

*Review of Approach for Development of  
New Federal Reference Method (FRM)  
for Pb-TSP*

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## *Current FRM for Pb-TSP*

- Overall method for Pb-TSP consists of the sampling method and the analysis method combined
  - Sampling method based on high-volume TSP per 40 CFR Part 50, Appendix B
  - Analysis method based on Atomic Absorption Spectroscopy (AAS) per 40 CFR Part 50, Appendix G

## *Need for a new FRM for Pb-TSP*

- Advances in new analytical measurement technologies warrant a revision and update to the existing AAS FRM analysis method
  - Improved analytical sensitivity (detection limits) to support much lower NAAQS
  - Improved and more efficient extraction methods
  - Wider use and availability of newer analytical instrumentation
- Focus of new FRM is on the analysis method only and will not address sampling

## *Proposed FRM for Pb-TSP*

- Extraction Methods
  - Heated ultrasonic water bath – EQL-0510-191
    - $80 \pm 5^{\circ}\text{C}$  with 1.02M nitric/2.23M hydrochloric
  - Hot block digestion – EQL-0710-192
    - $95 \pm 5^{\circ}\text{C}$  with 3.5% nitric (v/v)
- Analysis Method
  - Inductively-coupled mass spectrometry (ICP-MS)
  - Advantages:
    - Very low method detection limits (MDLs)
      - On the order of  $0.2 \text{ ng/m}^3$  or less for high-volume samples
    - Commonly used

## *FRM and Method Performance*

- Based on following guidance documents and references:
  - EQL-0510-191, Determination of Lead in TSP by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with Heated Ultrasonic Nitric and Hydrochloric Acid Filter Extraction.
  - EQL-0710-192, Heated Nitric Acid Hot Block Digestion and ICP-MS Analysis for Lead(Pb) on TSP High-Volume Filters.
  - Validation and Peer Review of U.S. Environmental Protection Agency Chemical Methods of Analysis, prepared for The EPA Forum on Environmental Measurements (FEM); FEM Document Number 2005-01, October 14, 2005.
  - Guidance for Methods Development and Methods Validation for the RCRA Program; Development and Validation of SW-846 Methods Phase 2: Formal Validation, April 6, 1992.
  - EPA's Office of Solid Waste (OSW) compendium of sampling and analytical methods for Evaluating Solid Waste, SW-846 Method 6020A, "Inductively Coupled Plasma-Mass Spectrometry", Revision 1, February 2007.
  - Harper et al., (1983). Simplex Optimization of Multi-element Ultrasonic Extraction of Atmospheric Particulates; Anal. Chem., 55 (9), 1553-1557.
  - Long et al., (1979). Lead Analysis of Ambient Air Particulates: Inter-laboratory Evaluation of EPA Lead Reference Method; APCA Journal, 29, 28-31.

## *Method Performance*

- Analysis of Standard Reference Materials (SRMs)
- Analysis of filters spiked with NIST-traceable Pb salts solutions
- Effects of Interferences and filter matrix effects
- Determination of MDL (40 CFR part 136, appendix B)
- Intra-laboratory method performance
  - Testing to assess bias and precision
    - Bias 10% and Precision 15%
  - Evaluation of glass and quartz filter matrices
  - Analysis of spiked filter strips, SRMs and real world samples
  - Test small variations in extraction temperature and time
  - Evaluate extract storage stability

## *Method Performance*

- Inter-laboratory (between-lab) method performance
  - Purpose to assess the performance of the method when applied by other laboratories
  - Need at least four laboratories to participate
  - Labs will be asked to analyze filter samples and spiked filter strips using both extraction options and the ICP-MS analysis method
  - The coefficient of variation (CV) will be used to determine the variability at the 95% confidence interval

## *Charge Questions*

- What are the panel's views on the two extraction method options of heated ultrasonic with nitric/hydrochloric acids and graphitic hot block with nitric acid for the extraction of Pb from TSP?
- What are the panel's views on ICP-MS as the analysis method for Pb-TSP as the FRM?
- What are the panel's views on the approach described for evaluating the performance the method prior to proposing it through the rule making process as a new FRM for Pb-TSP?
- Inter-laboratory testing will be done to assess between-laboratory variability. What are the panel's views on a reasonable level of variability (CV) at the 95% confidence interval?

## *Next Steps*

- Consider and incorporate advice
- Complete intra-laboratory performance tests
- Complete inter-laboratory performance tests
- Proposed and Final Rule within 18 months