *Email:* Ms. Ashley Mohr at [mohr.ashley@epa.gov](mailto:mohr.ashley@epa.gov).

(3) *Fax:* Ms. Ashley Mohr, Air Permits Section (6PD-R), at fax number 214-665-6762.

(4) *Mail:* Ms. Ashley Mohr, Air Permits Section (6PD-R), Environmental Protection Agency, 1445 Ross Avenue, Suite 1200, Dallas, Texas 75202-2733.

(5) *Hand or Courier Delivery:* Ms. Ashley Mohr, Air Permits Section (6PD-R), Environmental Protection Agency, 1445 Ross Avenue, Suite 1200, Dallas, Texas 75202-2733. Such deliveries are accepted only between the hours of 8:30 a.m. and 4:30 p.m. weekdays except for legal holidays. Special arrangements should be made for deliveries of boxed information.

*Instructions:* Direct your comments to Docket ID No. EPA-R06-OAR-2006-0600. EPA's policy is that all comments received will be included in the public docket without change and may be made available online at <http://www.regulations.gov>, including any