Evaluation of Methods for Analysis of Lead in Air Particulates: An Intra-Laboratory and Inter-Laboratory Comparison

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James M. Harrington,[1*] Clay M. Nelson,[2] Frank X. Weber,[1] Karen D. Bradham,[2] Keith E. Levine,[1] Joann Rice[3]

[1] Trace Inorganics Department, Environmental and Industrial Sciences Division, RTI International, 3040 E Cornwallis Rd., PO Box 12194, Research Triangle Park, NC 27709
[2] U.S. Environmental Protection Agency, Office of Research and Development, National Exposure Research Laboratory, Research Triangle Park, NC 27711 USA
[3] U.S. Environmental Protection Agency, Office of Air Quality Planning & Standards, Research Triangle Park, NC 27711 USA
* Corresponding author: jharrington@rti.org, phone 1-919-541-8777

Abstract

In 2008, the United States Environmental Protection Agency (USEPA) set a new National Ambient Air Quality Standard (NAAQS) for lead in total suspended particulate matter (Pb-TSP) which called for significant decreases in the allowable limits. The Federal Reference Method (FRM) for Pb-TSP promulgated in 1978 prescribes analysis of Pb by flame atomic absorption spectroscopy (FAAS), but the new limits approach the limits of quantitation of FAAS. On August 2, 2013, the USEPA finalized a new FRM for Pb-TSP. This new FRM describes two extraction methods and analysis by inductively coupled plasma-mass spectrometry (ICP-MS). The study described here was performed to evaluate the use of ICP-MS in the analysis of Pb-TSP for implementation of this new FRM. A multi-laboratory study of the new FRM demonstrated acceptable intra- and inter-laboratory precision and comparability for glass fiber, quartz, and PTFE filters, and acceptable accuracy for the analysis of three National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs). A comparison was made between analytical results obtained using the 1978 FRM and those obtained using the new FRM. The results demonstrate that the ICP-MS method performs acceptably for the determination of Pb-TSP with lower limits of quantitation and strong inter- and intra-laboratory precision.

1.0 Introduction

In 2008, the United States Environmental Protection Agency (USEPA) revised the guidelines on the allowable concentration of lead (Pb) in total suspended particulate matter (TSP) set forth in the National Ambient Air Quality Standards (NAAQS), decreasing it from the previous limit of 1.5 µg/m^3 to 0.15 µg/m^3 [1]. Lead is found in suspended particles due to its emission from airports and airplanes, industrial activities, and from other point sources, and is associated with a variety of potential public health impacts. Of particular concern are adverse neurological effects in both children and adults, and the potential for respiratory problems in individuals of all ages, including asthma and lung cancer [2]. Additional biochemical and cellular effects have been observed in animal models exposed to lead. Observed levels of lead in air have been gradually declining over the past 30 years due to the phasing out of leaded fuels in many areas of the developed world [3]. However, lead can still be found in the atmosphere due to resuspension of historically contaminated particulate matter, partially-controlled metal-based industries (e.g., smelting), and lead emissions from piston-engine aircraft operating on leaded aviation gas.

The previous Federal Reference Method (FRM) for the determination of Pb as TSP in air samples (promulgated in 1978 and replaced in 2013) made use of Flame Atomic Absorption Spectroscopy (FAAS) as the analytical method. Although the previous FRM was adequate for most samples, the need for improved measurement sensitivity (detection limits) in response to the lower NAAQS, advances in measurement technology, and the availability of methods with improved precision, detection limits, throughput, and extraction efficiency supported the development of a new FRM for Pb-TSP.

This new FRM, described in 40 CFR Part 50, Appendix G, is intended to be used by laboratories for the collection of air quality data and for approving new Federal Equivalent Methods (FEMs) in support of NAAQS [4]. Sample collection for Pb-TSP analysis is performed according to 40 CFR Part 50, Appendix B. It is important to note that the method for sample collection described in Appendix B did not change when the analytical component described in Appendix G was revised. The new FRM applies to the analysis of Pb-TSP and features two extraction techniques: nitric acid (HNO_3) extraction in a hotblock and a combination nitric/hydrochloric acid (HCl) extraction in an ultrasonic bath. Both of these extraction techniques have been shown to be adequate for Pb analysis due to the acid solubility of this element as found in air particulates [5]. A previous study of the combination HNO_3/HCl ultrasonic extraction technique demonstrated that the increased oxidizing ability of the acid mixture made the method appropriate for the analysis of a number of elements in addition to Pb [6]. Since Pb solubility is heavily influenced by pH changes, it is generally not necessary to employ more rigorous sample preparation techniques, such as closed vessel microwave extraction [7, 8]. Two Federal Equivalent Methods (FEM's) have been evaluated against the 1978 FRM and are currently approved for analysis of Pb-TSP: EQL-0510-191 and EQL-0710-192. These designated methods make use of both extraction techniques prior to inductively coupled plasma-mass spectrometry (ICP-MS) analysis [9, 10]. ICP-MS exhibits much lower effective quantitation ranges and limits than FAAS, making it appropriate for the decreased NAAQS limits. Additionally, ICP-MS has the sensitivity to accommodate any future reductions in the NAAQS. The European Standard EN 14902 for measurement of Pb, amongst other metals, in PM_{10} sampled air filters was revised in 2005 to include ICP-MS as an acceptable analytical technique,

and an interlaboratory comparison of the results obtained from extraction using ICP-MS and GFAAS produced favorable results [11, 12].

The purpose of this study was to evaluate the suitability of the two FEM extraction methods, 1) heated graphite block with HNO_3, and 2) heated ultrasonic water bath with a HNO_3/HCl mixture, for the ICP-MS determination of Pb in TSP for a new FRM. To this end, a multi-laboratory evaluation was performed using reference materials and lead-spiked quartz, glass fiber, and PTFE sample air filters to determine intra- and inter-laboratory accuracy, precision, and reproducibility for Pb-TSP analysis. Both extraction approaches were evaluated, and results were compared between the methods for agreement. As part of the FEM approval process, the two methods were proven to be comparable to FAAS and, therefore, retain consistency with the 1978 FRM.

2.0 Results and Discussion

MDLs were established for both extraction methods performed on all three types of filters through the analysis of Pb-spiked samples and are presented in Table 1. Established MDLs are all far below the limit (less than 5%) of lead in TSP established in the updated NAAQS (0.15 $\mu g/m^3$). While lead solution-spiked samples alone may not be used as a direct comparison to the application of the technique on real-world samples, they can provide a much simpler sample matrix that can be used in the reliable development of quantitation limits and as a demonstration of the reproducibility of the ICP-MS analysis technique in the presence of the filter matrix. In addition, lead solution-spiked filters are the accepted matrix for demonstration of method proficiency by the USEPA.Complex botanical, geological, and industrial standard reference materials (SRMs) were selected to provide a robust challenge to assess method performance at or

below the concentration range of real-world samples. Recoveries of the SRMs extracted by both methods in the presence of all three filter types are also shown in Table 1. For all four SRM materials, the observed recoveries ranged from 91-108%, successfully fulfilling the pre-defined acceptance criteria of 90-110%.

The filter samples that had been extracted with each method were analyzed non-sequentially to determine extraction precision. For all filter types and extraction conditions, the determined %CV values for extraction samples with Pb concentrations exceeding 1 µg/L are shown in Table 1. Excellent precision was observed, with %CV values of 2% or less, which is within the maximum allowable limit of 3% CV for triplicate measurements.

The measured analytical bias and precision results from the intra-laboratory study (as defined in 40 CFR Part 53.33) are shown in Table 1. Bias is calculated as a signless value since it is calculated using absolute values, but it is assigned a sign based on its 25th and 75th percentile values. If both values have the same sign, the bias has that sign. If the values have opposite signs, the bias is assigned a ± sign. The bias values for the intra-laboratory study are all within 8%, demonstrating good agreement between the values determined at different concentration levels. Table 1 also shows the bias determined for the inter-laboratory study. The bias values ranged from 3.78 to 6.89%, demonstrating good agreement of the results between the laboratories of this study.

The results of the stability measurements are shown in Table 1, with extracts obtained from all three filter media using both extraction methods exhibiting average percent differences that met the acceptance criteria of ±10% difference. This demonstrates that samples prepared by the new FRM are acceptably stable over the course of eight calendar months.

Inter- and intra-laboratory reproducibility data are presented in Table 2. Intra-laboratory precision was excellent (less than the target 10% CV), demonstrating highly reproducible results within a testing facility over a broad range of concentrations. The results for the inter-laboratory analysis were found to exhibit less than the target of 20% CV, demonstrating that the results obtained between two laboratories did not vary significantly. Data from the decoupled analysis of samples are also shown in Table 2, as represented by the %CV of the results obtained for samples produced at different laboratories that were then analyzed at a single laboratory. The mean %CV of measured Pb in samples ranged from 3.38 to 7.80%, demonstrating that variation in recovered Pb concentrations was likely due to differences in sample collection technique rather than differences in the analytical method used at different laboratories.

Finally, a comparison was made between the results of the sample analyses performed by ICP-MS and sample analyses performed by FAAS on samples prepared using both extraction methods. Comparability was defined in 40 CFR Part 53.33 as the percent difference between the ICP-MS results and the FAAS results for identical samples.

$$D = \frac{C_{ij} - R_{jk}}{R_{jk}} \times 100 \tag{3}$$

where D is the percent difference, C is the concentration of each filter sample as determined by the candidate method and R is the concentration determined by the reference method, i is the filter number, j is the replicate of the candidate method (A, B, or C), and k is the replicate of the reference method (A, B, or C). The samples that were extracted and analyzed were all found to fall within a concentration range that is appropriate for both analytical techniques. The determined comparability of the lead content for both extraction methods are shown in Table 3. For all sample filters, the comparability values fall within the acceptance criteria of ±20% comparability, demonstrating equivalency of the results obtained by the two methods.

3.0 Experimental

Materials and equipment used in both extraction and measurement methods are described in detail in EQL-0510-191 and EQL-0710-192. National Institute of Standards and Technology (NIST) traceable Pb standards (High Purity Standards, Charleston, SC, USA) from two sources or bottles produced with two different lot numbers were used to prepare calibration standards and spiked samples. NIST-traceable scandium, indium, praseodymium, terbium, holmium, and bismuth standards (High Purity Standards) were used to prepare internal standard solutions for ICP-MS analysis. Trace Metals Grade HNO_3 and HCl (SCP Science, Champlain, NY, USA) were used to prepare extraction solutions and calibration standards. Solid NIST (Gaithersburg, MD, USA) standard reference materials (SRMs) were purchased and used as received in preparation of samples. Where necessary, chemical reagents of similar purity were used in sample and standard preparation.

Quartz and glass fiber filters (Whatman International Ltd, Maidstone, England) with dimensions of 8" x 10" were used for blanks, audit samples, and TSP samples provided to each laboratory taking part in the study. A selection of lab-prepared samples and of real-world test samples was used for extraction and analysis in the intra-laboratory study. There were no PTFE filters available that had been sampled for TSP according to 40 CFR Part 50, Appendix B, to provide samples to all of the laboratories taking part in the inter-laboratory study described below. Therefore, PTFE filters (Whatman International Ltd) that had been used to sample PM_{10} as described in 40 CFR Part 50, Appendix O were used for the study. Seven filters were extracted at the reference laboratory by the ultrasonic extraction method, and portions of the extracts were sent to each laboratory for analysis. Fifty milliliter polypropylene digestion tubes

(Environmental Express, Charleston, SC, USA or equivalent) were used for extraction of filter samples. A Thermo (Franklin, MA, USA) X-Series II ICP-MS instrument or equivalent was used for ICP-MS analysis of extracted samples.

3.1 Intra-laboratory study

The intra-laboratory method performance study consisted of analysis of a series of SRM and laboratory control samples that were prepared to mimic "real-world" samples. A number of quartz and glass fiber air filter samples were prepared by the methods described in 40 CFR Part 50, Appendix B (active air flow through a filter mounted in a sampling device at a flow rate of 1.1-1.7 m^3/min), and by spiking the filters with a reference Pb salt solution (SRM 3128). Samples were extracted by the methods described in EQL-0510-191 (heated ultrasonic water bath at 80 ± 5 °C in a 1.03 M HNO_3/2.23 M HCl solution) and EQL-0710-192 (3.5% (v/v) HNO_3 solution heated in a graphite block at 95 ± 5 °C). Additionally, a selection of filters of all three types were extracted in digestion vessels that contained massed samples of solid NIST SRMs 1547 (peach leaves), 2709 (San Joaquin soil), 2583 (trace elements in indoor dust), and 2582 (powdered paint) and analyzed for extractable Pb content [13-16]. Sample extracts were analyzed by ICP-MS following the EPA Office of Solid Waste SW846 method 6020A [17], which includes steps for calibration, calibration verification, and quality control sample preparation.

Method detection limits were established by analyzing the extracts of Pb salt solution-spiked sample filters (PTFE, quartz, and glass fiber) using 40 CFR Part 136, Appendix B. Method detection limits (MDLs) were established by multiplying the standard deviation of replicate analyses (n = 7) of each filter type by 3.146 (as defined in Appendix B). Method performance was also evaluated by triplicate analysis of spiked and sample strips taken from

quartz, glass fiber, and PTFE filters (n = 7 each) using either the hotblock or ultrasonic extraction method.

Analyses were evaluated for bias and precision and compared to pre-defined acceptance criteria (listed in Tables 1 and 2). Bias ($\left|AB\right|$) was defined in 40 CFR Part 58, Appendix A, 4.1.3, as an upper bound of the mean absolute value of the percent differences (Eq. 1).

$$\left|AB\right| = AB + t_{0.95,n-1}\frac{AS}{\sqrt{n}} \qquad (1)$$

where AB is the average difference between the nominal and measured lead concentrations, $t_{0.95, n-1}$ represents the Student's t-value at a 95% confidence interval with n-1 degrees of freedom, AS represents the standard deviation of the absolute value of the deviation of the measured values, and n represents the number of samples measured.

Precision was defined as described in 40 CFR Part 53.33, as the difference between the maximum and minimum determinations, divided by the average of the triplicate measurements and converted to a percentage (Eq. 2) [18].

$$P = \frac{C_{i\max} - C_{i\min}}{C_{avg}} \times 1000 \qquad (2)$$

where P represents precision, C_{imax} represents the maximum measured concentration of a filter, C_{imin} represents the minimum measured concentration of a filter, and C_{avg} represents the average concentration measured in all filters.

Sample stability was assessed in extracts of spiked filter strips and of sampled field filters with concentrations between 0.045 and 0.375 µg/m^3. Samples of glass fiber and quartz filter strips extracted by both methods and PTFE filters extracted by the ultrasonic method were assessed. Samples were measured immediately after extraction as time=0, and the extracts were stored at ambient room temperature (~23 °C). Extracts were reanalyzed after a period of 246

calendar days and the percent difference from the initial measurement was determined. After the final measurement, the results for all measurements were averaged and compared to the acceptance criterion of ±10% difference (Table 1).

3.2 Inter-laboratory study

The inter-laboratory comparison was performed in a manner consistent with a previous FRM evaluation [19]. Four laboratories participated in the inter-laboratory assessment of the new FRM. Each laboratory was provided with copies of the standard operating procedures (SOPs) for both FEMs and with samples of glass fiber, quartz, and PTFE filters that had been cut into strips of approximately equivalent width. Each filter was cut into eight strips, with a pair of adjacent strips being sent to each laboratory. One strip was extracted by the hotblock method, while the second was extracted by the ultrasonic method, and each extract was analyzed by ICP-MS for total soluble lead content. Method performance was evaluated by comparison of extracts of audit filter strips spiked at three concentrations (0.045, 0.150, and 0.375 $\mu g/m^3$ or 7.582, 25.275, and 63.693 μg/strip) and triplicate analysis of strips taken from both types of filters (quartz or glass fiber, n = 7) using either of the extraction methods (hotblock or ultrasonic). The results obtained from all laboratories were compared to each other and evaluated for bias and precision. Following the inter-laboratory analysis of samples, a decoupled analysis was performed by collection of the solutions extracted from the TSP filter samples in each laboratory and analysis of these solutions at the reference laboratory to determine the percent coefficient of variation (%CV) of each sample and extraction technique. This method of data analysis provides an estimate of the variability that arises due to sampling and extraction technique and minimizes bias that arises due to analysis on different instruments by different analysts.

4.0 Conclusions

The results shown in this study demonstrate that the analysis of Pb-TSP extracts can be accurately and reproducibly performed using ICP-MS. This analytical technique provides the versatility and low limits of quantitation that are required to meet the new, lower federal health standards for Pb-TSP. While the previous FRM for Pb-TSP, which features analysis by FAAS, is acceptable for determining the lead content of air particulates, ICP-MS is able to operate at significantly lower lead concentrations, making it more appropriate for application to the new limit for Pb-TSP, 0.15 $\mu g/m^3$. The application of both ultrasonic and hotblock extraction methods for three types of filter samples provides satisfactory results when applied to the accepted filter materials. The acidic conditions found in both extraction methods are able to effectively solubilize Pb from quartz, glass fiber, and PTFE filter media for analysis. Data obtained from both ICP-MS and FAAS are comparable and exhibit good reproducibility and accuracy, making the new FRM an effective method of determining Pb-TSP.

does not constitute endorsement or recommendation for use. The authors acknowledge no

significant conflicts of interest.

6.0 References

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Tables

Table 1. Intra-Laboratory Method Performance

Test Description	Acceptance Criteria	Heated Ultrasonic			Hotblock	
		Glass Fiber Filter	Quartz Filter	PTFE Filter	Glass Fiber Filter	Quartz Filter
Method Detection Limit[1]	5% of the NAAQS or 0.0075 μg/m^3	0.0000161 μg/m^3	0.000174 μg/m^3	0.000097 μg/m^3	0.000131 μg/m^3	0.000021 μg/m^3
SRM 1547 Recovery	90-110%	100±4	101±6	104±5	92±7	106±3
SRM 2709 Recovery	90-110%	98±1	95±1	93±1	98±3	104±3
SRM 2583 Recovery	90-110%	103±8	91±5	108±11	103±4	92±6
SRM 2582 Recovery	90-110%	101±0	93±1	96±3	94±4	95±2
RSD of replicate measurements	RSD of 3 consecutive replicates ≤ 3 %	1.50	1.44	0.81	0.43	1.93
Analytical Bias[2]	≤ 7%	-3.78	-6.89	±1.61	+4.12	-6.41
Analytical Precision[2]	≤ 10%	0.62	0.66	0.17	1.30	1.56
Intra-Laboratory Method Precision[3]	≤10%	1.15	5.76	1.11	2.70	1.73
Spiked Filter Extract Stability Average % Difference[4]	±10% of the original concentration	-1.75	-5.01	-0.38	6.55	1.50
Sample Filter Extract Stability Average % Difference[4]	±10% of the original concentration	-1.84	-1.88	4.04	8.76	-7.66

[1] 40 CFR Part 136, Appendix B

[2] 40 CFR Part 58, Appendix A

[3] 40 CFR part 53.33

[4] Stability of extracts tested for up to 246 days at room temperature; average % difference between original and final concentration

Table 2. Experimental Bias, Reproducibility, and Variability

Test Description	Acceptance Criteria	Heated Ultrasonic			Hotblock	
		Glass Fiber Filter	Quartz Filter	PTFE Filter	Glass Fiber Filter	Quartz Filter
Bias[1]	≤15%	±4.54	-7.39	-6.55	±4.40	-5.28
Intra-Laboratory Reproducibility[2]	≤20%	2.68	2.98	N/A[4]	3.37	3.29
Inter-Laboratory Reproducibility[3]	≤20%	9.82	5.51	6.59	7.69	7.56
Decoupled Extraction Method Variability	N/A[5]	7.04	3.38	N/A[4]	4.02	7.80

[1] 40 CFR Part 58, Appendix A

[2] Within laboratory method reproducibility for the four participating laboratories computed as %CV (Long et al., 1979).

[3] Between-laboratory method reproducibility across the four participating laboratories computed as %CV (Long et al., 1979).

[4] Insufficient PTFE filter extract was available to perform this test.

[5] The goal was to assess the variability due to the sampling and preparation (extraction) methods; therefore no acceptance criterion was specified.

Table 3. Comparability to the Existing FRM and Method Performance[1]

Test Description	Acceptance Criteria	Heated Ultrasonic			Hotblock	
		Glass Fiber Filter	Quartz Filter	PTFE Filter	Glass Fiber Filter	Quartz Filter
FEM Approval Precision	15%	< 2.3 %	NA[2]	NA	< 6.6 %	NA
FEM Approval Comparability	±20%	> - 13.1 % < 17.0 %	NA	NA	> - 6.1 % < 12.5 %	NA

[1] 40 CFR, Part 53.33

[2] NA = Comparability analysis between ICP-MS and FAAS analysis was not performed for this filter material.