Metal Sampling Group 1 (METALSSG-1)
Metals Collected on Mixed Cellulose Ester Filters

Method number:	5003
Version number:	1.0

Validated analytes:

Analyte	CAS No.
Arsenic	7440-38-2
Cadmium	7440-43-9
Lead	7439-92-1

Note: CAS numbers listed are for arsenic, cadmium, and lead in their elemental forms only. CAS numbers and molecular weights for compounds of these elements vary. This method is only intended for the sampling and analysis of inorganic arsenic, cadmium and lead; it is not intended for the sampling and analysis of volatile or organic compounds that contain these elements.

Procedure: Collect air samples by drawing workplace air through a 37-mm diameter, 0.8 micron pore size, mixed-cellulose ester (MCE) filter contained in a closed-face polystyrene cassette using a personal sampling pump. Collect wipe samples on smear tabs. Digest the samples with nitric acid using microwave digestion and dilute with 18 MΩ-RO water to a solution of 6% nitric acid/1% hydrochloric acid (v/v). Dilute digested sample solution by a factor of ten and analyze by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) instrumentation.

Recommended sampling time and sampling rate: 240 min at 2 L/min (480 L)

Special requirements: This method is designed to collect particulate inorganic arsenic. Some species of inorganic arsenic are volatile, like arsine gas (AsH_3) and arsenic trioxide (As_2O_3). To sample and analyze for arsine gas see the instructions found in NIOSH Method 6001[1]. Arsenic trioxide is only partially collected[2] on the MCE filter used in this method. When workplace processing temperatures exceed 800 °C, arsenic may convert to arsenic trioxide. To sample and analyze for arsenic trioxide see the instructions found in NIOSH Method 7901[3].

Validation status: Data found in the respective method appendices have been subjected to the established validation procedures of the OSHA Method Development Team. The method is considered to be fully validated for all analytes so designated.

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[1] Hull, R. D. Arsine (NIOSH Method 6001), 1994. Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health web site. https://www.cdc.gov/niosh/docs/2003-154/pdfs/6001.pdf (accessed November 2019).

[2] Costello, R.J.; Eller, P.M.; Hull, R.D. Measurement of Multiple Inorganic Arsenic Species. *Am. Ind. Hyg. Assoc. J*. **1983**, 44, 21-28.

[3] Millson, M; Eller, P. M. Arsenic Trioxide (NIOSH Method 7901), 1994. Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health web site. https://www.cdc.gov/niosh/docs/2003-154/pdfs/7901.pdf (accessed November 2019).

1 Introduction

For assistance with accessibility problems in using figures and illustrations presented in this method, please contact the Salt Lake Technical Center (SLTC) at (801) 233-4900. This procedure was designed and tested for internal use by OSHA personnel. Mention of any company name or commercial product does not constitute endorsement by OSHA.

This method harmonizes the preparation and analysis of various metal analytes collected on 37-mm diameter, 0.8 micron pore size, mixed-cellulose ester (MCE) filters. Validation data for each analyte are located in the relevant appendices. The acid matrix of the calibration standards is 0.4%/0.1% (v/v) nitric acid/hydrochloric acid in an 18 MΩ-RO water solution while the final acid matrix of the digested samples is 0.6%/0.1% (v/v) nitric acid/hydrochloric acid in an 18 MΩ-RO water solution. The slight difference in acid matrices arises due to the requirement for a minimum volume of undiluted acid to fully digest an MCE filter in a 10-mL microwave vessel. The validation data included in relevant appendices, which were all obtained using the above listed matrices for samples and standards, show that this difference does not impact analytical results.

2 Sampling Procedure

Follow all safety practices that apply to the work area being sampled. Attach sampling equipment to the worker in a manner that will not interfere with work performance or safety.

2.1 Apparatus

37-mm diameter, 0.8 micron pore size, MCE filter, with support pad in two-piece polystyrene cassette, with end plugs and a gel band. Commercially prepared cassettes may be purchased from SKC Inc. (catalog no. 225-508).

A personal sampling pump calibrated to within ±5% of the recommended flow rate is used with a representative sampling device in-line with flexible pump tubing.

Smear tabs (SKC 225-24), 20-mL glass scintillation vials and disposable gloves, for wipe sampling.

2.2 Reagents

- Deionized water for wipe sampling

2.3 Technique

Air Samples

Remove the bottom plug from a prepared cassette, attach the calibrated personal sampling pump (the support pad should face the tubing to the pump) with flexible tubing, and position the apparatus in the appropriate workplace area or in the worker's breathing zone in an approximately vertical position with the inlet facing down. Sample closed face by removing the inlet plug from the cassette and drawing air directly into the inlet. Position the sampling pump, cassette and tubing so they do not impede work performance or safety. The air being sampled should not pass through any hose or tubing before entering the cassette. Care should be taken to avoid overloading the filter.

Sample at 2 L/min for 240 min (480 L).

After sampling, replace the plugs at both ends of the cassette. Seal each sample end-to-end with a Form OSHA-21 as soon as possible.

Submit at least one field blank sample with each set of air samples. Handle the blank sample in the same manner as the other air samples except draw no air through it.

Record sample air volume (liters), sampling time (min) and sampling rate (L/min) for each sample, along with any potential interference on the Form OSHA-91A.

Submit the samples to the laboratory for analysis as soon as possible after sampling.

Wipe Samples

Use a smear tabs moistened with deionized water prior to use. Wear clean, impervious, disposable gloves while handling or collecting wipe samples. Change gloves between samples to minimize cross-contamination.

Wipe a 10-cm by 10-cm surface area in a horizontal side-to-side pattern, applying firm pressure. If possible, fold the smear tab in half with the exposed side in, and use it to wipe the same area again in a vertical up-and-down pattern.

After sampling transfer the wipe sample to a clean 20-mL scintillation vial. Cap the vial securely and seal with a Form OSHA-21. Use 20-mL glass scintillation vials to transport and ship wipe samples. It may be convenient to preload vials with moist smear tabs prior to field work.

Submit at least one field blank sample with each set of wipe samples. Handle, store, and ship blank samples in the same manner as other wipe samples.

Note any known substance present or potential interferences on the form OSHA-91A.

3 Analytical Procedure

3.1 Apparatus

- Digestion microwave vessels (10-mL Pyrex) and caps
- MCE filters (37-mm for wiping cassette interior)
- Microwave system capable of reaching 130 °C without sample loss
- Class-A flat bottom 50-mL polypropylene containers
- Disposable syringes (10-mL) and syringe filters (0.8-µm)
- Auto-diluter
- Vials for sample analysis (15-mL)
- ICP-MS instrument with collision cell technology (CCT)
- Mixing “Y” fitting to add the internal standard solution
- Wash bottles, forceps, and stir bars

3.2 Reagents

- 18 MΩ-RO water
- Arsenic (As) standard solution (1000 µg/mL)
- Cadmium (Cd) standard solution (1000 µg/mL)
- Lead (Pb) standard solution (1000 µg/mL)
- Germanium (Ge) standard solution (1000 µg/mL)
- Rhodium (Rh) standard solution (1000 µg/mL)
- Lutetium (Lu) standard solution (1000 µg/mL)
- Concentrated nitric acid (69-70%) (reagent grade or better)
- Concentrated hydrochloric acid (36.5-38%) (reagent grade or better)

3.3 Reagent Preparation

Sample diluent (0.4%/0.1% (v/v) nitric acid/hydrochloric acid in water): To a 1000-mL volumetric flask add 800 mL of 18 MΩ-RO water, 4.0 mL of nitric acid, 1.0 mL of hydrochloric acid, then 18 MΩ-RO water to the mark.

Instrument rinse (2% (v) nitric acid in water): To a 1000-mL volumetric flask add 800 mL of 18 MΩ-RO water, 20 mL nitric acid, then 18 MΩ-RO water to the mark.

Internal standard solution (ISTD): Dilute germanium, rhodium, and lutetium standards in an acid stabilized matrix (1-2% nitric acid) to concentrations that will provide a signal in the middle of pulse counting range. The signal count intensities of these internal standard measurements (or interpolated signal count intensities between them) are used to correct signal counts for analytes of interest. The signal for ^{73}Ge is used to correct ^{75}As; ^{103}Rh is used for ^{111}Cd, and ^{114}Cd; ^{175}Lu is used for ^{206}Pb, ^{207}Pb, and ^{208}Pb. The internal standard (ISTD) mix is introduced with a mixing "Y" fitting immediately before the standard reaches the plasma.

3.4 Standard Preparation

Purchase or prepare an intermediate stock standard solution containing arsenic, cadmium, and lead at desired concentrations. Ensure the intermediate standard has a final acid matrix of 0.4%/0.1% (v/v) nitric acid/hydrochloric acid in an 18 MΩ-RO water solution. This intermediate stock standard is good for twelve months.

Dilute the intermediate stock standard to working range concentrations prior to each analysis using the sample diluent. The acid matrix of the working range calibration standards is 0.4%/0.1% (v/v) nitric acid/hydrochloric acid in an 18 MΩ-RO water solution.

3.5 Sample Preparation

For air samples, carefully transfer any loose particulate from the cassette into a 10-mL Pyrex microwave digestion vessel. Use forceps to transfer the filter to the same vessel. Wipe the interior of the cassette top with a clean MCE filter, moistened with 18 MΩ-RO water, and add it to the same vessel. Other interior surfaces of the cassette should be wiped if visibly contaminated.

For smear tab samples, carefully transfer each smear tab into a 10-mL Pyrex microwave digestion vessel using forceps. If material remains in the scintillation vial, rinse with a small amount (up to 2 mL) of 18 MΩ-RO water into the same vessel.

Add a stir bar to each vessel. To digest the samples, add 3 mL of concentrated nitric acid. Cap the vessel and place it in the microwave sample tray. Program the microwave to ramp the temperature over a period of 2 minutes to 130 °C and hold at 130 °C for 8 minutes with medium speed stirring (570 rpm). Programmed pressure stages (set for pressure release by venting vessels) are unnecessary.

<u>Microwave settings</u>

stage:	1
temperature:	130 °C
ramp time:	2 min
hold time:	8 min
pressure:	450 psi
power:	300 W
stirring:	570 rpm

After samples have cooled, quantitatively transfer each solution to a Class-A container using 18 MΩ-RO water from a rinse bottle or an auto-diluter. Add 0.5 mL of concentrated hydrochloric acid. Bring each sample solution to a final volume of 50 mL with 18 MΩ-RO water (Alternatively, dilute to final volume with a 1% hydrochloric acid solution). Cap

the container and stir or shake each sample well. The final acid matrix for all prepared samples is 6%/1% (v/v) nitric acid/hydrochloric acid in an 18 MΩ-RO water solution.

3.6 Analysis

Analyze samples using an ICP-MS instrument and analytical conditions similar to those described below. Use an ISTD calibration method. For each analyte construct a least-squares linear regression curve by plotting ISTD-corrected response of standard injections versus ppb concentrations of analyte per sample. A weighted least-squares linear regression, using a 1/RSD or $1/RSD^2$ weight, can also be used. Sample aliquots used for instrumental analysis should be free of particulate. Sample solutions should remain undisturbed for long enough for particulates to settle if present. Alternatively, solutions may be filtered. Dilute each sample solution by a factor of ten with 18 MΩ-RO water and pour an aliquot of each diluted sample solution into an appropriate vial for analysis. Dilution by factors greater than ten may be required for very concentrated samples to ensure sample measurement is within the calibration range.

ICP-MS Conditions

detector mode:	peak jumping
runs:	3
sweeps per run:	100
dwell time:	1-100 milliseconds
channel spacing:	0.02 *m/z*
channels per *m/z*:	1
plasma flow:	13 L/min
aux. flow:	0.7-0.8 L/min
nebulizer flow:	0.6-0.7 L/min
power:	1400 W
peristaltic pump:	0.675 mL/min sample flow
	0.675 mL/min ISTD flow
	20 s sample uptake delay
autosampler:	2.25 mL/min rinse flow
	60 s rinse time

Collision Cell (CCT)

^{75}As:	Kinetic energy discrimination (KED) mode –
	8% H_2 in He, 5-10 mL/min, 20 s time delay
^{111}Cd, ^{114}Cd:	Off
^{206}Pb, ^{207}Pb, ^{208}Pb:	Off

ICP-MS instrumentation must be tuned and checked with a tuning solution. Instrument and plasma conditions can generally be altered to minimize analytical interferences. Follow manufacturer's recommendations to tune the instrument. Table 1 below summarizes common interferences of the analytes for which this method is validated. Use a tuning solution containing barium to ensure that the ratio of the doubly charged barium ion to the singly charged $^{137}Ba^+$ ion remains less than 0.03. Barium is chosen for this test due to its low secondary ionization potential. This minimizes the effects of interferences from doubly charged ions, such as $^{150}Nd^{++}$ on $^{75}As^+$, listed in the second column of Table 1. Use a tuning solution that contains cerium to ensure that the ratio of $^{146}Ce^{16}O^+$ to $^{140}Ce^+$ remains less than 0.01 in KED mode (or 0.02 in standard mode). Cerium is chosen for this test due to its high affinity for oxygen and the stability of its oxide in a plasma. This removes the effects of polyatomic ions, such as $^{190}Pt^{16}O^+$ on $^{206}Pb^+$, listed in the third column of Table 1. Analytical interferences in ICP-MS also include isobaric interferences, ions that have the same *m/z* ratio (such as $^{114}Sn^+$ as an interference for $^{114}Cd^+$), listed in the fourth column of Table 1. These interferences are corrected using correction equations which are usually included in instrument operating software.

Table 1. Common interferences of validated analytes[4].

isotope of interest	analytical interferences: doubly charged ions	analytical interferences: polyatomic ions	analytical interferences: Isobaric ions	correction equations (note *d*)	notes
^{75}As	$^{150}Nd^{++}$, $^{150}Sm^{++}$	$^{40}Ar^{35}Cl^{+}$, $^{59}Co^{16}O^{+}$, $^{36}Ar^{38}Ar^{1}H^{+}$, $^{38}Ar^{37}Cl^{+}$, $^{36}Ar,^{39}K^{+}$, $^{43}Ca^{16}O_2^{+}$, $^{23}Na^{12}C^{40}Ar^{+}$, $^{12}C^{31}P^{16}O_2^{+}$	None	$^{75}As^{+} = {}^{75}Total - 2.9033 \times {}^{40}Ar^{37}Cl^{+}$	*a*
^{111}Cd	None	$^{95}Mo^{16}O^{+}$, $^{94}Zr^{16}O^{1}H^{+}$, $^{39}K_2{}^{16}O_2{}^{1}H^{+}$	None	$^{111}Cd^{+} = {}^{111}Total - 0.00040 \times {}^{95}Mo^{+}$	*b*
^{114}Cd	None	$^{98}Mo^{16}O$, $^{98}Ru^{16}O^{+}$	^{114}Sn	$^{114}Cd^{+} = {}^{114}Total - 0.00070 \times {}^{95}Mo^{+} - 0.024 \times {}^{118}Sn^{+}$	*b*
^{206}Pb	None	$^{190}Pt^{16}O^{+}$	None	$^{Total}Pb = {}^{206}Pb^{+} + {}^{207}Pb^{+} + {}^{208}Pb^{+}$	*c*
^{207}Pb	None	$^{191}Ir^{16}O^{+}$	None	$^{Total}Pb = {}^{206}Pb^{+} + {}^{207}Pb^{+} + {}^{208}Pb^{+}$	*c*
^{208}Pb	None	$^{192}Pt^{16}O^{+}$	None	$^{Total}Pb = {}^{206}Pb^{+} + {}^{207}Pb^{+} + {}^{208}Pb^{+}$	*c*

a. Neodymium and samarium are rare elements and the particular isotopic abundances that interfere with ^{75}As are not plentiful. Polyatomic ion interference is greatly reduced through the use of collision cell technology (CCT) in KED mode. The use of such technology eliminates the need for any correction equations. Without the application of collision cell technology ^{75}As requires correction for $^{40}Ar^{35}Cl$.

b. ^{111}Cd is the preferred *m/z* for analysis. Although the isotopic abundance of the interfering tin isotope for ^{114}Cd is less than one percent, ^{114}Cd results are only used for verification; variation from the ^{111}Cd results may be monitored along with the Sn results for interference determination. Results for ^{114}Cd should always be corrected by an interference correction equation.

c. The three stable isotopes of lead validated herein are the endpoint of the radiologic decay of ^{232}Th, ^{235}U, and ^{238}U. The abundance ratio of these lead isotopes to each other may change slightly depending on the source of origin, but together they constitute 98.6% of all stable lead found in nature. Summing the isotopes together negates the impact of abundance ratio differences on results.

d. The correction equations shown are from Thermo Fisher PlasmaLab Software Ver. 2.6.2.337.

Because cadmium has an isobaric interference, three interference check solution (ICS) mixtures were prepared and analyzed. These solutions were each spiked with tin to achieve a concentration equivalent to the PEL. No cadmium was added to the first solution (ICS_B). The other two solutions ($ICS_{A,PEL}$ and $ICS_{A,action\ level}$) were then spiked with cadmium to achieve a concentration equivalent to the PEL or the action limit for cadmium based on the same sampling parameters. These solutions demonstrate that samples containing reasonably high levels of interfering element still give acceptable results for cadmium, the analyte of interest. Results are summarized in Table 2.

Table 2. Interference check solutions for cadmium.

solution	ppb		µg/sample		result (µg/sample)		result (%)	
	Sn	Cd	Sn	Cd	^{114}Cd	^{111}Cd	^{114}Cd	^{111}Cd
ICS_B	1920	0.0	960	0.0	0.168	0.006	N/A	N/A
$ICS_{A,PEL}$	1920	4.8	960	2.4	2.634	2.447	109.8	102.0
$ICS_{A,action\ level}$	1920	2.4	960	1.2	1.379	1.226	114.9	102.2

[4] May, T.W.; Wiedmeyer, R.H. A Table of Polyatomic Interferences in ICP-MS. *Atomic Spec.* **1998**, 19, 150-155.

3.7 Calculations

The analyte air concentration (C_a) is calculated in micrograms per cubic meter (µg/m^3) using Equation 1, where C_s is the concentration of analyte found in the sample as reported by the instrument in µg/L, V_a is the volume of air sampled (L), V_s is the final diluted volume of the digested sample solution (mL), and D_F is dilution factor applied for the analysis. If desired, C_s can be corrected by subtracting the concentration of analyte (if any) found on the sample blank.

$$C_a = \frac{C_s V_s}{V_a} D_F \qquad \text{Equation 1}$$

For wipe samples, the mass (m) in µg is obtained using Equation 2, where C_s is the analyte concentration of the sample as reported by the instrument (µg/L), V_s is the final diluted volume of the digested sample solution (mL), and D_F is dilution factor applied for the analysis.

$$m = \frac{C_s V_s}{1000} D_F \qquad \text{Equation 2}$$

Molar masses *(M*) and analytical mass to charge ratios (*m/z*) are listed in Table 3 along with the OSHA Integrated Management Information System (IMIS) numbers for each analyte.

Table 3. Analytical mass to charge ratios and OSHA Integrated Management Information System (IMIS) numbers for Method 5003 analytes.

	arsenic	cadmium	lead
m/z	75	111, 114	206, 207, 208
IMIS	0260	C141	1591

OSHA 5003, Appendix A
Inorganic Arsenic

Version:	1.0
OSHA PEL:	10 µg/m^3 TWA, 5 µg/m^3 action level Note: Arsenic has an expanded standard requiring biological monitoring and/or medical examinations (29 CFR 1910.1018).
ACGIH TLV:	0.01 mg/m^3
Recommended sampling time and sampling rate:	240 min at 2.0 L/min (480 L)
Reliable quantitation limit:	4.56×10^{-2} µg/m^3 (^{75}As)
Standard error of estimate:	5.10% (^{75}As)
Status:	Fully validated. Method 5003 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of inorganic arsenic.

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1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Arsenic

Particulate metals have been analyzed by a variety of methods throughout OSHA's history ranging from early methods that employed hot plate digestion techniques and flame atomic absorption (FAA) through more recently developed technologies such as microwave digestion techniques paired with inductively coupled plasma mass spectrometry (ICP-MS) instrumentation. In 2005, OSHA published Method 1006[1] which specified the use of an open vessel microwave digestion for sample preparation. While useful, the open vessel microwave digestion technique is inferior to the closed vessel microwave system because acids in a closed system can be heated higher than their boiling points enabling digestion of some metal compounds that would otherwise require the use of more caustic or higher boiling acids.

OSHA Method 5003 seeks to establish a routine metal digestion that can be used for arsenic and its compounds in a matrix that is useful for many metals and their compounds without the use of extremely caustic or high boiling acids such as perchloric acid and sulfuric acid. The acid matrix specified here is well suited for ICP-MS instrumentation.

1.2 Changes to the Previously-used Method

This method differs significantly from previously used methods. Changes to analytical conditions, and digestion acid volume have been made to allow standardized collection of arsenic with the other analytes found in the Metals Sampling Group 1, described in Method 5003. The detection limit of the analytical procedure (DLAP), detection limit of the overall procedure (DLOP), reliable quantitation limit (RQL), instrument response to arsenic, recovery, and stability of digested samples, storage stability, and reproducibility were all reevaluated.

[1] Giles, P. Arsenic, Cadmium, Cobalt, Copper, Lead, and Nickel (Open Vessel Microwave Digestion/ICP-MS Analysis) (OSHA 1006) 2005. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/mdt/mdt1006/1006.pdf (accessed November 2019).

1.3 Validation Parameters

Where applicable, this method follows validation protocols drawing from the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Spectroscopic Analysis".[2] These Guidelines detail required validation tests, show examples of statistical calculations, list validation acceptance criteria, and define analytical parameters. The target concentration for method evaluation was the analyte concentration equivalent to sampling for the recommended time at the OSHA time-weighted average (TWA) permissible exposure limit (PEL) for arsenic. Validation data were collected using a Thermo X-series 2 ICP-MS instrument, with collision cell technology (CCT), and a Fisher Scientific "Y" fitting (Part no. NC9380620). Samples were prepared with a CEM Discover SP-D digestion microwave.

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure (DLAP)

The DLAP is measured as the concentration of analyte that produces a response significantly greater than a reagent blank. Ten analytical standards were prepared with approximately equal descending increments of analyte such that the highest standard concentration would produce a peak approximately 10 times the response of a blank at the mass to charge ratio of the analyte. These standards and a reagent blank were analyzed with the analytical parameters. The data obtained were used to determine the required parameters (standard error of estimate ($S_{y/x}$) and slope) for the calculation of the DLAP. Results obtained for the blank and each standard are listed below in Table A-1 and are plotted in Figure A-1.

Table A-1. DLAP data for ^{75}As.

concentration (µg/L)	response (counts/s)
0.000	292.905
0.025	351.674
0.050	394.609
0.075	446.379
0.100	487.514
0.125	538.151
0.150	610.189
0.175	661.426
0.200	721.865
0.225	786.237
0.250	839.976

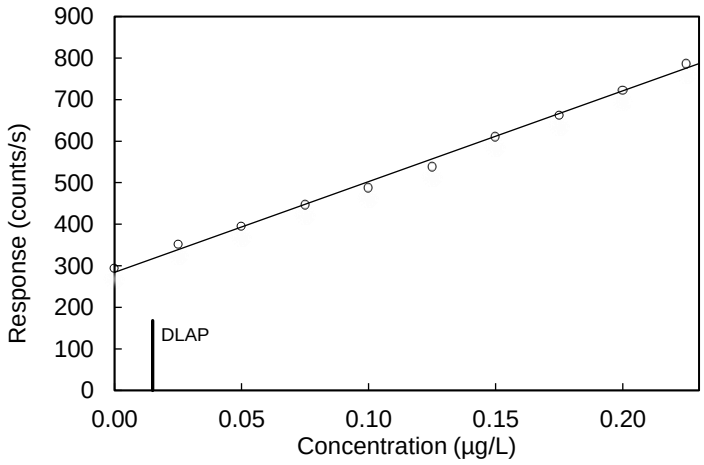

Figure A-1. Plot of data used to determine the DLAP for arsenic at ^{75}As ($y = 2.18 \times 10^3 x + 2.84 \times 10^2$, $S_{y/x} = 1.09 \times 10^1$, DLAP = 1.50×10^{-2} µg/L).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is measured as mass per sample that produces a response significantly different than a sample blank. The RQL is the lowest level of analyte mass per sample for precise quantitative measurements and expressed as an air concentration based on the recommended sampling parameters. Ten samplers were spiked with approximately equal descending increments of analyte, such that the highest sampler loading would produce a peak approximately 10 times the response of a sample blank at the mass to charge ratio of the analyte. These spiked samplers and a sample blank were analyzed with the analytical parameters. The data obtained were used to calculate the required parameters ($S_{y/x}$

[2] Eide, M.; Giles, P.; Simmons, M.; Hendricks, W. Evaluation Guidelines for Air Sampling Methods Utilizing Spectroscopic Analysis, 2005. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/spectroguide/spectroguide.pdf (accessed November 2019).

and the slope) for the calculation of the DLOP and RQL. Results obtained for the sample blank and the ten spiked samplers are listed below in Table A-2 and plotted in Figure A-2.

Table A-2. DLOP and RQL data for ^{75}As.

concentration (µg/sample)	response (counts/s)
0.0000	687.628
0.0125	744.367
0.0250	783.303
0.0375	869.145
0.0500	913.983
0.0625	974.724
0.0750	1046.299
0.0875	1108.040
0.1000	1159.781
0.1125	1226.390
0.1250	1309.070

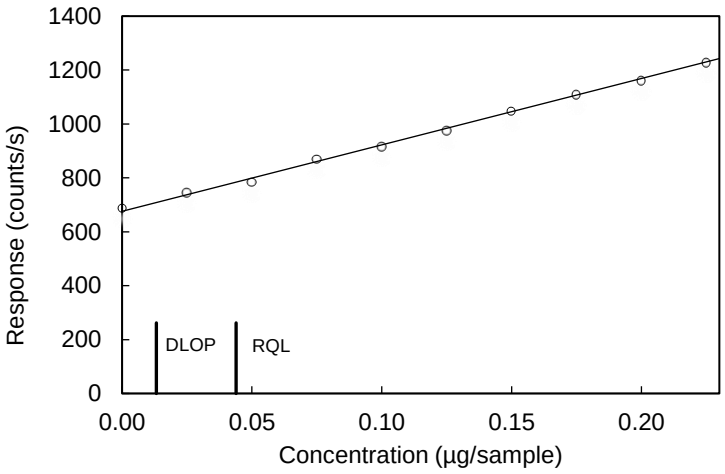

Figure A-2. Plot of data used to determine the DLOP and RQL for arsenic at ^{75}As (y = 4.93 × 10^{3}x + 6.76 × 10^2, $S_{y/x}$ = 1.08 × 10^1, DLOP = 6.57 × 10^{-3} µg/sample, RQL = 2.19 × 10^{-2} µg/sample (4.56 × 10^{-2} µg/m^3)).

3 Analytical Calibration

Fifteen analytical standards over a range of 0.05 to 2.0× the target concentration were prepared and analyzed with the analytical parameters. A least-squares linear regression curve was constructed by plotting the analyte mass per sample versus the internal standard (ISTD)-corrected analyte peak area. The data obtained were used to calculate the analytical calibration precision ($S_{y/x}$). Results are listed below in Table A-3 and plotted in Figure A-3.

Table A-3. Analytical precision data for ^{75}As.

× target (µg/L)	0.05× 0.5	0.5× 5	1.0× 10	1.5× 15	2.0× 20
response	2125	12436	23955	35798	47242
(corrected	2110	12321	23766	35276	46705
counts/s)	2115	12547	24193	35519	47077

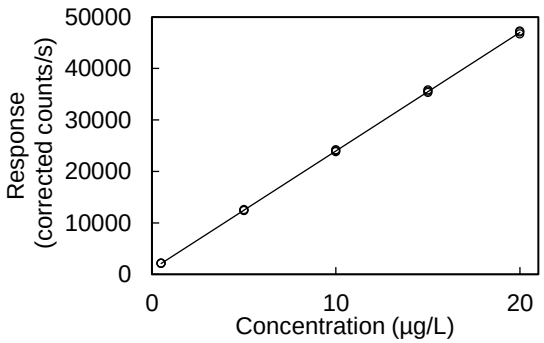

Figure A-3. Plot of the data used to estimate precision of the analytical method for ^{75}As (y = 2.30 × 10^{3}x + 9.45 × 10^2, $S_{y/x}$ = 1.78 × 10^2).

4 Sampler Storage Stability

Thirty-six samples were prepared by direct spiking, eighteen at the PEL (4.8 µg/sample) and eighteen at action level (2.4 µg/sample). The samplers were stored at ambient temperature (about 24 °C). Three samples were selected from each of the two storage sets and analyzed at the intervals noted in Table A-4. Sample results were not corrected for digestion efficiency. Results obtained for the PEL and action level storage tests are listed below in Table A-4. Results are plotted in Figures A-4 and A-5.

Table A-4. Sampler storage stability data for arsenic.

time (days)	PEL storage recovery (%)			action level storage recovery (%)		
0	99.1	100.9	100.6	102.5	103.5	99.8
3	99.8	99.6	99.3	99.2	97.7	98.0
8	98.7	100.2	99.9	101.5	102.6	103.7
11	101.3	101.0	101.8	102.5	100.7	98.7
15	100.0	100.8	100.3	98.9	100.8	101.0
18	101.0	101.8	98.2	100.3	103.5	102.3

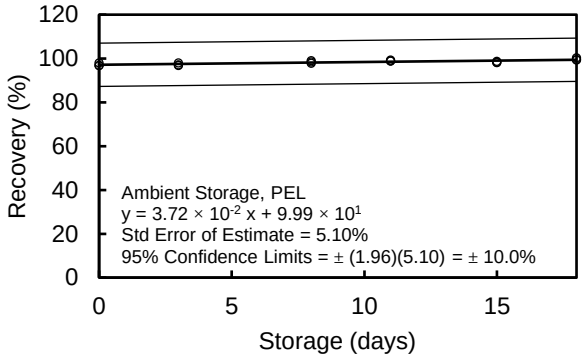

Figure A-4. Plot of storage stability data for arsenic at the PEL.

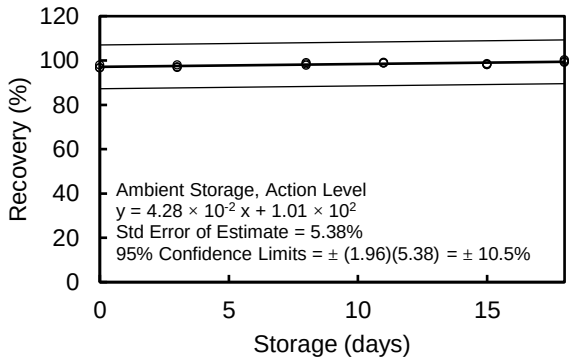

Figure A-5. Plot of storage stability data for arsenic at the action level.

5 Precision

The precision of the overall procedure at the 95% confidence level is obtained by multiplying the overall standard error of estimate by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). This provides ninety-five percent confidence intervals which are drawn about the regression lines in the storage stability figures shown in Section 4.

The precision of the overall procedure at the 95% confidence level for the ambient temperature 18-day storage test (at the PEL concentration) is ± 10.0%. The precision of the overall procedure at the 95% confidence level for the ambient temperature 18-day storage test (at the action level concentration) is ± 10.5%. These data were obtained from the overall standard errors of estimate (5.10% and 5.38%) derived from the data shown in Figures A-4 and A-5, with an additional 5% added for sampling pump error.

The recovery of arsenic from samples used in the 18-day storage test at the PEL was 100.6% when samples were stored at ambient temperature. The recovery of arsenic from samples used in the storage test at the action level was 101.8% when samples were stored at ambient temperature.

6 Recovery and Stability of Prepared Samples

6.1 Soluble Forms

Quantitative digestion is affected by the acid matrix, the sampling medium, and the technique used to digest the samples. For the use of reagents and techniques other than those described here, testing specified in current OSHA evaluation guidelines must be completed.

A value for digestion efficiency (D_E) was determined by liquid-spiking four MCE filters at a range of analyte concentrations equivalent to sampling at 0.05 to 2 times the target concentration value for 4 hours. For a single set of filters spiked with analyte equivalent to sampling at the 1.0× target concentration value for 4 hours, humid air (74.9%

relative humidity at 22.3 °C) was passed through the filters for 240 min at 2 L/min prior to spiking. Another set of filters was spiked at the RQL level. The spiked samples were stored overnight at ambient temperature and then analyzed. An overall mean D_E value of 99.0% was obtained across the analyte concentration range studied for ^{75}As. The results of these tests, along with the D_E values at the RQL, are provided in Table A-5, and they demonstrate that the presence of water on the filter had no significant effect on D_E. The D_E values for the RQL and wet sampler testing were not included in the overall mean.

Table A-5. Digestion efficiency data for ^{75}As.

level		sample recovery (%)				
× target concn	µg per sample	1	2	3	4	mean rec (%)
0.05	0.25	98.1	99.2	100.6	98.7	99.2
0.5	2.5	98.6	98.3	100.8	101.0	99.7
1.0	5.0	101.0	101.7	99.3	99.6	100.4
1.5	7.5	99.9	97.1	96.1	98.5	97.9
2.0	10.0	97.2	97.7	97.7	99.2	98.0
RQL	0.025	101.4	100.3	102.1	101.9	101.4
1.0 (wet)	5.0	101.5	101.5	102.3	100.4	101.4

Based on available solubility data[3] for hot water, it is assumed that the following arsenic compounds will solubilize in the acid matrix at concentrations of twice the PEL: arsenic acid hemihydrate, arsenic pentafluoride, arsenous acid (solution), arsonoacetic acid, arsphenamine, sodium arsenate (dibasic), sodium arsenite, potassium arsenite, sodium arsenate (dibasic heptahydrate), potassium arsenate, and arsenic triiodide.

6.2 Insoluble Forms

Digestion efficiencies of selected insoluble arsenic compounds were tested due to their likely presence in work environments or industrial importance. Efficiencies were determined by digesting and analyzing a known amount of each compound material in triplicate. The compounds tested were measured by mass onto a tared MCE filter and then prepared and analyzed. The compounds and data obtained are shown in Table A-6.

Table A-6. Digestion efficiency of arsenic from selected arsenic compounds.

compound	level						% recovery by sample			mean
	total mass (µg)			As mass (µg)			1	2	3	rec (%)
arsenic (elemental)	191	274	239	191	274	239	97.6	99.1	98.1	98.3
arsenic trisulfide	244	99	133	148	60.1	80.8	94.9	102.2	94.4	97.2
arsenic trioxide	108	103	252	81.6	77.8	190	98.9	104.9	100.4	101.4
gallium arsenide	103	388	314	53.2	200	162	94.5	103.1	103.2	100.3
indium arsenide	218	166	112	85.9	65.4	44.1	107.2	108.7	107.0	107.6

6.3 Digestion Efficiency of Smear Tabs

The digestion efficiency of soluble arsenic from liquid-spiked smear tabs was determined at the PEL and action level (5.0 and 2.5 µg/sample), as well as at the RQL (0.025 µg/sample). Liquid was spiked directly onto the four smear tabs and allowed to dry at ambient temperature. A liquid solution was also prepared at a concentration corresponding to each level of the test samples; these solutions were diluted from an arsenic solution and were not digested. Each corresponding liquid solution, used for reference, was analyzed 3 times on the same day as the samples. The mean result of each corresponding solution was used to apply a correction to the corresponding sample results. Results in Tables A-7 reflect the corrected recoveries of the samples.

[3] *The Merck Index*; 14th ed.; O'Neil, M., Ed.; Merck & Co. Inc.: Whitehouse Station, NJ, 2006 pp 936-939.

Table A-7. Corrected arsenic recovery from smear tabs for ^{75}As.

level	mass spiked (µg)	sample recovery (%) 1	2	3	4	mean rec (%)
PEL	5.0	97.9	98.5	99.0	98.0	98.4
action level	2.5	97.2	98.8	100.0	99.2	98.8
RQL	0.025	102.3	101.1	101.4	100.6	101.4

6.4 Stability of Digested Samples

The stability of digested samples was examined by reanalyzing the 1.0× target concentration samples 24, 48, and 72 hours after the initial analysis. After the original analysis was performed two vials and their contents were discarded and replaced by freshly diluted aliquots from a closed polypropylene container for each reanalysis event. The other two vials remained in the auto-sampler tray at ambient conditions throughout the duration of the test. Sample digestates were stored at room temperature. Freshly prepared standards were used for each reanalysis event. Results calculated from instrument calibration curves similar to the calibration curve presented in section 3 are listed in Table A-8.

Table A-8. Digested sample stability data for ^{75}As.

	fresh dilution recovery (%)		exposed diluted sample recovery (%)	
time (days)	1	2	1	2
0	100.2	99.6	99.9	99.5
1	101.1	98.9	103.3	100.4
2	99.8	101.5	103.6	102.6
3	101.3	99.8	104.8	105.6

7 Sampler Capacity

Because a test atmosphere was not generated a full sampler capacity study could not be performed. Instead a retention efficiency study was performed. The retention efficiency of an MCE filter was tested by spiking six filters at twice the PEL equivalent (10 µg). After drying, the filters were each placed in a two-piece cassette with the ends plugged, equipped with a support pad under the filter. Three of the filter cassettes were set aside and used as controls, with no air pulled through these cassettes. Air with approximately 75.1% relative humidity, at 23.2 °C, was drawn through three of the samplers, each lined up with a blank (un-spiked) sampler placed downstream, for 240 minutes at 2 L/min. No analyte was detected on any of the blanks. The mean recovery for the three test filters was 100.3% for ^{75}As. The mean recovery for the three control filters, through which air was not drawn, was 100.3% for ^{75}As.

8 Low Humidity

A low humidity recovery test was not performed.

9 Interferences

A sampling interference study was not performed.

10 Reproducibility

Reproducibility was determined by preparing and analyzing 6 MCE filters each at the PEL and action level (4.8, and 2.4 µg/sample). The samples were analyzed 16 days after preparation. Sample results were not corrected for digestion efficiency. No sample result for arsenic had a deviation greater than the precision of the overall procedure determined in Section 5. The data are presented in Tables A-9 and A-10.

Table A-9. Reproducibility for arsenic at the PEL.

theoretical (µg/sample)	result (µg/sample)	recovery (%)	deviation (%)
4.8	4.804	100.1	0.1
4.8	4.860	101.3	1.3
4.8	4.804	100.1	0.1
4.8	4.786	99.7	-0.3
4.8	4.826	100.5	0.5
4.8	4.737	98.7	-1.3

Table A-10. Reproducibility for arsenic at the action level.

theoretical (µg/sample)	result (µg/sample)	recovery (%)	deviation (%)
2.4	2.378	99.1	-0.9
2.4	2.432	101.3	1.3
2.4	2.420	100.8	0.8
2.4	2.416	100.7	0.7
2.4	2.370	98.8	-1.2
2.4	2.427	101.1	1.1

11 Additional Testing

11.1 Recovery from Wiping Cassette Interior

Recovery of soluble arsenic from a cassette was determined by spiking 4 cassettes each at the PEL and action level (5 and 2.5 µg/sample). Liquid was spiked onto the interior surface of a top cassette piece, allowed to dry at ambient temperature, and then wiped with a damp MCE filter. The data obtained are shown in Table A-11.

Table A-11. Arsenic recovery from cassettes for ^{75}As.

level	mass spiked (µg)	sample recovery (%) 1	2	3	4	mean rec (%)
PEL	5.0	97.7	97.5	97.6	88.4	95.3
action level	2.5	90.0	91.9	88.4	88.2	89.6

11.2 Smear Tab Wipe Sampling Efficiency

Wipe efficiency was tested on twelve glass surface areas. Each area measured 10 cm by 10 cm square. A liquid solution was spiked at 5 and 2.5 µg/sample, in a spiral pattern of droplets, onto each surface and allowed to dry overnight at ambient temperature. Each surface area was wiped in an up-and-down pattern with a damp smear tab. The smear tab was folded in half, keeping the wiped side folded together, and then used to wipe the same area in a side-to-side pattern. Results are shown in Table A-12.

Table A-12. Arsenic recovery from glass for ^{75}As.

level	mass spiked (µg)	sample recovery (%) 1	2	3	4	5	6	mean rec (%)
PEL	5.0	89.5	84.6	91.3	88.7	87.7	87.7	88.3
action level	2.5	83.7	83.2	87.2	83.8	92.0	90.2	86.7

12 Estimation of Uncertainty

Estimation of uncertainty was not performed. Instead the overall standard error of estimate was calculated from the ambient storage test as prescribed by the OSHA validation guidelines[2].

13 Sampler Testing Procedure

A test atmosphere was not generated.

OSHA 5003, Appendix B
Cadmium

Version:	1.0
OSHA PEL:	5 µg/m^3 TWA, 2.5 µg/m^3 action level Note: Cadmium has an expanded standard requiring biological monitoring and/or medical examinations (29 CFR 1910.1027).
ACGIH TLV:	0.01 mg/m^3
Recommended sampling time and sampling rate:	240 min at 2.0 L/min (480 L)
Reliable quantitation limit:	5.69×10^{-2} µg/m^3 (^{111}Cd) 3.65×10^{-2} µg/m^3 (^{114}Cd)
Standard error of estimate:	5.08% (^{111}Cd)
Status:	Fully validated. Method 5003 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of inorganic cadmium.

November 2019 Brian J. Albrecht & Tyler J. Erickson

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Cadmium

Particulate metals have been analyzed by a variety of methods throughout OSHA's history ranging from early methods that employed hot plate digestion techniques and flame atomic absorption (FAA) through more recently developed technologies such as microwave digestion techniques paired with inductively coupled plasma mass spectrometry (ICP-MS) instrumentation. In 2005, OSHA published Method 1006[1] which specified the use of an open vessel microwave digestion for sample preparation. While useful, the open vessel microwave digestion technique is inferior to the closed vessel microwave system because acids in a closed system can be heated higher than their boiling points enabling digestion of some metal compounds that would otherwise require the use of more caustic or higher boiling acids.

OSHA Method 5003 seeks to establish a routine metal digestion that can be used for cadmium and its compounds in a matrix that is useful for many metals and their compounds without the use of extremely caustic or high boiling acids such as perchloric acid and sulfuric acid. The acid matrix specified here is well suited for ICP-MS instrumentation.

1.2 Changes to the Previously-used Method

This method differs significantly from previously used methods. Changes to analytical conditions, and digestion acid volume have been made to allow standardized collection of cadmium with the other analytes found in the Metals Sampling Group 1, described in Method 5003. The detection limit of the analytical procedure (DLAP), detection limit of the overall procedure (DLOP), reliable quantitation limit (RQL), instrument response to cadmium, recovery, and stability of digested samples, storage stability, and reproducibility were all reevaluated.

[1] Giles, P. Arsenic, Cadmium, Cobalt, Copper, Lead, and Nickel (Open Vessel Microwave Digestion/ICP-MS Analysis) (OSHA 1006) 2005. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/mdt/mdt1006/1006.pdf (accessed November 2019).

1.3 Validation Parameters

Where applicable, this method follows validation protocols drawing from the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Spectroscopic Analysis".[2] These Guidelines detail required validation tests, show examples of statistical calculations, list validation acceptance criteria, and define analytical parameters. The target concentration for method evaluation was the analyte concentration equivalent to sampling for the recommended time at the OSHA time-weighted average (TWA) permissible exposure limit (PEL) for cadmium. Validation data were collected using a Thermo X-series 2 ICP-MS instrument,with collision cell technology (CCT) and a Fisher Scientific "Y" fitting (Part no. NC9380620). Samples were prepared with a CEM Discover SP-D digestion microwave.

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure (DLAP)

The DLAP is measured as the concentration of analyte that produces a response significantly greater than a reagent blank. Ten analytical standards were prepared with approximately equal descending increments of analyte such that the highest standard concentration would produce a peak approximately 10 times the response of a blank at the mass to charge ratio of the analyte. These standards and a reagent blank were analyzed with the analytical parameters. The data obtained were used to determine the required parameters (standard error of estimate ($S_{y/x}$) and slope) for the calculation of the DLAP. Results obtained for the blank and each standard are listed below in Tables B-1 and B-2 and are plotted in Figures B-1 and B-2.

Table B-1. DLAP data for ^{111}Cd.

concentration (µg/L)	response (counts/s)
0.000	7.667
0.050	217.336
0.100	304.006
0.150	461.679
0.200	596.021
0.250	774.369
0.300	913.383
0.350	1059.067
0.400	1201.753
0.450	1381.114
0.500	1391.116

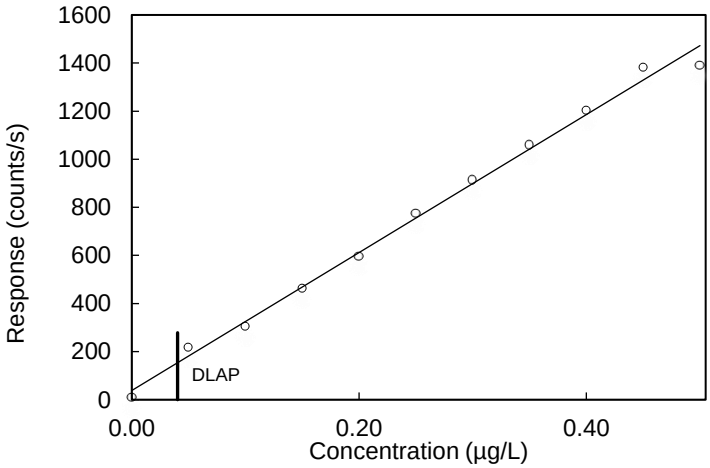

Figure B-1. Plot of data used to determine the DLAP for cadmium at ^{111}Cd (y = 2.87 × 10^{3}x + 3.81 × 10^1, $S_{y/x}$ = 3.86 × 10^1, DLAP = 4.03 × 10^{-2} µg/L).

[2] Eide, M.; Giles, P.; Simmons, M.; Hendricks, W. Evaluation Guidelines for Air Sampling Methods Utilizing Spectroscopic Analysis, 2005. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/spectroguide/spectroguide.pdf (accessed November 2019).

Table B-2. DLAP data for ^{114}Cd.

concentration (µg/L)	response (counts/s)
0.000	20.667
0.050	502.682
0.100	705.363
0.150	1087.071
0.200	1451.126
0.250	1751.184
0.300	2218.962
0.350	2488.038
0.400	2799.804
0.450	3262.639
0.500	3403.695

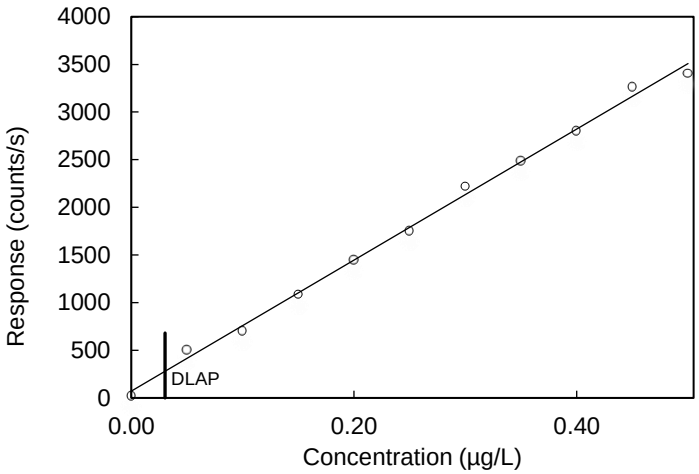

Figure B-2. Plot of data used to determine the DLAP for cadmium at ^{114}Cd ($y = 6.87 \times 10^{3}x + 7.16 \times 10^{1}$, $S_{y/x} = 6.93 \times 10^{1}$, DLAP $= 3.03 \times 10^{-2}$ µg/L).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is measured as mass per sample that produces a response significantly different than a sample blank. The RQL is the lowest level of analyte mass per sample for precise quantitative measurements and expressed as an air concentration based on the recommended sampling parameters. Ten samplers were spiked with approximately equal descending increments of analyte, such that the highest sampler loading would produce a peak approximately 10 times the response of a sample blank at the mass to charge ratio of the analyte. These spiked samplers and a sample blank were analyzed with the analytical parameters. The data obtained were used to calculate the required parameters ($S_{y/x}$ and the slope) for the calculation of the DLOP and RQL. Results obtained for the sample blank and the ten spiked samplers are listed below in Tables B-3 and B-4 and plotted in Figures B-3 and B-4.

Table B-3. DLOP and RQL data for ^{111}Cd.

concentration (µg/sample)	response (counts/s)
0.0000	16.667
0.0250	164.002
0.0500	350.007
0.0750	496.015
0.1000	634.691
0.1250	829.708
0.1500	970.390
0.1750	1140.411
0.2000	1340.108
0.2250	1449.793
0.2500	1614.156

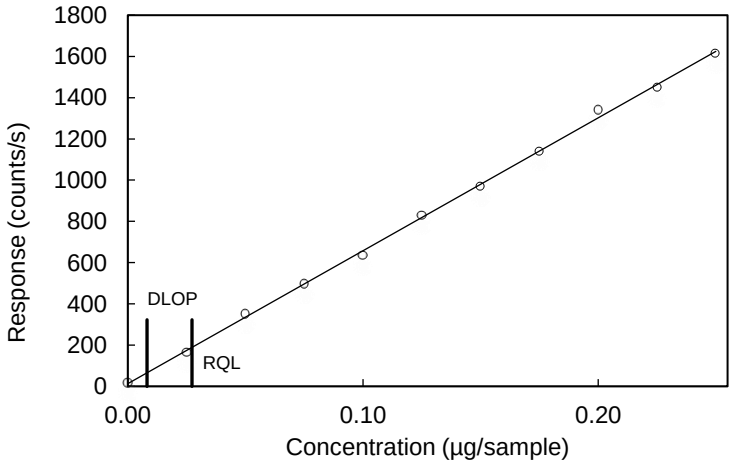

Figure B-3. Plot of data used to determine the DLOP and RQL for cadmium at ^{111}Cd ($y = 6.45 \times 10^{3}x + 1.30 \times 10^{1}$, $S_{y/x} = 1.76 \times 10^{1}$, DLOP $= 8.19 \times 10^{-3}$ µg/sample, RQL $= 2.73 \times 10^{-2}$ µg/sample (5.69×10^{-2} µg/m^3)).

Table B-4. DLOP and RQL data for ^{114}Cd.

concentration (µg/sample)	response (counts/s)
0.0000	60.667
0.0250	404.343
0.0500	811.039
0.0750	1214.088
0.1000	1539.142
0.1250	1917.221
0.1500	2279.979
0.1750	2728.780
0.2000	3111.247
0.2250	3473.057
0.2500	3857.559

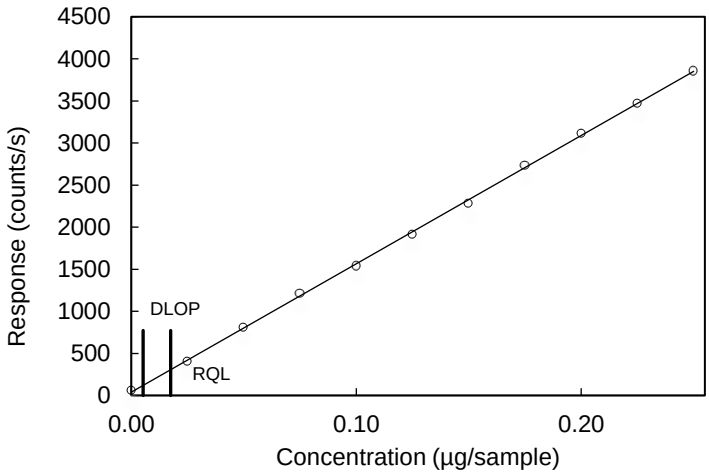

Figure B-4. Plot of data used to determine the DLOP and RQL for cadmium at ^{114}Cd ($y = 1.52 \times 10^{4}x + 3.93 \times 10^{1}$, $S_{y/x} = 2.66 \times 10^{1}$, DLOP $= 5.25 \times 10^{-3}$ µg/sample, RQL $= 1.75 \times 10^{-2}$ µg/sample (3.65×10^{-2} µg/m^3)).

3 Analytical Calibration

Fifteen analytical standards over a range of 0.05 to 2.0× the target concentration were prepared and analyzed with the analytical parameters. A least-squares linear regression curve was constructed by plotting the analyte mass per sample versus the internal standard (ISTD)-corrected analyte peak area. The data obtained were used to calculate the analytical calibration precision ($S_{y/x}$). Results are listed below in Tables B-5 and B-6 and plotted in Figures B-5 and B-6.

Table B-5. Analytical precision data for ^{111}Cd.

× target (µg/L)	0.05× 0.25	0.5× 2.5	1.0× 5	1.5× 7.5	2.0× 10
response	759	7439	14900	22404	29664
(corrected	743	7490	14836	22357	29631
counts/s)	771	7549	14978	22320	29969

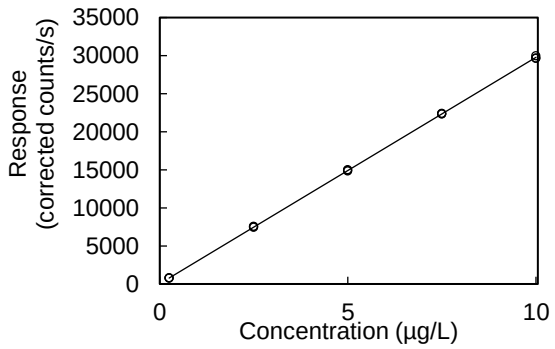

Figure B-5. Plot of the data used to estimate precision of the analytical method for ^{111}Cd ($y = 2.97 \times 10^{3}x + 3.60 \times 10^{1}$, $S_{y/x} = 8.54 \times 10^{1}$).

Table B-6. Analytical precision data for ^{114}Cd.

× target (µg/L)	0.05× 0.25	0.5× 2.5	1.0× 5	1.5× 7.5	2.0× 10
response (corrected counts/s)	1682	17520	35201	52996	70185
	1761	17656	35233	52746	70113
	1768	17687	35469	52638	70929

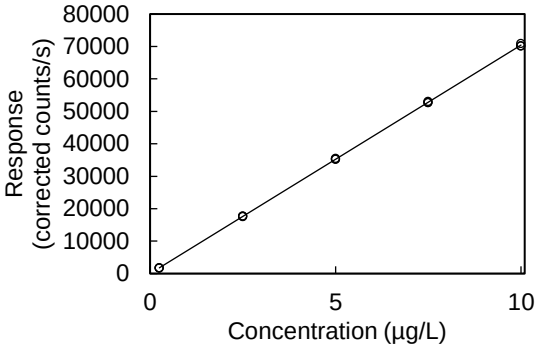

Figure B-6. Plot of the data used to estimate precision of the analytical method for ^{114}Cd ($y = 7.04 \times 10^{3}x + 1.35 \times 10^{1}, S_{y/x} = 2.09 \times 10^{2}$).

4 Sampler Storage Stability

The results for cadmium used for the sampler storage stability section are from ^{111}Cd, which is preferred over ^{114}Cd (see Method 5003 3.8 Analysis).

Thirty-six samples were prepared by direct spiking, eighteen at the PEL (2.4 µg/sample) and eighteen at action level (1.2 µg/sample). The samplers were stored at ambient temperature (about 24 °C). Three samples were selected from each of the two storage sets and analyzed at the intervals noted in Table B-7. Sample results were not corrected for digestion efficiency. Results obtained for the PEL and action level storage tests are listed below in Table B-7. Results are plotted in Figures B-7 and B-8.

Table B-7. Sampler storage stability data for cadmium.

time (days)	PEL storage recovery (%)			action level storage recovery (%)		
0	99.0	99.5	98.5	100.6	101.1	97.2
3	99.2	100.1	98.3	99.1	98.7	99.8
8	97.4	99.0	99.5	99.9	102.4	100.1
11	100.4	100.2	100.6	100.8	100.0	102.0
15	99.7	100.3	99.4	100.0	99.7	101.5
18	100.3	102.5	101.3	99.7	102.4	99.6

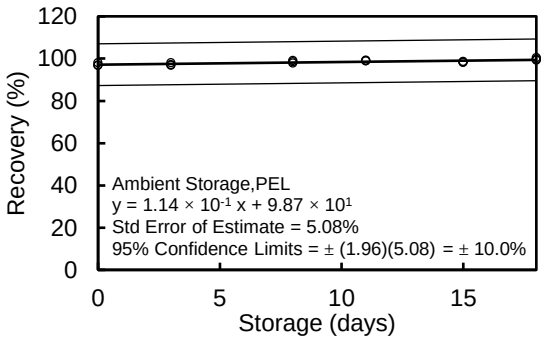

Figure B-7. Plot of storage stability data for cadmium at the PEL.

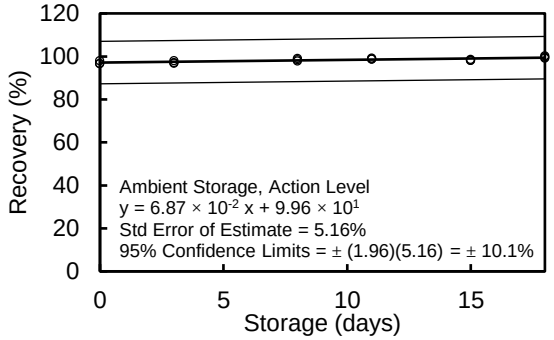

Figure B-8. Plot of storage stability data for cadmium at the action level.

5 Precision

The precision of the overall procedure at the 95% confidence level is obtained by multiplying the overall standard error of estimate by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). This provides ninety-five percent confidence intervals which are drawn about the regression lines in the storage stability figures shown in Section 4.

The precision of the overall procedure at the 95% confidence level for the ambient temperature 18-day storage test (at the PEL concentration) is $\pm$ 10.0%. The precision of the overall procedure at the 95% confidence level for the ambient temperature 18-day storage test (at the action level concentration) is $\pm$ 10.1%. These data were obtained from the overall standard errors of estimate (5.08% and 5.16%) derived from the data shown in Figures B-7 and B-8, with an additional 5% added for sampling pump error.

The recovery of cadmium from samples used in the 18-day storage test at the PEL was 100.8% when samples were stored at ambient temperature. The recovery of cadmium from samples used in the storage test at the action level was 100.8% when samples were stored at ambient temperature.

6 Recovery and Stability of Prepared Samples

6.1 Soluble Forms

Quantitative digestion is affected by the acid matrix, the sampling medium, and the technique used to digest the samples. For the use of reagents and techniques other than those described here, testing specified in current OSHA evaluation guidelines must be completed.

A value for digestion efficiency (D_E) was determined by liquid-spiking four MCE filters at a range of analyte concentrations equivalent to sampling at 0.05 to 2 times the target concentration value for 4 hours. For a single set of filters spiked with analyte equivalent to sampling at the 1.0× target concentration value for 4 hours, humid air (79.3% relative humidity at 23.2 °C) was passed through the filters for 240 min at 2 L/min prior to spiking. Another set of filters was spiked at the RQL level. The spiked samples were stored overnight at ambient temperature and then analyzed. An overall mean D_E value of 97.5% was obtained across the analyte concentration range studied for ^{111}Cd, and 98.1% was obtained for ^{114}Cd. The results of these tests, along with the D_E values at the RQL, are provided in Tables B-8 and B-9, and they demonstrate that the presence of water on the filter had no significant effect on D_E. The D_E values for the RQL and wet sampler testing were not included in the overall mean.

Table B-8. Digestion efficiency data for ^{111}Cd.

level		sample recovery (%)				
× target concn	µg per sample	1	2	3	4	mean rec (%)
0.05	0.125	95.1	94.9	96.4	95.1	95.4
0.5	1.25	97.3	97.1	99.1	98.6	98.0
1.0	2.50	99.7	100.3	98.6	100.0	99.7
1.5	3.75	97.1	95.7	95.3	97.4	96.4
2.0	5.00	98.3	97.1	97.8	98.2	97.9
RQL	0.025	103.2	99.8	107.6	107.3	104.5
1.0 (wet)	2.50	99.6	99.1	98.9	101.1	99.7

Table B-9. Digestion efficiency data for ^{114}Cd.

level		sample recovery (%)				
× target concn	µg per sample	1	2	3	4	mean rec (%)
0.05	0.125	97.3	95.0	96.8	98.7	97.0
0.5	1.25	98.3	97.7	99.7	99.6	98.8
1.0	2.50	100.2	100.5	98.2	100.5	99.9
1.5	3.75	97.5	96.2	95.3	97.6	96.7
2.0	5.00	98.2	97.4	98.2	98.8	98.2
RQL	0.025	93.1	94.7	97.7	95.4	95.2
1.0 (wet)	2.50	99.7	99.8	98.8	100.5	99.7

Based on available solubility data[3] for hot water, it is assumed that the following cadmium compounds will solubilize in the acid matrix at concentrations of twice the PEL: cadmium acetate dihydrate, cadmium bromide, cadmium chloride, cadmium chloride hemipentahydrate, cadmium iodide, cadmium salicylate monohydrate, cadmium sulfate hydrate, cadmium cyanide, cadmium bitrate tetrahydrate, cadmium potassium cyanide, cadmium fluoride, and cadmium sulfide.

6.2 Insoluble Forms

Digestion efficiencies of selected insoluble cadmium compounds were tested due to their likely presence in work environments or industrial importance. Efficiencies were determined by digesting and analyzing a known amount of each compound material in triplicate. The compounds tested were measured by mass onto a tared MCE filter and then prepared and analyzed. The compounds and data obtained are shown in Table B-10.

Table B-10. Digestion efficiency of cadmium from selected cadmium compounds.

compound	level						% recovery by sample			mean
	total mass (µg)			Cd mass (µg)			1	2	3	rec (%)
cadmium (metal)	98	244	125	98.0	244	125	100.6	92.8	99.3	97.6
cadmium oxide	138	118	109	121	103	95.4	96.1	106.8	99.7	100.9
cadmium hydroxide	149	139	218	114	107	167	104.3	106.6	101.7	104.2
cadmium selenide	142	70	107	83.4	41.1	62.9	97.8	107.9	95.7	100.5
cadmium telluride	165	139	85	77.3	65.1	39.8	90.5	92.7	98.6	93.9
cadmium tungstate	169	181	192	52.7	56.5	59.9	99.6	99.1	98.6	99.1

6.3 Digestion Efficiency of Smear Tabs

The digestion efficiency of soluble cadmium from liquid-spiked smear tabs was determined at the PEL and action level (2.5 and 1.25 µg/sample), as well as at the RQL (0.025 µg/sample). Liquid was spiked directly onto the four smear tabs and allowed to dry at ambient temperature. A liquid solution was also prepared at a concentration corresponding to each level of the test samples; these solutions were diluted from a cadmium solution and were not digested. Each corresponding liquid solution, used for reference, was analyzed 3 times on the same day as the samples. The mean result of each corresponding solution was used to apply a correction to the corresponding sample results. Results in Tables B-11 and B-12 reflect the corrected recoveries of the samples.

[3] *The Merck Index*; 14th ed.; O'Neil, M., Ed.; Merck & Co. Inc.: Whitehouse Station, NJ, 2006 pp 936-939.

Table B-11. Corrected cadmium recovery from smear tabs for ^{111}Cd.

level	mass spiked (µg)	sample recovery (%) 1	2	3	4	mean rec (%)
PEL	2.5	100.0	98.7	99.8	100.7	99.8
action level	1.25	97.5	99.4	99.4	99.1	98.9
RQL	0.025	94.0	96.1	91.2	99.0	95.1

Table B-12. Corrected cadmium recovery from smear tabs for ^{114}Cd.

level	mass spiked (µg)	sample recovery (%) 1	2	3	4	mean rec (%)
PEL	2.5	100.0	99.2	99.5	99.4	99.5
action level	1.25	97.2	99.1	99.9	99.7	99.0
RQL	0.025	99.8	104.7	100.5	103.2	102.1

6.4 Stability of Digested Samples

The stability of digested samples was examined by reanalyzing the 1.0× target concentration samples 24, 48, and 72 hours after the initial analysis. After the original analysis was performed two vials and their contents were discarded and replaced by freshly diluted aliquots from a closed polypropylene container for each reanalysis event. The other two vials remained in the auto-sampler tray at ambient conditions throughout the duration of the test. Sample digestates were stored at room temperature. Freshly prepared standards were used for each reanalysis event. Results calculated from instrument calibration curves similar to the calibration curve presented in section 3 are listed in Tables B-13 and B-14.

Table B-13. Digested sample stability data for ^{111}Cd.

	fresh dilution recovery (%)		exposed diluted sample recovery (%)	
time (days)	1	2	1	2
0	98.3	99.9	101.7	100.1
1	99.2	99.1	102.4	101.1
2	97.2	100.6	104.8	102.9
3	101.8	100.5	106.2	106.4

Table B-14. Digested sample stability data for ^{114}Cd.

	fresh dilution recovery (%)		exposed diluted sample recovery (%)	
time (days)	1	2	1	2
0	98.4	100.9	100.8	101.8
1	98.9	99.5	102.6	101.3
2	97.5	100.4	103.4	103.0
3	100.6	100.2	105.7	105.1

7 Sampler Capacity

Because a test atmosphere was not generated a full sampler capacity study could not be performed. Instead a retention efficiency study was performed. The retention efficiency of an MCE filter was tested by spiking six filters at twice the PEL equivalent (5 µg). After drying, the filters were each placed in a two-piece cassette with the ends plugged, equipped

with a support pad under the filter. Three of the filter cassettes were set aside and used as controls, with no air pulled through these cassettes. Air with approximately 74.9% relative humidity, at 22.3 °C, was drawn through three of the samplers, each lined up with a blank (un-spiked) sampler placed downstream, for 240 minutes at 2 L/min. No analyte was detected on any of the blanks. The mean recoveries for the three test filters were 97.2, and 96.7% for ^{111}Cd, and ^{114}Cd respectively. The mean recoveries for the three control filters, through which air was not drawn, were 97.2, and 96.4% for ^{111}Cd, and ^{114}Cd respectively.

8 Low Humidity

A low humidity recovery test was not performed.

9 Interferences

A sampling interference study was not performed.

10 Reproducibility

The results for cadmium used for the reproducibility section are from ^{111}Cd which is preferred over ^{114}Cd.

Reproducibility was determined by preparing and analyzing 6 MCE filters each at the PEL and action level (2.4, and 1.2 µg/sample). The samples were analyzed 16 days after preparation. Sample results were not corrected for digestion efficiency. No sample result for cadmium had a deviation greater than the precision of the overall procedure determined in Section 5. The data are presented in Tables B-15 and B-16.

Table B-15. Reproducibility for cadmium at the PEL.

theoretical (µg/sample)	result (µg/sample)	recovery (%)	deviation (%)
2.4	2.372	98.8	-1.2
2.4	2.401	100.0	0.0
2.4	2.394	99.8	-0.2
2.4	2.398	99.9	-0.1
2.4	2.417	100.7	0.7
2.4	2.352	98.0	-2.0

Table B-16. Reproducibility for cadmium at the action level.

theoretical (µg/sample)	result (µg/sample)	recovery (%)	deviation (%)
1.2	1.178	98.2	-1.8
1.2	1.214	101.2	1.2
1.2	1.198	99.8	-0.2
1.2	1.188	99.0	-1.0
1.2	1.200	100.0	0.0
1.2	1.202	100.2	0.2

11 Additional Testing

11.1 Recovery from Wiping Cassette Interior

Recovery of soluble cadmium from a cassette was determined by spiking 4 cassettes each at the PEL and action level (2.5 and 1.25 µg/sample). Liquid was spiked onto the interior surface of a top cassette piece, allowed to dry at ambient temperature, and then wiped with a damp MCE filter. The data obtained are shown in Tables B-17 and B-18.

Table B-17. Cadmium recovery from cassettes for ^{111}Cd.

level	mass spiked (µg)	sample recovery (%) 1	2	3	4	mean rec (%)
PEL	2.5	88.5	90.8	88.4	86.8	88.6
action level	1.25	96.2	94.8	95.8	87.6	93.6

Table B-18. Cadmium recovery from cassettes for ^{114}Cd.

level	mass spiked (µg)	sample recovery (%) 1	2	3	4	mean rec (%)
PEL	2.5	96.0	95.1	95.7	87.2	93.5
action level	1.25	88.6	90.8	87.6	87.2	88.6

11.2 Smear Tab Wipe Sampling Efficiency

Wipe efficiency was tested on twelve glass surface areas. Each area measured 10 cm by 10 cm square. A liquid solution was spiked at 2.5 and 1.25 µg/sample, in a spiral pattern of droplets, onto each surface and allowed to dry overnight at ambient temperature. Each surface area was wiped in an up-and-down pattern with a damp smear tab. The smear tab was folded in half, keeping the wiped side folded together, and then used to wipe the same area in a side-to-side pattern. Results are shown in Tables B-19 and B-20.

Table B-19. Cadmium recovery from glass for ^{111}Cd.

level	mass spiked (µg)	sample recovery (%) 1	2	3	4	5	6	mean rec (%)
PEL	2.5	83.2	82.5	86.0	82.8	91.5	89.1	85.9
action level	1.25	88.8	84.3	89.9	88.4	87.6	86.4	87.6

Table B-20. Cadmium recovery from glass for ^{114}Cd.

level	mass spiked (µg)	sample recovery (%) 1	2	3	4	5	6	mean rec (%)
PEL	2.5	88.0	83.0	90.4	87.8	87.6	87.7	87.4
action level	1.25	83.0	83.1	86.2	83.4	91.6	89.2	86.1

12 Estimation of Uncertainty

Estimation of uncertainty was not performed. Instead the overall standard error of estimate was calculated from the ambient storage test as prescribed by the OSHA validation guidelines[2].

13 Sampler Testing Procedure

A test atmosphere was not generated.

OSHA 5003, Appendix C
Lead

Version:	1.0
OSHA PEL:	50 µg/m^3 TWA, 30 µg/m^3 action level Note: Lead has an expanded standard requiring biological monitoring and/or medical examinations (29 CFR 1910.1025 and 29 CFR 1926.62).
ACGIH TLV:	50 µg/m^3
Recommended sampling time and sampling rate:	240 min at 2.0 L/min (480 L)
Reliable quantitation limit:	2.40×10^{-1} µg/m^3 (^{206}Pb) 1.90×10^{-1} µg/m^3 (^{207}Pb) 2.25×10^{-1} µg/m^3 (^{208}Pb)
Standard error of estimate:	5.04% (^{206}Pb, ^{207}Pb, and ^{208}Pb)
Status:	Fully validated. Method 5003 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of inorganic lead.

November 2019 Brian J. Albrecht & Tyler J. Erickson

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Lead

Particulate metals have been analyzed by a variety of methods throughout OSHA's history ranging from early methods that employed hot plate digestion techniques and flame atomic absorption (FAA) through more recently developed technologies such as microwave digestion techniques paired with inductively coupled plasma mass spectrometry (ICP-MS) instrumentation. In 2005, OSHA published Method 1006[1] which specified the use of an open vessel microwave digestion for sample preparation. While useful, the open vessel microwave digestion technique is inferior to the closed vessel microwave system because acids in a closed system can be heated higher than their boiling points enabling digestion of some metal compounds that would otherwise require the use of more caustic or higher boiling acids.

OSHA Method 5003 seeks to establish a routine metal digestion that can be used for lead and its compounds in a matrix that is useful for many metals and their compounds without the use of extremely caustic or high boiling acids such as perchloric acid and sulfuric acid. The acid matrix specified here is well suited for ICP-MS instrumentation.

1.2 Changes to the Previously-used Method

This method differs significantly from previously used methods. Changes to analytical conditions, and digestion acid volume have been made to allow standardized collection of lead with the other analytes found in the Metals Sampling Group 1, described in Method 5003. The detection limit of the analytical procedure (DLAP), detection limit of the overall procedure (DLOP), reliable quantitation limit (RQL), instrument response to lead, recovery, and stability of digested samples, storage stability, and reproducibility were all reevaluated.

[1] Giles, P. Arsenic, Cadmium, Cobalt, Copper, Lead, and Nickel (Open Vessel Microwave Digestion/ICP-MS Analysis) (OSHA 1006) 2005. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/mdt/mdt1006/1006.pdf (accessed November 2019).

1.3 Validation Parameters

Where applicable, this method follows validation protocols drawing from the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Spectroscopic Analysis".[2] These Guidelines detail required validation tests, show examples of statistical calculations, list validation acceptance criteria, and define analytical parameters. The target concentration for method evaluation was the analyte concentration equivalent to sampling for the recommended time at the OSHA time-weighted average (TWA) permissible exposure limit (PEL) for lead. Validation data were collected using a Thermo X-series 2 ICP-MS instrument, with collision cell technology (CCT) and a Fisher Scientific "Y" fitting (Part no. NC9380620). Samples were prepared with a CEM Discover SP-D digestion microwave.

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure (DLAP)

The DLAP is measured as the concentration of analyte that produces a response significantly greater than a reagent blank. Ten analytical standards were prepared with approximately equal descending increments of analyte such that the highest standard concentration would produce a peak approximately 10 times the response of a blank at the mass to charge ratio of the analyte. These standards and a reagent blank were analyzed with the analytical parameters. The data obtained were used to determine the required parameters (standard error of estimate ($S_{y/x}$) and slope) for the calculation of the DLAP. Results obtained for the blank and each standard are listed below in Tables C-1 through C-3 and are plotted in Figures C-1 through C-3.

Table C-1. DLAP data for ^{206}Pb.

concentration (µg/L)	response (counts/s)
0.000	39.000
0.100	123.334
0.200	224.003
0.300	440.012
0.400	578.687
0.500	771.703
0.600	993.060
0.700	1337.442
0.800	1490.134
0.900	1913.554
1.000	2054.922

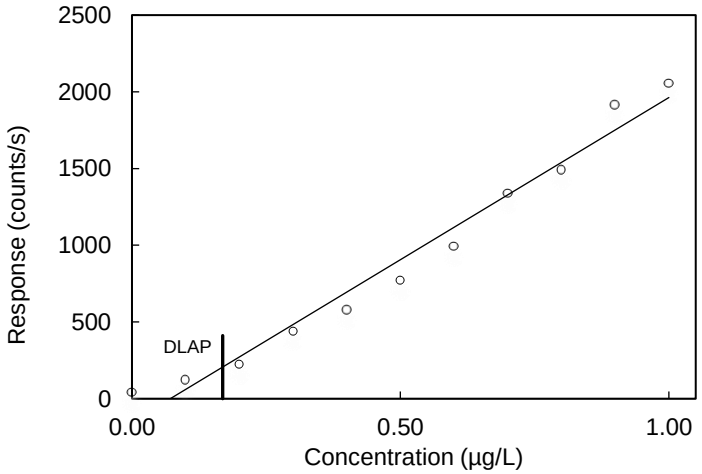

Figure C-1. Plot of data used to determine the DLAP for lead at ^{206}Pb ($y = 2.11 \times 10^3 x - 1.51 \times 10^2$, $S_{y/x} = 1.19 \times 10^2$, DLAP $= 1.69 \times 10^{-1}$ µg/L).

[2] Eide, M.; Giles, P.; Simmons, M.; Hendricks, W. Evaluation Guidelines for Air Sampling Methods Utilizing Spectroscopic Analysis, 2005. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/spectroguide/spectroguide.pdf (accessed November 2019).

Table C-2. DLAP data for ^{207}Pb.

concentration (µg/L)	response (counts/s)
0.000	28.333
0.100	115.001
0.200	181.335
0.300	373.008
0.400	522.350
0.500	654.026
0.600	882.381
0.700	1133.079
0.800	1305.436
0.900	1689.506
1.000	1833.536

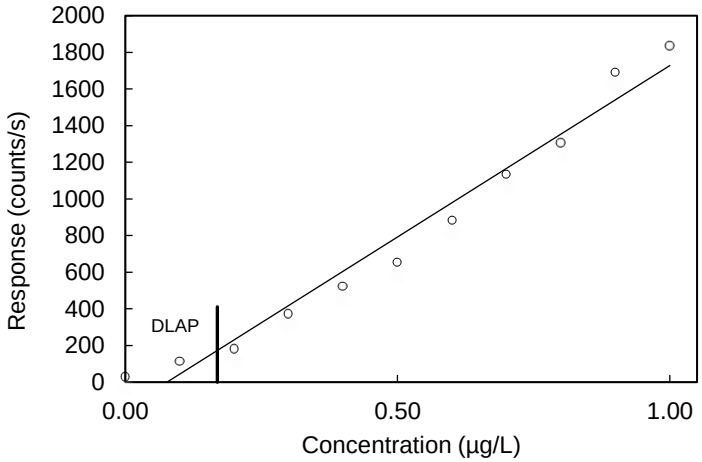

Figure C-2. Plot of data used to determine the DLAP for lead at ^{207}Pb ($y = 1.87 \times 10^{3}x - 1.43 \times 10^{2}$, $S_{y/x} = 1.11 \times 10^{2}$, DLAP $= 1.78 \times 10^{-1}$ µg/L).

Table C-3. DLAP data for ^{208}Pb.

concentration (µg/L)	response (counts/s)
0.000	66.667
0.100	266.671
0.200	458.013
0.300	899.049
0.400	1205.755
0.500	1567.817
0.600	2107.603
0.700	2708.447
0.800	3186.281
0.900	3985.292
1.000	4355.144

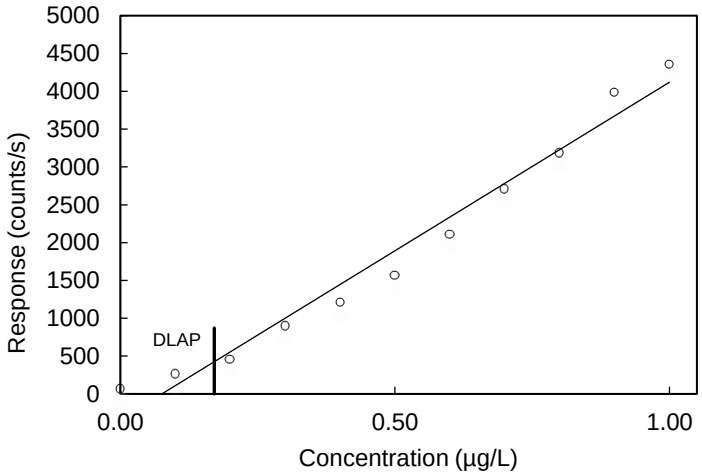

Figure C-3. Plot of data used to determine the DLAP for lead at ^{208}Pb ($y = 4.46 \times 10^{3}x - 3.37 \times 10^{2}$, $S_{y/x} = 2.54 \times 10^{2}$, DLAP $= 1.71 \times 10^{-1}$ µg/L).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is measured as mass per sample that produces a response significantly different than a sample blank. The RQL is the lowest level of analyte mass per sample for precise quantitative measurements and expressed as an air concentration based on the recommended sampling parameters. Ten samplers were spiked with approximately equal descending increments of analyte, such that the highest sampler loading would produce a peak approximately 10 times the response of a sample blank at the mass to charge ratio of the analyte. These spiked samplers and a sample blank were analyzed with the analytical parameters. The data obtained were used to calculate the required parameters ($S_{y/x}$ and the slope) for the calculation of the DLOP and RQL. Results obtained for the sample blank and the ten spiked samplers are listed below in Tables C-4 through C-6 and plotted in Figures C-4 through C-6.

Table C-4. DLOP and RQL data for ^{206}Pb.

concentratio (µg/sample)	response (counts/s)
0.0000	501.682
0.0500	638.024
0.1000	947.721
0.1500	1199.420
0.2000	1518.472
0.2500	1799.195
0.3000	2151.945
0.3500	2487.038
0.4000	2599.072
0.4500	3040.221
0.5000	3305.322

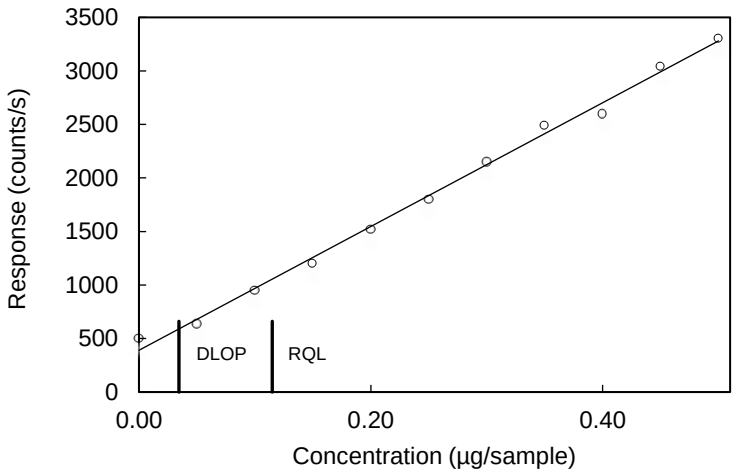

Figure C-4. Plot of data used to determine the DLOP and RQL for lead at ^{206}Pb ($y = 5.78 \times 10^{3}x + 3.90 \times 10^{2}$, $S_{y/x} = 6.65 \times 10^{1}$, DLOP $= 3.45 \times 10^{-2}$ µg/sample, RQL $= 1.15 \times 10^{-1}$ µg/sample (2.40×10^{-1} µg/m^3)).

Table C-5. DLOP and RQL data for ^{207}Pb.

concentratio (µg/sample)	response (counts/s)
0.0000	398.676
0.0500	540.684
0.1000	839.042
0.1500	1059.734
0.2000	1325.439
0.2500	1614.823
0.3000	1916.220
0.3500	2108.267
0.4000	2326.992
0.4500	2700.438
0.5000	2862.492

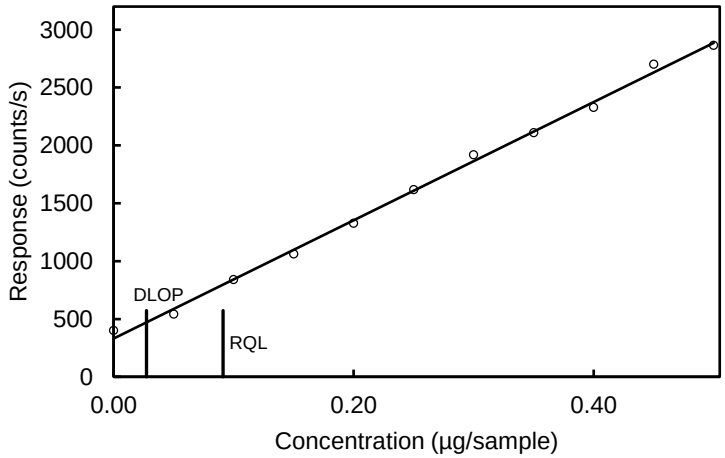

Figure C-5. Plot of data used to determine the DLOP and RQL for lead at ^{207}Pb ($y = 5.11 \times 10^{3}x + 3.31 \times 10^{2}$, $S_{y/x} = 4.66 \times 10^{1}$, DLOP $= 2.74 \times 10^{-2}$ µg/sample, RQL $= 9.12 \times 10^{-2}$ µg/sample (1.90×10^{-1} µg/m^3)).

Table C-6. DLOP and RQL data for ^{208}Pb.

concentratio (µg/sample)	response (counts/s)
0.0000	1019.729
0.0500	1347.442
0.1000	1974.234
0.1500	2574.731
0.2000	3191.945
0.2500	3786.193
0.3000	4557.913
0.3500	4995.831
0.4000	5613.557
0.4500	6564.251
0.5000	6870.164

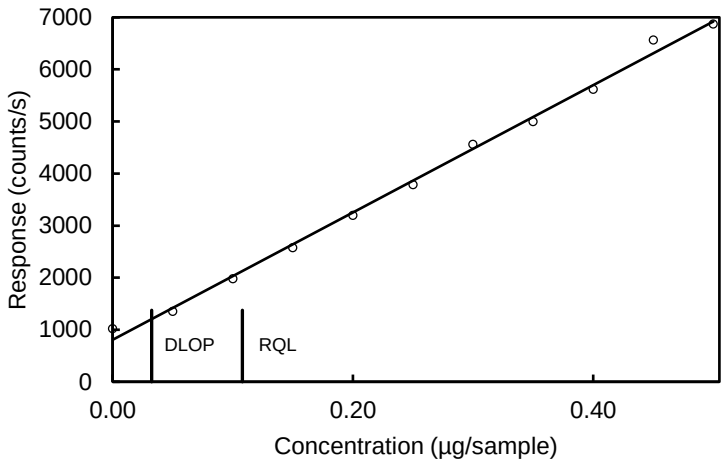

Figure C-6. Plot of data used to determine the DLOP and RQL for lead at ^{208}Pb ($y = 1.22 \times 10^{4}x + 8.07 \times 10^{2}$, $S_{y/x} = 1.32 \times 10^{2}$, DLOP $= 3.25 \times 10^{-2}$ µg/sample, RQL $= 1.08 \times 10^{-1}$ µg/sample (2.25×10^{-1} µg/m^3)).

3 Analytical Calibration

Fifteen analytical standards over a range of 0.05 to 2.0× the target concentration were prepared and analyzed with the analytical parameters. A least-squares linear regression curve was constructed by plotting the analyte mass per sample versus the internal standard (ISTD)-corrected analyte peak area. The data obtained were used to calculate the analytical calibration precision ($S_{y/x}$). Results are listed below in Tables C-7 through C-9 and plotted in Figures C-7 through C-9.

Table C-7. Analytical precision data for ^{206}Pb.

× target (µg/L)	0.05× 2.5	0.5× 25	1.0× 50	1.5× 75	2.0× 100
response	4086	40444	81822	122731	164270
(corrected	4212	41685	83116	124609	166147
counts/s)	4146	41889	83550	125599	168235

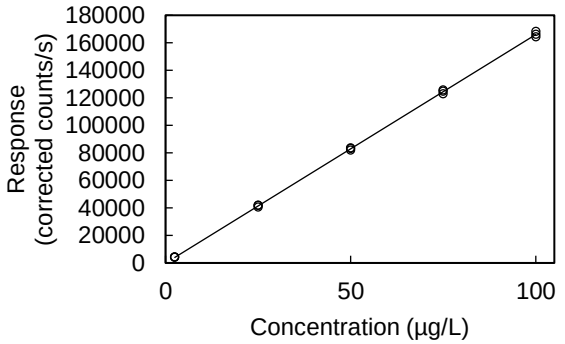

Figure C-7. Plot of the data used to estimate precision of the analytical method for ^{206}Pb ($y = 1.66 \times 10^{3}x - 1.49 \times 10^{2}$, $S_{y/x} = 1.08 \times 10^{3}$).

Table C-8. Analytical precision data for ^{207}Pb.

× target (µg/L)	0.05× 2.5	0.5× 25	1.0× 50	1.5× 75	2.0× 100
response	3525	35704	72091	108153	145202
(corrected	3643	36561	73285	109895	145888
counts/s)	3720	36851	73383	110539	149352

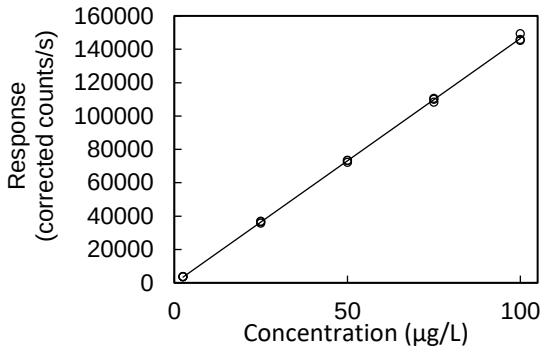

Figure C-8. Plot of the data used to estimate precision of the analytical method for ^{207}Pb ($y = 1.47 \times 10^3 x - 2.58 \times 10^2$, $S_{y/x} = 1.09 \times 10^3$).

Table C-9. Analytical precision data for ^{208}Pb.

× target (µg/L)	0.05× 2.5	0.5× 25	1.0× 50	1.5× 75	2.0× 100
response	8482	84533	17181	258756	344295
(corrected	8877	87022	17389	261608	348787
counts/s)	8861	87443	17519	262265	353908

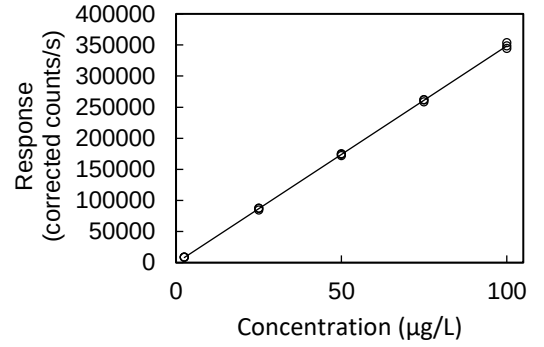

Figure C-9. Plot of the data used to estimate precision of the analytical method for ^{208}Pb ($y = 3.49 \times 10^3 x - 5.42 \times 10^2$, $S_{y/x} = 2.27 \times 10^3$).

4 Sampler Storage Stability

The results for lead used for the sampler storage stability section represent a mathematically calculated result obtained from analytical software. Each result accounts for the sum of all three *m/z* ratios (^{206}Pb, ^{207}Pb, and ^{208}Pb).

Thirty-six samples were prepared by direct spiking, eighteen at the PEL (24 µg/sample) and eighteen at action level (12 µg/sample). The samplers were stored at ambient temperature (about 24 °C). Three samples were selected from each of the two storage sets and analyzed at the intervals noted in Table C-10. Sample results were not corrected for digestion efficiency. Results obtained for the PEL and action level storage tests are listed below in Table C-10. Results are plotted in Figures C-10 and C-11.

Table C-10. Sampler storage stability data for lead.

time (days)	PEL storage recovery (%)			action level storage recovery (%)		
0	96.7	98.0	96.7	96.8	98.0	97.0
3	97.1	98.0	96.8	98.3	97.6	96.3
8	97.8	99.0	98.4	98.1	97.5	96.6
11	98.8	98.8	99.2	98.7	97.8	99.0
15	98.1	98.6	98.2	97.3	98.1	100.3
18	99.2	100.3	99.6	98.5	99.4	99.7

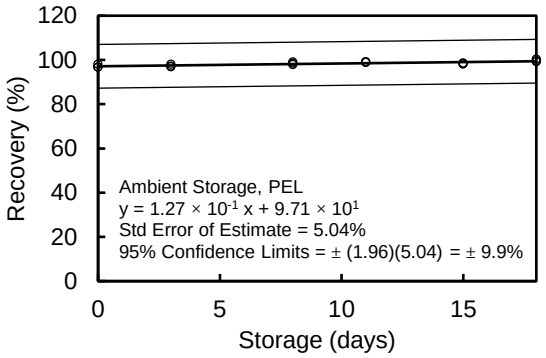

Figure C-10. Plot of storage stability data for lead at the PEL.

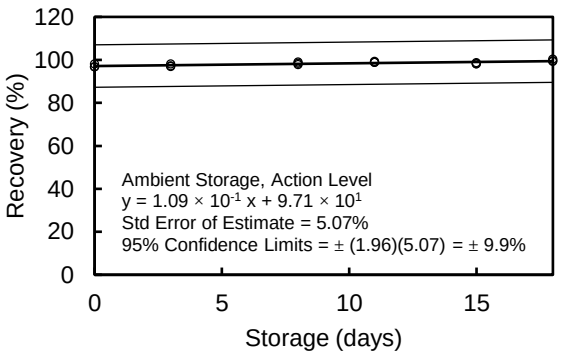

Figure C-11. Plot of storage stability data for lead at the action level.

5 Precision

The precision of the overall procedure at the 95% confidence level is obtained by multiplying the overall standard error of estimate by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). This provides ninety-five percent confidence intervals which are drawn about the regression lines in the storage stability figures shown in Section 4.

The precision of the overall procedure at the 95% confidence level for the ambient temperature 18-day storage test (at the PEL concentration) is ± 9.9%. The precision of the overall procedure at the 95% confidence level for the ambient temperature 18-day storage test (at the action level concentration) is ± 9.9%. These data were obtained from the overall standard errors of estimate (5.04% and 5.07%) derived from the data shown in Figures C-10 and C-11, with an additional 5% added for sampling pump error.

The recovery of lead from samples used in the 18-day storage test at the PEL was 99.4% when samples were stored at ambient temperature. The recovery of lead from samples used in the storage test at the action level was 99.1% when samples were stored at ambient temperature.

6 Recovery and Stability of Prepared Samples

6.1 Soluble Forms

Quantitative digestion is affected by the acid matrix, the sampling medium, and the technique used to digest the samples. For the use of reagents and techniques other than those described here, testing specified in current OSHA evaluation guidelines must be completed.

A value for digestion efficiency (D_E) was determined by liquid-spiking four MCE filters at a range of analyte concentrations equivalent to sampling at 0.05 to 2 times the target concentration value for 4 hours. For a single set of filters spiked with analyte equivalent to sampling at the 1.0× target concentration value for 4 hours, humid air (79.3% relative humidity at 23.2 °C) was passed through the filters for 240 min at 2 L/min prior to spiking. Another set of filters was spiked at the RQL level. The spiked samples were stored overnight at ambient temperature and then analyzed. An overall mean D_E value of 98.3% was obtained across the analyte concentration range studied for ^{206}Pb, ^{207}Pb, and ^{208}Pb. The results of these tests, along with the D_E values at the RQL, are provided in Tables C-11 through C-13, and they demonstrate that the presence of water on the filter had no significant effect on D_E. The D_E values for the RQL and wet sampler testing were not included in the overall mean.

Table C-11. Digestion efficiency data for ^{206}Pb.

level		sample recovery (%)				
× target concn	µg per sample	1	2	3	4	mean rec (%)
0.05	1.25	100.5	98.0	96.9	98.1	98.4
0.5	12.5	98.4	98.6	99.6	99.3	99.0
1.0	25.0	97.6	98.2	97.1	98.2	97.8
1.5	37.5	98.4	96.7	99.4	98.5	98.3
2.0	50.0	98.2	97.7	98.5	98.8	98.3
RQL	0.125	109.6	107.4	100.7	99.8	104.4
1.0 (wet)	25.0	101.3	101.5	100.5	102.4	101.4

Table C-12. Digestion efficiency date for ^{207}Pb.

level		sample recovery (%)				
× target concn	µg per sample	1	2	3	4	mean rec (%)
0.05	1.25	99.8	97.1	96.9	99.2	98.3
0.5	12.5	98.6	99.0	98.7	98.9	98.8
1.0	25.0	97.9	98.8	97.0	98.4	98.0
1.5	37.5	98.1	96.5	99.3	98.5	98.1
2.0	50.0	97.9	97.6	98.6	98.8	98.2
RQL	0.125	111.8	105.6	100.4	103.4	105.3
1.0 (wet)	25.0	98.1	98.0	97.6	99.2	98.2

Table C-13. Digestion efficiency data for ^{208}Pb.

level		sample recovery (%)				
× target concn	µg per sample	1	2	3	4	mean rec (%)
0.05	1.25	99.2	97.1	97.3	99.2	98.2
0.5	12.5	99.0	98.4	99.2	99.3	99.0
1.0	25.0	98.4	98.9	97.2	98.5	98.3
1.5	37.5	98.2	95.8	98.8	98.2	97.8
2.0	50.0	97.9	97.6	98.3	98.6	98.1
RQL	0.125	107.6	106.9	99.8	98.2	103.1
1.0 (wet)	25.0	99.7	99.8	99.1	100.8	99.9

Based on available solubility data[3] for hot water, it is assumed that the following lead compounds will solubilize in the acid matrix at concentrations of twice the PEL: lead citrate, lead ethylsulfate, lead fluorosilicate, lead lactate, lead nitrite, lead phenolsulfonate, lead peroxydisulfate, lead perchlorate, lead chlorate, lead dithionate, lead acetate, lead nitrate, lead isobutyrate, lead formate, lead chloride, lead bromate, lead picrate, lead bromide, lead monoiodide, lead chlorite, lead fluoride, lead thiocyanate, lead fluorochloride, lead diiodide, lead thiosulfate, lead azide, lead stearate, lead hydroxide, lead oxychloride, lead laurate, lead myristate, lead tartrate, lead palmitate, and lead iodate.

6.2 Insoluble Forms

Digestion efficiencies of selected insoluble lead compounds were tested due to their likely presence in work environments or industrial importance. Efficiencies were determined by digesting and analyzing a known amount of each compound material in triplicate. The compounds tested were measured by mass onto a tared MCE filter and then

[3] *The Merck Index*; 14th ed.; O'Neil, M., Ed.; Merck & Co. Inc.: Whitehouse Station, NJ, 2006 pp 936-939.

prepared and analyzed. The compounds and data obtained are shown in Table C-14.

Table C-14. Digestion efficiency of lead from selected lead compounds.

compound	level						% recovery by sample			mean
	total mass (µg)			Pb mass (µg)			1	2	3	rec (%)
lead (metal)	474	308	368	474	308	368	103.2	106.0	106.9	105.4
lead sulfide	619	561	420	537	486	364	103.1	102.9	102.1	102.7
lead chromate	412	570	436	264	366	280	104.1	96.4	109.2	103.2
lead molybdate	295	652	402	166	368	227	108.5	105.1	106.6	106.7
lead dioxide	600	720	687	520	624	595	106.8	105.3	93.5	101.9
lead telluride	372	355	480	230	220	297	107.5	101.2	108.6	105.8

6.3 Digestion Efficiency of Smear Tabs

The digestion efficiency of soluble lead from liquid-spiked smear tabs was determined at the PEL and action level (25 and 12.5 µg/sample), as well as at the RQL (0.125 µg/sample). Liquid was spiked directly onto the four smear tabs and allowed to dry at ambient temperature. A liquid solution was also prepared at a concentration corresponding to each level of the test samples; these solutions were diluted from a lead solution and were not digested. Each corresponding liquid solution, used for reference, was analyzed 3 times on the same day as the samples. The mean result of each corresponding solution was used to apply a correction to the corresponding sample results. Results in Tables C-15 through C-17 reflect the corrected recoveries of the samples.

Table C-15. Corrected lead recovery from smear tabs for ^{206}Pb.

level	mass spiked (µg)	sample recovery (%) 1	2	3	4	mean rec (%)
PEL	25	100.3	100.3	100.8	100.8	100.6
action level	12.5	98.6	100.2	100.6	99.6	99.8
RQL	0.125	108.1	107.8	108.5	106.1	107.6

Table C-16. Corrected lead recovery from smear tabs for ^{207}Pb.

level	mass spiked (µg)	sample recovery (%) 1	2	3	4	mean rec (%)
PEL	25	100.8	100.4	100.8	100.5	100.6
action level	12.5	99.0	100.6	100.6	100.1	100.1
RQL	0.125	106.2	106.9	107.3	109.7	107.5

Table C-17. Corrected lead recovery from smear tabs for ^{208}Pb.

level	mass spiked (µg)	sample recovery (%) 1	2	3	4	mean rec (%)
PEL	25	100.1	100.3	100.8	100.9	100.5
action level	12.5	99.2	100.8	100.5	100.2	100.2
RQL	0.125	107.6	107.0	105.4	106.3	106.6

6.4 Stability of Digested Samples

The stability of digested samples was examined by reanalyzing the 1.0× target concentration samples 24, 48, and 72 hours after the initial analysis. After the original analysis was performed two vials and their contents were discarded and replaced by freshly diluted aliquots from a closed polypropylene container for each reanalysis event. The other two vials remained in the auto-sampler tray at ambient conditions throughout the duration of the test. Sample digestates were stored at room temperature. Freshly prepared standards were used for each reanalysis event. Results calculated

from instrument calibration curves similar to the calibration curve presented in section 3 are listed in Table C-18 through C-20.

Table C-18. Digested sample stability data for ^{206}Pb.

	fresh dilution recovery (%)		exposed diluted sample recovery (%)	
time (days)	1	2	1	2
0	99.8	101.0	101.4	101.3
1	98.2	98.7	102.3	101.5
2	98.5	101.2	104.6	103.7
3	100.5	100.7	105.2	105.7

Table C-19. Digested sample stability data for ^{207}Pb.

	fresh dilution recovery (%)		exposed diluted sample recovery (%)	
time (days)	1	2	1	2
0	99.1	100.4	101.3	101.0
1	98.1	99.8	102.5	100.8
2	98.3	101.1	104.4	102.3
3	100.4	100.2	105.2	105.6

Table C-20. Digested sample stability data for ^{208}Pb.

	fresh dilution recovery (%)		exposed diluted sample recovery (%)	
time (days)	1	2	1	2
0	99.4	100.9	101.2	101.3
1	98.1	99.1	102.4	100.5
2	98.7	101.2	104.5	102.5
3	100.3	100.4	105.1	105.8

7 Sampler Capacity

Because a test atmosphere was not generated a full sampler capacity study could not be performed. Instead a retention efficiency study was performed. The retention efficiency of an MCE filter was tested by spiking six filters at twice the PEL equivalent (50 µg). After drying, the filters were each placed in a two-piece cassette with the ends plugged, equipped with a support pad under the filter. Three of the filter cassettes were set aside and used as controls, with no air pulled through these cassettes. Air with approximately 74.9% relative humidity, at 22.3 °C, was drawn through three of the samplers, each lined up with a blank (un-spiked) sampler placed downstream, for 240 minutes at 2 L/min. No analyte was detected on any of the blanks. The mean recoveries for the three test filters were 99.4, 96.8, and 98.4% for ^{206}Pb, ^{207}Pb, and ^{208}Pb respectively. The mean recoveries for the three control filters, through which air was not drawn, were 99.2, 96.4, and 98.0% for ^{206}Pb, ^{207}Pb, and ^{208}Pb respectively.

8 Low Humidity

A low humidity recovery test was not performed.

9 Interferences

A sampling interference study was not performed.

10 Reproducibility

The results for lead used for the reproducibility section represent a mathematically calculated result obtained from analytical software. Each result accounts for the sum of all three *m/z* ratios (^{206}Pb, ^{207}Pb, and ^{208}Pb).

Reproducibility was determined by preparing and analyzing 6 MCE filters each at the PEL and action level (24, and 12 µg/sample). The samples were analyzed 16 days after preparation. Sample results were not corrected for digestion efficiency. No sample result for lead had a deviation greater than the precision of the overall procedure determined in Section 5. The data are presented in Tables C-21 and C-22.

Table C-21. Reproducibility for lead at the PEL.

theoretical (µg/sample)	result (µg/sample)	recovery (%)	deviation (%)
24.0	23.085	96.2	-3.8
24.0	23.575	98.2	-1.8
24.0	23.225	96.8	-3.2
24.0	23.245	96.9	-3.1
24.0	23.460	97.8	-2.2
24.0	22.865	95.3	-4.7

Table C-22. Reproducibility for lead at the action level.

theoretical (µg/sample)	result (µg/sample)	recovery (%)	deviation (%)
12.0	11.260	93.8	-6.2
12.0	11.610	96.8	-3.2
12.0	11.630	96.9	-3.1
12.0	11.445	95.4	-4.6
12.0	11.640	97.0	-3.0
12.0	11.545	96.2	-3.8

11 Additional Testing

11.1 Recovery from Wiping Cassette Interior

Recovery of soluble lead from a cassette was determined by spiking 4 cassettes each at the PEL and action level (25 and 12.5 µg/sample). Liquid was spiked onto the interior surface of a top cassette piece, allowed to dry at ambient temperature, and then wiped with a damp MCE filter. The data obtained are shown in Tables C-23 through C-25.

Table C-23. Lead recovery from cassettes for ^{206}Pb.

level	mass spiked (µg)	sample recovery (%) 1	2	3	4	mean rec (%)
PEL	25	95.8	95.2	95.7	88.0	93.7
action level	12.5	88.8	90.4	87.5	87.8	88.6

Table C-24. Lead recovery from cassettes for ^{207}Pb.

level	mass spiked (µg)	sample recovery (%) 1	2	3	4	mean rec (%)
PEL	25	93.0	92.6	93.0	85.3	91.0
action level	12.5	86.2	88.2	85.0	85.2	86.2

Table C-25. Lead recovery from cassettes for ^{208}Pb.

level	mass spiked (µg)	sample recovery (%) 1	2	3	4	mean rec (%)
PEL	25	94.3	93.9	94.2	86.4	92.2
action level	12.5	87.0	88.9	85.9	86.0	87.0

11.2 Smear Tab Wipe Sampling Efficiency

Wipe efficiency was tested on twelve glass surface areas. Each area measured 10 cm by 10 cm square. A liquid solution was spiked at 25 and 12.5 µg/sample, in a spiral pattern of droplets, onto each surface and allowed to dry overnight at ambient temperature. Each surface area was wiped in an up-and-down pattern with a damp smear tab. The smear tab was folded in half, keeping the wiped side folded together, and then used to wipe the same area in a side-to-side pattern. Results are shown in Tables C-26 through C-28.

Table C-26. Lead recovery from glass for ^{206}Pb.

level	mass spiked (µg)	sample recovery (%)						mean rec (%)
		1	2	3	4	5	6	
PEL	25	83.6	84.9	86.4	84.1	91.5	89.2	86.6
action level	12.5	89.4	85.8	92.0	88.9	88.0	88.1	88.7

Table C-27. Lead recovery from glass for ^{207}Pb.

level	mass spiked (µg)	sample recovery (%)						mean rec (%)
		1	2	3	4	5	6	
PEL	25	81.7	82.5	84.0	81.9	89.2	87.1	84.4
action level	12.5	86.7	83.1	88.6	86.2	86.1	85.8	86.1

Table C-28. Lead recovery from glass for ^{208}Pb.

level	mass spiked (µg)	sample recovery (%)						mean rec (%)
		1	2	3	4	5	6	
PEL	25	82.4	83.3	85.0	82.8	90.2	88.1	85.3
action level	12.5	87.8	84.3	89.9	87.2	86.8	86.8	87.1

12 Estimation of Uncertainty

Estimation of uncertainty was not performed. Instead the overall standard error of estimate was calculated from the ambient storage test as prescribed by the OSHA validation guidelines[2].

13 Sampler Testing Procedure

A test atmosphere was not generated.