



Occupational Safety and Health Administration

- **Part Number:** 1910
Part Number
 - **Title:** Occupational Safety and Health Standards
 - **Subpart:** 1910 Subpart Z
 - **Subpart Title:** Toxic and Hazardous Substances
Standard
 - **Number:** 1910.1027 App E
 - **Title:** Cadmium in Workplace Atmospheres
 - **GPO Source:** e-CFR
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Appendix E to § 1910.1027 - Cadmium in Workplace Atmospheres

Method Number: ID-189

Matrix: Air

OSHA Permissible Exposure Limits: 5 $\mu\text{g}/\text{m}^3$ (TWA), 2.5 $\mu\text{g}/\text{m}^3$ (Action Level TWA)

Collection Procedure: A known volume of air is drawn through a 37-mm diameter filter cassette containing a 0.8- μm mixed cellulose ester membrane filter (MCEF).

Recommended Air Volume: 960 L

Recommended Sampling Rate: 2.0 L/min

Analytical Procedure: Air filter samples are digested with nitric acid. After digestion, a small amount of hydrochloric acid is added. The samples are then diluted to volume with deionized water and analyzed by either flame atomic absorption spectroscopy (AAS) or flameless atomic absorption spectroscopy using a heated graphite furnace atomizer (AAS-HGA).

Detection Limits:

Qualitative: 0.2 $\mu\text{g}/\text{m}^3$ for a 200 L sample by Flame AAS, 0.007 $\mu\text{g}/\text{m}^3$ for a 60 L sample by AAS-HGA

Quantitative: 0.70 $\mu\text{g}/\text{m}^3$ for a 200 L sample by Flame AAS, 0.025 $\mu\text{g}/\text{m}^3$ for a 60 L sample by AAS-HGA

Precision and Accuracy: (Flame AAS Analysis and AAS-HGA Analysis):

Validation Level: 2.5 to 10 $\mu\text{g}/\text{m}^3$ for a 400 L air vol, 1.25 to 5.0 $\mu\text{g}/\text{m}^3$ for a 60 L air vol

CV₁ (pooled): 0.010, 0.043

Analytical Bias: + 4.0%, -5.8%

Overall Analytical Error: $\pm 6.0\%$, $\pm 14.2\%$

Method Classification: Validated

Date: June, 1992

Inorganic Service Branch II, OSHA Salt Lake Technical Center, Salt Lake City, Utah

Commercial manufacturers and products mentioned in this method are for descriptive use only and do not constitute endorsements by USDOL-OSHA. Similar products from other sources can be substituted.

1. Introduction

1.1. Scope

This method describes the collection of airborne elemental cadmium and cadmium compounds on 0.8- μm mixed cellulose ester membrane filters and their subsequent analysis by either flame atomic absorption spectroscopy (AAS) or flameless atomic absorption spectroscopy using a heated graphite furnace atomizer (AAS-HGA). It is applicable for both TWA and Action Level TWA Permissible Exposure Level (PEL) measurements. The two atomic absorption analytical techniques included in the method do not differentiate between cadmium fume and cadmium dust samples. They also do not differentiate between elemental cadmium and its compounds.

1.2. Principle

Airborne elemental cadmium and cadmium compounds are collected on a 0.8- μm mixed cellulose ester membrane filter (MCEF). The air filter samples are digested with concentrated nitric acid to destroy the organic matrix and dissolve the cadmium analytes. After digestion, a small amount of concentrated hydrochloric acid is added to help dissolve other metals which may be present. The samples are diluted to volume with deionized water and then aspirated into the oxidizing air/acetylene flame of an atomic absorption spectrophotometer for analysis of elemental cadmium. If the concentration of cadmium in a sample solution is too low for quantitation by this flame AAS analytical technique, and the sample is to be averaged with other samples for TWA calculations, aliquots of the sample and a matrix modifier are later injected onto a L'vov platform in a pyrolytically-coated graphite tube of a Zeeman atomic absorption

spectrophotometer/graphite furnace assembly for analysis of elemental cadmium. The matrix modifier is added to stabilize the cadmium metal and minimize sodium chloride as an interference during the high temperature charring step of the analysis (5.1., 5.2.).

1.3. History

Previously, two OSHA sampling and analytical methods for cadmium were used concurrently (5.3., 5.4.). Both of these methods also required 0.8- μ m mixed cellulose ester membrane filters for the collection of air samples. These cadmium air filter samples were analyzed by either flame atomic absorption spectroscopy (5.3.) or inductively coupled plasma/atomic emission spectroscopy (ICP-AES) (5.4.). Neither of these two analytical methods have adequate sensitivity for measuring workplace exposure to airborne cadmium at the new lower TWA and Action Level TWA PEL levels when consecutive samples are taken on one employee and the sample results need to be averaged with other samples to determine a single TWA.

The inclusion of two atomic absorption analytical techniques in the new sampling and analysis method for airborne cadmium permits quantitation of sample results over a broad range of exposure levels and sampling periods. The flame AAS analytical technique included in this method is similar to the previous procedure given in the General Metals Method ID-121 (5.3.) with some modifications. The sensitivity of the AAS-HGA analytical technique included in this method is adequate to measure exposure levels at $\frac{1}{10}$ the Action Level TWA, or lower, when less than full-shift samples need to be averaged together.

1.4. Properties (5.5.)

Elemental cadmium is a silver-white, blue-tinged, lustrous metal which is easily cut with a knife. It is slowly oxidized by moist air to form cadmium oxide. It is insoluble in water, but reacts readily with dilute nitric acid. Some of the physical properties and other descriptive information of elemental cadmium are given below:

CAS No.	7440-43-9
Atomic Number	48
Atomic Symbol	Cd
Atomic Weight	112.41
Melting Point	321 °C
Boiling Point	765 °C
Density	8.65 g/mL (25 °C)

The properties of specific cadmium compounds are described in reference 5.5.

1.5. Method Performance

A synopsis of method performance is presented below. Further information can be found in Section 4.

1.5.1. The qualitative and quantitative detection limits for the flame AAS analytical technique are 0.04 μg (0.004 $\mu\text{g}/\text{mL}$) and 0.14 μg (0.014 $\mu\text{g}/\text{mL}$) cadmium, respectively, for a 10 mL solution volume. These correspond, respectively, to 0.2 $\mu\text{g}/\text{m}^3$ and 0.70 $\mu\text{g}/\text{m}^3$ for a 200 L air volume.

1.5.2. The qualitative and quantitative detection limits for the AAS-HGA analytical technique are 0.44 ng (0.044 ng/mL) and 1.5 ng (0.15 ng/mL) cadmium, respectively, for a 10 mL solution volume. These correspond, respectively, to 0.007 $\mu\text{g}/\text{m}^3$ and 0.025 $\mu\text{g}/\text{m}^3$ for a 60 L air volume.

1.5.3. The average recovery by the flame AAS analytical technique of 17 spiked MCEF samples containing cadmium in the range of 0.5 to 2.0 times the TWA target concentration of 5 $\mu\text{g}/\text{m}^3$ (assuming a 400 L air volume) was 104.0% with a pooled coefficient of variation (CV_1) of 0.010. The flame analytical technique exhibited a positive bias of + 4.0% for the validated concentration range. The overall analytical error (OAE) for the flame AAS analytical technique was $\pm 6.0\%$.

1.5.4. The average recovery by the AAS-HGA analytical technique of 18 spiked MCEF samples containing cadmium in the range of 0.5 to 2.0 times the Action Level TWA target concentration of 2.5 $\mu\text{g}/\text{m}^3$ (assuming a 60 L air volume) was 94.2% with a pooled coefficient of variation (CV_1) of 0.043. The AAS-HGA analytical technique exhibited a negative bias of -5.8% for the validated concentration range. The overall analytical error (OAE) for the AAS-HGA analytical technique was $\pm 14.2\%$.

1.5.5. Sensitivity in flame atomic absorption is defined as the characteristic concentration of an element required to produce a signal of 1% absorbance (0.0044 absorbance units). Sensitivity values are listed for each element by the atomic absorption spectrophotometer manufacturer and have proved to be a very valuable diagnostic tool to determine if instrumental parameters are optimized and if the instrument is performing up to specification. The sensitivity of the spectrophotometer used in the validation of the flame AAS analytical technique agreed with the manufacturer specifications (5.6.); the 2 $\mu\text{g}/\text{mL}$ cadmium standard gave an absorbance reading of 0.350 abs. units.

1.5.6. Sensitivity in graphite furnace atomic absorption is defined in terms of the characteristic mass, the number of picograms required to give an integrated absorbance value of 0.0044 absorbance-second (5.7.). Data suggests that under Stabilized Temperature Platform Furnace (STPF) conditions (see Section 1.6.2.), characteristic mass values are transferable between properly functioning instruments to an accuracy of about 20% (5.2.). The characteristic mass for

STPF analysis of cadmium with Zeeman background correction listed by the manufacturer of the instrument used in the validation of the AAS-HGA analytical technique was 0.35 pg. The experimental characteristic mass value observed during the determination of the working range and detection limits of the AAS-HGA analytical technique was 0.41 pg.

1.6. Interferences

1.6.1. High concentrations of silicate interfere in determining cadmium by flame AAS (5.6.). However, silicates are not significantly soluble in the acid matrix used to prepare the samples.

1.6.2. Interferences, such as background absorption, are reduced to a minimum in the AAS-HGA analytical technique by taking full advantage of the Stabilized Temperature Platform Furnace (STPF) concept. STPF includes all of the following parameters (5.2.):

- a. Integrated Absorbance,
- b. Fast Instrument Electronics and Sampling Frequency,
- c. Background Correction,
- d. Maximum Power Heating, e. Atomization off the L'vov platform in a pyrolytically coated graphite tube,
- f. Gas Stop during Atomization,
- g. Use of Matrix Modifiers.

1.7. Toxicology (5.14.)

Information listed within this section is synopsis of current knowledge of the physiological effects of cadmium and is not intended to be used as the basis for OSHA policy. IARC classifies cadmium and certain of its compounds as Group 2A carcinogens (probably carcinogenic to humans). Cadmium fume is intensely irritating to the respiratory tract. Workplace exposure to cadmium can cause both chronic and acute effects. Acute effects include tracheobronchitis, pneumonitis, and pulmonary edema. Chronic effects include anemia, rhinitis/anosmia, pulmonary emphysema, proteinuria and lung cancer. The primary target organs for chronic disease are the kidneys (non-carcinogenic) and the lungs (carcinogenic).

2. Sampling

2.1. Apparatus

2.1.1. Filter cassette unit for air sampling: A 37-mm diameter mixed cellulose ester membrane filter with a pore size of 0.8- μ m contained in a 37-mm polystyrene two- or three-piece cassette filter holder (part no. MAWP 037 A0, Millipore Corp., Bedford, MA). The filter is supported with a

cellulose backup pad. The cassette is sealed prior to use with a shrinkable gel band.

2.1.2. A calibrated personal sampling pump whose flow is determined to an accuracy of $\pm 5\%$ at the recommended flow rate with the filter cassette unit in line.

2.2. Procedure

2.2.1. Attach the prepared cassette to the calibrated sampling pump (the backup pad should face the pump) using flexible tubing. Place the sampling device on the employee such that air is sampled from the breathing zone.

2.2.2. Collect air samples at a flow rate of 2.0 L/min. If the filter does not become overloaded, a full-shift (at least seven hours) sample is strongly recommended for TWA and Action Level TWA measurements with a maximum air volume of 960 L. If overloading occurs, collect consecutive air samples for shorter sampling periods to cover the full workshift.

2.2.3. Replace the end plugs into the filter cassettes immediately after sampling. Record the sampling conditions.

2.2.4. Securely wrap each sample filter cassette end-to-end with an OSHA Form 21 sample seal.

2.2.5. Submit at least one blank sample with each set of air samples. The blank sample should be handled the same as the other samples except that no air is drawn through it.

2.2.6. Ship the samples to the laboratory for analysis as soon as possible in a suitable container designed to prevent damage in transit.

3. Analysis

3.1. Safety Precautions

3.1.1. Wear safety glasses, protective clothing and gloves at all times.

3.1.2. Handle acid solutions with care. Handle all cadmium samples and solutions with extra care (see Sect. 1.7.). Avoid their direct contact with work area surfaces, eyes, skin and clothes. Flush acid solutions which contact the skin or eyes with copious amounts of water.

3.1.3. Perform all acid digestions and acid dilutions in an exhaust hood while wearing a face shield. To avoid exposure to acid vapors, do not remove beakers containing concentrated acid solutions from the exhaust hood until they have returned to room temperature and have been diluted or emptied.

3.1.4. Exercise care when using laboratory glassware. Do not use chipped pipets, volumetric flasks, beakers or any glassware with sharp edges exposed in order to avoid the possibility of cuts or abrasions.

3.1.5. Never pipet by mouth.

3.1.6. Refer to the instrument instruction manuals and SOPs (5.8., 5.9.) for proper and safe operation of the atomic absorption spectrophotometer, graphite furnace atomizer and associated equipment.

3.1.7. Because metallic elements and other toxic substances are vaporized during AAS flame or graphite furnace atomizer operation, it is imperative that an exhaust vent be used. Always ensure that the exhaust system is operating properly during instrument use.

3.2. Apparatus for Sample and Standard Preparation

3.2.1. Hot plate, capable of reaching 150 °C, installed in an exhaust hood.

3.2.2. Phillips beakers, 125 mL.

3.2.3. Bottles, narrow-mouth, polyethylene or glass with leakproof caps: used for storage of standards and matrix modifier.

3.2.4. Volumetric flasks, volumetric pipets, beakers and other associated general laboratory glassware.

3.2.5. Forceps and other associated general laboratory equipment.

3.3. Apparatus for Flame AAS Analysis

3.3.1. Atomic absorption spectrophotometer consisting of a(an):

Nebulizer and burner head

Pressure regulating devices capable of maintaining constant oxidant and fuel pressures

Optical system capable of isolating the desired wavelength of radiation (228.8 nm)

Adjustable slit

Light measuring and amplifying device

Display, strip chart, or computer interface for indicating the amount of absorbed radiation

Cadmium hollow cathode lamp or electrodeless discharge lamp (EDL) and power supply

3.3.2. Oxidant: compressed air, filtered to remove water, oil and other foreign substances.

3.3.3. Fuel: standard commercially available tanks of acetylene dissolved in acetone; tanks should be equipped with flash arresters.

CAUTION: Do not use grades of acetylene containing solvents other than acetone because they may damage the PVC tubing used in some instruments.

3.3.4. Pressure-reducing valves: two gauge, two-stage pressure regulators to maintain fuel and oxidant pressures somewhat higher than the controlled operating pressures of the instrument.

3.3.5. Exhaust vent installed directly above the spectrophotometer burner head.

3.4. Apparatus for AAS-HGA Analysis

3.4.1. Atomic absorption spectrophotometer consisting of a(an):

Heated graphite furnace atomizer (HGA) with argon purge system

Pressure-regulating devices capable of maintaining constant argon purge pressure

Optical system capable of isolating the desired wavelength of radiation (228.8 nm)

Adjustable slit

Light measuring and amplifying device

Display, strip chart, or computer interface for indicating the amount of absorbed radiation (as integrated absorbance, peak area)

Background corrector: Zeeman or deuterium arc. The Zeeman background corrector is recommended

Cadmium hollow cathode lamp or electrodeless discharge lamp (EDL) and power supply

Autosampler capable of accurately injecting 5 to 20 μL sample aliquots onto the L'vov Platform in a graphite tube

3.4.2. Pyrolytically coated graphite tubes containing solid, pyrolytic L'vov platforms.

3.4.3. Polyethylene sample cups, 2.0 to 2.5 mL, for use with the autosampler.

3.4.4. Inert purge gas for graphite furnace atomizer: compressed gas cylinder of purified argon.

3.4.5. Two gauge, two-stage pressure regulator for the argon gas cylinder.

3.4.6. Cooling water supply for graphite furnace atomizer.

3.4.7. Exhaust vent installed directly above the graphite furnace atomizer.

3.5. Reagents

All reagents should be ACS analytical reagent grade or better.

3.5.1. Deionized water with a specific conductance of less than 10 μS .

3.5.2. Concentrated nitric acid, HNO_3 .

3.5.3. Concentrated hydrochloric acid, HCl .

3.5.4. Ammonium phosphate, monobasic, $\text{NH}_4 \text{H}_2 \text{PO}_4$.

3.5.5. Magnesium nitrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2 \text{O}$.

3.5.6. Diluting solution (4% HNO_3 , 0.4% HCl): Add 40 mL HNO_3 and 4 mL HCl carefully to approximately 500 mL deionized water and dilute to 1 L with deionized water.

3.5.7. Cadmium standard stock solution, 1,000 $\mu\text{g}/\text{mL}$: Use a commercially available certified 1,000 $\mu\text{g}/\text{mL}$ cadmium standard or, alternatively, dissolve 1.0000 g of cadmium metal in a minimum volume of 1:1 HCl and dilute to 1 L with 4% HNO_3 . Observe expiration dates of commercial standards. Properly dispose of commercial standards with no expiration dates or prepared standards one year after their receipt or preparation date.

3.5.8. Matrix modifier for AAS-HGA analysis: Dissolve 1.0 g $\text{NH}_4 \text{H}_2 \text{PO}_4$ and 0.15 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2 \text{O}$ in approximately 200 mL deionized water. Add 1 mL HNO_3 and dilute to 500 mL with deionized water.

3.5.9 Nitric Acid, 1:1 $\text{HNO}_3/\text{DI H}_2 \text{O}$ mixture: Carefully add a measured volume of concentrated HNO_3 to an equal volume of $\text{DI H}_2 \text{O}$.

3.5.10. Nitric acid, 10% v/v: Carefully add 100 mL of concentrated HNO_3 to 500 mL of $\text{DI H}_2 \text{O}$ and dilute to 1 L.

3.6. Glassware Preparation

3.6.1. Clean Phillips beakers by refluxing with 1:1 nitric acid on a hot plate in a fume hood. Thoroughly rinse with deionized water and invert the beakers to allow them to drain dry.

3.6.2. Rinse volumetric flasks and all other glassware with 10% nitric acid and deionized water prior to use.

3.7. Standard Preparation for Flame AAS Analysis

3.7.1. Dilute stock solutions: Prepare 1, 5, 10 and 100 $\mu\text{g}/\text{mL}$ cadmium standard stock solutions by making appropriate serial dilutions of 1,000 $\mu\text{g}/\text{mL}$ cadmium standard stock solution with the diluting solution described in Section 3.5.6.

3.7.2. Working standards: Prepare cadmium working standards in the range of 0.02 to 2.0 µg/mL by making appropriate serial dilutions of the dilute stock solutions with the same diluting solution. A suggested method of preparation of the working standards is given below.

Working standard	Std solution	Aliquot	Final vol.
(µg/mL)	(µg/mL)	(mL)	(mL)
0.02	1	10	500
0.05	5	5	500
0.1	10	5	500
0.2	10	10	500
0.5	10	25	500
1	100	5	500
2	100	10	500

Store the working standards in 500-mL, narrow-mouth polyethylene or glass bottles with leak proof caps. Prepare every twelve months.

3.8. Standard Preparation for AAS-HGA Analysis

3.8.1. Dilute stock solutions: Prepare 10, 100 and 1,000 ng/mL cadmium standard stock solutions by making appropriate ten-fold serial dilutions of the 1,000 µg/mL cadmium standard stock solution with the diluting solution described in Section 3.5.6.

3.8.2. Working standards: Prepare cadmium working standards in the range of 0.2 to 20 ng/mL by making appropriate serial dilutions of the dilute stock solutions with the same diluting solution. A suggested method of preparation of the working standards is given below.

Working standard	Std solution	Aliquot	Final vol.
(ng/mL)	(ng/mL)	(mL)	(mL)
0.2	10	2	100
0.5	10	5	100
1	10	10	100
2	100	2	100
5	100	5	100

Working standard	Std solution	Aliquot	Final vol.
10	100	10	100
20	1,000	2	100

Store the working standards in narrow-mouth polyethylene or glass bottles with leakproof caps. Prepare monthly.

3.9. Sample Preparation

3.9.1. Carefully transfer each sample filter with forceps from its filter cassette unit to a clean, separate 125-mL Phillips beaker along with any loose dust found in the cassette. Label each Phillips beaker with the appropriate sample number.

3.9.2. Digest the sample by adding 5 mL of concentrated nitric acid (HNO₃) to each Phillips beaker containing an air filter sample. Place the Phillips beakers on a hot plate in an exhaust hood and heat the samples until approximately 0.5 mL remains. The sample solution in each Phillips beaker should become clear. If it is not clear, digest the sample with another portion of concentrated nitric acid.

3.9.3. After completing the HNO₃ digestion and cooling the samples, add 40 µL (2 drops) of concentrated HCl to each air sample solution and then swirl the contents. Carefully add about 5 mL of deionized water by pouring it down the inside of each beaker.

3.9.4. Quantitatively transfer each cooled air sample solution from each Phillips beaker to a clean 10-mL volumetric flask. Dilute each flask to volume with deionized water and mix well.

3.10. Flame AAS Analysis

Analyze all of the air samples for their cadmium content by flame atomic absorption spectroscopy (AAS) according to the instructions given below.

3.10.1. Set up the atomic absorption spectrophotometer for the air/acetylene flame analysis of cadmium according to the SOP (5.8.) or the manufacturer's operational instructions. For the source lamp, use the cadmium hollow cathode or electrodeless discharge lamp operated at the manufacturer's recommended rating for continuous operation. Allow the lamp to warm up 10 to 20 min or until the energy output stabilizes. Optimize conditions such as lamp position, burner head alignment, fuel and oxidant flow rates, etc. See the SOP or specific instrument manuals for details. Instrumental parameters for the Perkin-Elmer Model 603 used in the validation of this method are given in Attachment 1.

3.10.2. Aspirate and measure the absorbance of a standard solution of cadmium. The standard concentration should be within the linear range. For the instrumentation used in the validation of this method a 2 µg/mL cadmium standard gives a net absorbance reading of about 0.350 abs. units (see Section 1.5.5.) when the instrument and the source lamp are performing to manufacturer specifications.

3.10.3. To increase instrument response, scale expand the absorbance reading of the aspirated 2 µg/mL working standard approximately four times. Increase the integration time to at least 3 seconds to reduce signal noise.

3.10.4. Autozero the instrument while aspirating a deionized water blank. Monitor the variation in the baseline absorbance reading (baseline noise) for a few minutes to insure that the instrument, source lamp and associated equipment are in good operating condition.

3.10.5. Aspirate the working standards and samples directly into the flame and record their absorbance readings. Aspirate the deionized water blank immediately after every standard or sample to correct for and monitor any baseline drift and noise. Record the baseline absorbance reading of each deionized water blank. Label each standard and sample reading and its accompanying baseline reading.

3.10.6. It is recommended that the entire series of working standards be analyzed at the beginning and end of the analysis of a set of samples to establish a concentration-response curve, ensure that the standard readings agree with each other and are reproducible. Also, analyze a working standard after every five or six samples to monitor the performance of the spectrophotometer. Standard readings should agree within ±10 to 15% of the readings obtained at the beginning of the analysis.

3.10.7. Bracket the sample readings with standards during the analysis. If the absorbance reading of a sample is above the absorbance reading of the highest working standard, dilute the sample with diluting solution and reanalyze. Use the appropriate dilution factor in the calculations.

3.10.8. Repeat the analysis of approximately 10% of the samples for a check of precision.

3.10.9. If possible, analyze quality control samples from an independent source as a check on analytical recovery and precision.

3.10.10. Record the final instrument settings at the end of the analysis. Date and label the output.

3.11. AAS-HGA Analysis

Initially analyze all of the air samples for their cadmium content by flame atomic absorption spectroscopy (AAS) according to the instructions given in Section 3.10. If the concentration of cadmium in a sample solution is less than three times the quantitative detection limit [0.04 µg/mL

(40 ng/mL) for the instrumentation used in the validation] and the sample results are to be averaged with other samples for TWA calculations, proceed with the AAS-HGA analysis of the sample as described below.

3.11.1. Set up the atomic absorption spectrophotometer and HGA for flameless atomic absorption analysis of cadmium according to the SOP (5.9.) or the manufacturer's operational instructions and allow the instrument to stabilize. The graphite furnace atomizer is equipped with a pyrolytically coated graphite tube containing a pyrolytic platform. For the source lamp, use a cadmium hollow cathode or electrodeless discharge lamp operated at the manufacturer's recommended setting for graphite furnace operation. The Zeeman background corrector and EDL are recommended for use with the L'vov platform. Instrumental parameters for the Perkin-Elmer Model 5100 spectrophotometer and Zeeman HGA-600 graphite furnace used in the validation of this method are given in Attachment 2.

3.11.2. Optimize the energy reading of the spectrophotometer at 228.8 nm by adjusting the lamp position and the wavelength according to the manufacturer's instructions.

3.11.3. Set up the autosampler to inject a 5- μ L aliquot of the working standard, sample or reagent blank solution onto the L'vov platform along with a 10- μ L overlay of the matrix modifier.

3.11.4. Analyze the reagent blank (diluting solution, Section 3.5.6.) and then autozero the instrument before starting the analysis of a set of samples. It is recommended that the reagent blank be analyzed several times during the analysis to assure the integrated absorbance (peak area) reading remains at or near zero.

3.11.5. Analyze a working standard approximately midway in the linear portion of the working standard range two or three times to check for reproducibility and sensitivity (see sections 1.5.5. and 1.5.6.) before starting the analysis of samples. Calculate the experimental characteristic mass value from the average integrated absorbance reading and injection volume of the analyzed working standard. Compare this value to the manufacturer's suggested value as a check of proper instrument operation.

3.11.6. Analyze the reagent blank, working standard, and sample solutions. Record and label the peak area (abs-sec) readings and the peak and background peak profiles on the printer/plotter.

3.11.7. It is recommended the entire series of working standards be analyzed at the beginning and end of the analysis of a set of samples. Establish a concentration-response curve and ensure standard readings agree with each other and are reproducible. Also, analyze a working standard after every five or six samples to monitor the performance of the system. Standard readings should agree within $\pm 15\%$ of the readings obtained at the beginning of the analysis.

3.11.8. Bracket the sample readings with standards during the analysis. If the peak area reading of a sample is above the peak area reading of the highest working standard, dilute the sample with the diluting solution and reanalyze. Use the appropriate dilution factor in the calculations.

3.11.9. Repeat the analysis of approximately 10% of the samples for a check of precision.

3.11.10. If possible, analyze quality control samples from an independent source as a check of analytical recovery and precision.

3.11.11. Record the final instrument settings at the end of the analysis. Date and label the output.

3.12. Calculations

Note: Standards used for HGA analysis are in ng/mL. Total amounts of cadmium from calculations will be in ng (not µg) unless a prior conversion is made.

3.12.1. Correct for baseline drift and noise in flame AAS analysis by subtracting each baseline absorbance reading from its corresponding working standard or sample absorbance reading to obtain the net absorbance reading for each standard and sample.

3.12.2. Use a least squares regression program to plot a concentration-response curve of net absorbance reading (or peak area for HGA analysis) versus concentration (µg/mL or ng/mL) of cadmium in each working standard.

3.12.3. Determine the concentration (µg/mL or ng/mL) of cadmium in each sample from the resulting concentration-response curve. If the concentration of cadmium in a sample solution is less than three times the quantitative detection limit [0.04 µg/mL (40 ng/mL) for the instrumentation used in the validation of the method] and if consecutive samples were taken on one employee and the sample results are to be averaged with other samples to determine a single TWA, reanalyze the sample by AAS-HGA as described in Section 3.11. and report the AAS-HGA analytical results.

3.12.4. Calculate the total amount (µg or ng) of cadmium in each sample from the sample solution volume (mL):

$$W = (C)(\text{sample vol, mL})(DF)$$

Where:

W = Total cadmium in sample

C = Calculated concentration of cadmium

DF = Dilution Factor (if applicable)

3.12.5. Make a blank correction for each air sample by subtracting the total amount of cadmium in the corresponding blank sample from the total amount of cadmium in the sample.

3.12.6. Calculate the concentration of cadmium in an air sample (mg/m^3 or $\mu\text{g}/\text{m}^3$) by using one of the following equations:

$$\text{mg}/\text{m}^3 = W_{bc}/(\text{Air vol sampled, L})$$

or

$$\mu\text{g}/\text{m}^3 = (W_{bc})(1,000 \text{ ng}/\mu\text{g})/(\text{Air vol sampled, L})$$

Where:

W_{bc} = blank corrected total μg cadmium in the sample. ($1\mu\text{g} = 1,000 \text{ ng}$)

4. Backup Data

4.1. Introduction

4.1.1. The purpose of this evaluation is to determine the analytical method recovery, working standard range, and qualitative and quantitative detection limits of the two atomic absorption analytical techniques included in this method. The evaluation consisted of the following experiments:

1. An analysis of 24 samples (six samples each at 0.1, 0.5, 1 and 2 times the TWA-PEL) for the analytical method recovery study of the flame AAS analytical technique.
2. An analysis of 18 samples (six samples each at 0.5, 1 and 2 times the Action Level TWA-PEL) for the analytical method recovery study of the AAS-HGA analytical technique.
3. Multiple analyses of the reagent blank and a series of standard solutions to determine the working standard range and the qualitative and quantitative detection limits for both atomic absorption analytical techniques.

4.1.2. The analytical method recovery results at all test levels were calculated from concentration-response curves and statistically examined for outliers at the 99% confidence level. Possible outliers were determined using the Treatment of Outliers test (5.10.). In addition, the sample results of the two analytical techniques, at 0.5, 1.0 and 2.0 times their target concentrations, were tested for homogeneity of variances also at the 99% confidence level. Homogeneity of the coefficients of variation was determined using the Bartlett's test (5.11.). The overall analytical error (OAE) at the 95% confidence level was calculated using the equation (5.12.):

$$\text{OAE} = \pm[|\text{Bias}| + (1.96)(\text{CV}_1(\text{pooled}))(100\%)]$$

4.1.3. A derivation of the International Union of Pure and Applied Chemistry (IUPAC) detection limit equation (5.13.) was used to determine the qualitative and quantitative detection limits for both atomic absorption analytical techniques:

$$C_{ld} = k(sd)/m \text{ (Equation 1)}$$

Where:

C_{ld} = the smallest reliable detectable concentration an analytical instrument can determine at a given confidence level.

$k = 3$ for the Qualitative Detection Limit at the 99.86% Confidence Level

$= 10$ for the Quantitative Detection Limit at the 99.99% Confidence Level.

sd = standard deviation of the reagent blank (Rbl) readings.

m = analytical sensitivity or slope as calculated by linear regression.

4.1.4. Collection efficiencies of metallic fume and dust atmospheres on 0.8- μm mixed cellulose ester membrane filters are well documented and have been shown to be excellent (5.11.). Since elemental cadmium and the cadmium component of cadmium compounds are nonvolatile, stability studies of cadmium spiked MCEF samples were not performed.

4.2. Equipment

4.2.1. A Perkin-Elmer (PE) Model 603 spectrophotometer equipped with a manual gas control system, a stainless steel nebulizer, a burner mixing chamber, a flow spoiler and a 10 cm. (one-slot) burner head was used in the experimental validation of the flame AAS analytical technique. A PE cadmium hollow cathode lamp, operated at the manufacturer's recommended current setting for continuous operation (4 mA), was used as the source lamp. Instrument parameters are listed in Attachment 1.

4.2.2. A PE Model 5100 spectrophotometer, Zeeman HGA-600 graphite furnace atomizer and AS-60 HGA autosampler were used in the experimental validation of the AAS-HGA analytical technique. The spectrophotometer was equipped with a PE Series 7700 professional computer and Model PR-310 printer. A PE System 2 cadmium electrodeless discharge lamp, operated at the manufacturer's recommended current setting for modulated operation (170 mA), was used as the source lamp. Instrument parameters are listed in Attachment 2.

4.3. Reagents

4.3.1. J.T. Baker Chem. Co. (Analyzed grade) concentrated nitric acid, 69.0-71.0%, and concentrated hydrochloric acid, 36.5-38.0%, were used to prepare the samples and standards.

4.3.2. Ammonium phosphate, monobasic, $\text{NH}_4 \text{H}_2 \text{PO}_4$ and magnesium nitrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2 \text{O}$, both manufactured by the Mallinckrodt Chem. Co., were used to prepare the matrix modifier for AAS-HGA analysis.

4.4. Standard Preparation for Flame AAS Analysis

4.4.1. Dilute stock solutions: Prepared 0.01, 0.1, 1, 10 and 100 $\mu\text{g}/\text{mL}$ cadmium standard stock solutions by making appropriate serial dilutions of a commercially available 1,000 $\mu\text{g}/\text{mL}$ cadmium standard stock solution (RICCA Chemical Co., Lot# A102) with the diluting solution (4% HNO_3 , 0.4% HCl).

4.4.2. Analyzed Standards: Prepared cadmium standards in the range of 0.001 to 2.0 $\mu\text{g}/\text{mL}$ by pipetting 2 to 10 mL of the appropriate dilute cadmium stock solution into a 100-mL volumetric flask and diluting to volume with the diluting solution. (See Section 3.7.2.)

4.5. Standard Preparation for AAS-HGA Analysis

4.5.1. Dilute stock solutions: Prepared 1, 10, 100 and 1,000 ng/mL cadmium standard stock solutions by making appropriate serial dilutions of a commercially available 1,000 $\mu\text{g}/\text{mL}$ cadmium standard stock solution (J.T. Baker Chemical Co., Instra-analyzed, Lot# D22642) with the diluting solution (4% HNO_3 , 0.4% HCl).

4.5.2. Analyzed Standards: Prepared cadmium standards in the range of 0.1 to 40 ng/mL by pipetting 2 to 10 mL of the appropriate dilute cadmium stock solution into a 100-mL volumetric flask and diluting to volume with the diluting solution. (See Section 3.8.2.)

4.6. Detection Limits and Standard Working Range for Flame AAS Analysis

4.6.1. Analyzed the reagent blank solution and the entire series of cadmium standards in the range of 0.001 to 2.0 $\mu\text{g}/\text{mL}$ three to six times according to the instructions given in Section 3.10. The diluting solution (4% HNO_3 , 0.4% HCl) was used as the reagent blank. The integration time on the PE 603 spectrophotometer was set to 3.0 seconds and a four-fold expansion of the absorbance reading of the 2.0 $\mu\text{g}/\text{mL}$ cadmium standard was made prior to analysis. The 2.0 $\mu\text{g}/\text{mL}$ standard gave a net absorbance reading of 0.350 abs. units prior to expansion in agreement with the manufacturer's specifications (5.6.).

4.6.2. The net absorbance readings of the reagent blank and the low concentration Cd standards from 0.001 to 0.1 $\mu\text{g}/\text{mL}$ and the statistical analysis of the results are shown in Table I. The standard deviation, sd, of the six net absorbance readings of the reagent blank is 1.05 abs. units. The slope, m, as calculated by a linear regression plot of the net absorbance readings (shown in Table II) of the 0.02 to 1.0 $\mu\text{g}/\text{mL}$ cadmium standards versus their concentration is 772.7 abs. units/ $(\mu\text{g}/\text{mL})$.

4.6.3. If these values for s_d and the slope, m , are used in Eqn. 1 (Sect. 4.1.3.), the qualitative and quantitative detection limits as determined by the IUPAC Method are:

$$C_{ld} = (3)(1.05 \text{ abs. units}) / (772.7 \text{ abs. units} / (\mu\text{g/mL}))$$

= 0.0041 $\mu\text{g/mL}$ for the qualitative detection limit.

$$C_{ld} = (10)(1.05 \text{ abs. units}) / (772.7 \text{ abs. units} / \mu\text{g/mL})$$

= 0.014 $\mu\text{g/mL}$ for the quantitative detection limit.

The qualitative and quantitative detection limits for the flame AAS analytical technique are 0.041 μg and 0.14 μg cadmium, respectively, for a 10 mL solution volume. These correspond, respectively, to 0.2 $\mu\text{g/m}^3$ and 0.70 $\mu\text{g/m}^3$ for a 200 L air volume.

4.6.4. The recommended Cd standard working range for flame AAS analysis is 0.02 to 2.0 $\mu\text{g/mL}$. The net absorbance readings of the reagent blank and the recommended working range standards and the statistical analysis of the results are shown in Table II. The standard of lowest concentration in the working range, 0.02 $\mu\text{g/mL}$, is slightly greater than the calculated quantitative detection limit, 0.014 $\mu\text{g/mL}$. The standard of highest concentration in the working range, 2.0 $\mu\text{g/mL}$, is at the upper end of the linear working range suggested by the manufacturer (5.6.). Although the standard net absorbance readings are not strictly linear at concentrations above 0.5 $\mu\text{g/mL}$, the deviation from linearity is only about 10% at the upper end of the recommended standard working range. The deviation from linearity is probably caused by the four-fold expansion of the signal suggested in the method. As shown in Table II, the precision of the standard net absorbance readings are excellent throughout the recommended working range; the relative standard deviations of the readings range from 0.009 to 0.064.

4.7. Detection Limits and Standard Working Range for AAS-HGA Analysis

4.7.1. Analyzed the reagent blank solution and the entire series of cadmium standards in the range of 0.1 to 40 ng/mL according to the instructions given in Section 3.11. The diluting solution (4% HNO_3 , 0.4% HCl) was used as the reagent blank. A fresh aliquot of the reagent blank and of each standard was used for every analysis. The experimental characteristic mass value was 0.41 pg, calculated from the average peak area (abs-sec) reading of the 5 ng/mL standard which is approximately midway in the linear portion of the working standard range. This agreed within 20% with the characteristic mass value, 0.35 pg, listed by the manufacturer of the instrument (5.2.).

4.7.2. The peak area (abs-sec) readings of the reagent blank and the low concentration Cd standards from 0.1 to 2.0 ng/mL and statistical analysis of the results are shown in Table III. Five of the reagent blank peak area readings were zero and the sixth reading was 1 and was an outlier.

The near lack of a blank signal does not satisfy a strict interpretation of the IUPAC method for determining the detection limits. Therefore, the standard deviation of the six peak area readings of the 0.2 ng/mL cadmium standard, 0.75 abs-sec, was used to calculate the detection limits by the IUPAC method. The slope, m , as calculated by a linear regression plot of the peak area (abs-sec) readings (shown in Table IV) of the 0.2 to 10 ng/mL cadmium standards versus their concentration is 51.5 abs-sec/(ng/mL).

4.7.3. If 0.75 abs-sec (sd) and 51.5 abs-sec/(ng/mL) (m) are used in Eqn. 1 (Sect. 4.1.3.), the qualitative and quantitative detection limits as determined by the IUPAC method are:

$$C_{ld} = (3)(0.75 \text{ abs-sec}) / (51.5 \text{ abs-sec}/(\text{ng/mL}))$$

= 0.044 ng/mL for the qualitative detection limit.

$$C_{ld} = (10)(0.75 \text{ abs-sec}) / (51.5 \text{ abs-sec}/(\text{ng/mL})) = 0.15 \text{ ng/mL for the quantitative detection limit.}$$

The qualitative and quantitative detection limits for the AAS-HGA analytical technique are 0.44 ng and 1.5 ng cadmium, respectively, for a 10 mL solution volume. These correspond, respectively, to 0.007 $\mu\text{g}/\text{m}^3$ and 0.025 $\mu\text{g}/\text{m}^3$ for a 60 L air volume.

4.7.4. The peak area (abs-sec) readings of the Cd standards from 0.2 to 40 ng/mL and the statistical analysis of the results are given in Table IV. The recommended standard working range for AAS-HGA analysis is 0.2 to 20 ng/mL. The standard of lowest concentration in the recommended working range is slightly greater than the calculated quantitative detection limit, 0.15 ng/mL. The deviation from linearity of the peak area readings of the 20 ng/mL standard, the highest concentration standard in the recommended working range, is approximately 10%. The deviations from linearity of the peak area readings of the 30 and 40 ng/mL standards are significantly greater than 10%. As shown in Table IV, the precision of the peak area readings are satisfactory throughout the recommended working range; the relative standard deviations of the readings range from 0.025 to 0.083.

4.8. Analytical Method Recovery for Flame AAS Analysis

4.8.1. Four sets of spiked MCEF samples were prepared by injecting 20 μL of 10, 50, 100 and 200 $\mu\text{g}/\text{mL}$ dilute cadmium stock solutions on 37 mm diameter filters (part no. AAWP 037 00, Millipore Corp., Bedford, MA) with a calibrated micropipet. The dilute stock solutions were prepared by making appropriate serial dilutions of a commercially available 1,000 $\mu\text{g}/\text{mL}$ cadmium standard stock solution (RICCA Chemical Co., Lot# A102) with the diluting solution (4% HNO_3 , 0.4% HCl). Each set contained six samples and a sample blank. The amount of cadmium in the prepared sets were equivalent to 0.1, 0.5, 1.0 and 2.0 times the TWA PEL target concentration of 5 $\mu\text{g}/\text{m}^3$ for a 400 L air volume.

4.8.2. The air-dried spiked filters were digested and analyzed for their cadmium content by flame atomic absorption spectroscopy (AAS) following the procedure described in Section 3. The 0.02 to 2.0 µg/mL cadmium standards (the suggested working range) were used in the analysis of the spiked filters.

4.8.3. The results of the analysis are given in Table V. One result at 0.5 times the TWA PEL target concentration was an outlier and was excluded from statistical analysis. Experimental justification for rejecting it is that the outlier value was probably due to a spiking error. The coefficients of variation for the three test levels at 0.5 to 2.0 times the TWA PEL target concentration passed the Bartlett's test and were pooled.

4.8.4. The average recovery of the six spiked filter samples at 0.1 times the TWA PEL target concentration was 118.2% with a coefficient of variation (CV_1) of 0.128. The average recovery of the spiked filter samples in the range of 0.5 to 2.0 times the TWA target concentration was 104.0% with a pooled coefficient of variation (CV_1) of 0.010. Consequently, the analytical bias found in these spiked sample results over the tested concentration range was + 4.0% and the OAE was $\pm 6.0\%$.

4.9. Analytical Method Recovery for AAS-HGA Analysis

4.9.1. Three sets of spiked MCEF samples were prepared by injecting 15 µL of 5, 10 and 20 µg/mL dilute cadmium stock solutions on 37 mm diameter filters (part no. AAWP 037 00, Millipore Corp., Bedford, MA) with a calibrated micropipet. The dilute stock solutions were prepared by making appropriate serial dilutions of a commercially available certified 1,000 µg/mL cadmium standard stock solution (Fisher Chemical Co., Lot# 913438-24) with the diluting solution (4% HNO₃, 0.4% HCl). Each set contained six samples and a sample blank. The amount of cadmium in the prepared sets were equivalent to 0.5, 1 and 2 times the Action Level TWA target concentration of 2.5 µg/m³ for a 60 L air volume.

4.9.2. The air-dried spiked filters were digested and analyzed for their cadmium content by flameless atomic absorption spectroscopy using a heated graphite furnace atomizer following the procedure described in Section 3. A five-fold dilution of the spiked filter samples at 2 times the Action Level TWA was made prior to their analysis. The 0.05 to 20 ng/mL cadmium standards were used in the analysis of the spiked filters.

4.9.3. The results of the analysis are given in Table VI. There were no outliers. The coefficients of variation for the three test levels at 0.5 to 2.0 times the Action Level TWA PEL passed the Bartlett's test and were pooled. The average recovery of the spiked filter samples was 94.2% with a pooled coefficient of variation (CV_1) of 0.043. Consequently, the analytical bias was -5.8% and the OAE was $\pm 14.2\%$.

4.10. Conclusions

The experiments performed in this evaluation show the two atomic absorption analytical techniques included in this method to be precise and accurate and have sufficient sensitivity to measure airborne cadmium over a broad range of exposure levels and sampling periods.

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Table I - Cd Detection Limit Study

[Flame AAS Analysis]

STD (µg/mL)	Absorbance reading at 228.8 nm	Statistical analysis
Reagent blank	5 2 4 3 4 3	n = 6. mean = 3.50. std dev = 1.05. CV = 0.30.
0.001	6 6 2 4 6 6	n = 6. mean = 5.00. std dev = 1.67. CV = 0.335.
0.002	5 7 7 3 7 4	n = 6. mean = 5.50. std dev = 1.76. CV = 0.320.
0.005	7 7 8 8 8 6	n = 6. mean = 7.33. std dev = 0.817. CV = 0.111.

STD ($\mu\text{g/mL}$)	Absorbance reading at 228.8 nm	Statistical analysis
0.010	10 9 10 13 10 10	n = 6. mean = 10.3. std dev = 1.37. CV = 0.133.
0.020	20 23 20 22 20 20	n = 6. mean = 20.8. std dev = 1.33. CV = 0.064.
0.050	42 42 42 42 42 45	n = 6. mean = 42.5. std dev = 1.22. CV = 0.029.
0.10	84 80 83	n = 3. mean = 82.3. std dev = 2.08. CV = 0.025.

Table II - Cd Standard Working Range Study

[Flame AAS Analysis]

STD ($\mu\text{g/mL}$)	Absorbance reading at 228.8 nm	Statistical analysis
Reagent blank	5 2 4 3 4 3	n = 6. mean = 3.50. std dev = 1.05. CV = 0.30.
0.020	20 23 20 22 20 20	n = 6. mean = 20.8. std dev = 1.33. CV = 0.064.
0.050	42 42 42 42 42 45	n = 6. mean = 42.5. std dev = 1.22. CV = 0.029.

STD ($\mu\text{g/mL}$)	Absorbance reading at 228.8 nm	Statistical analysis
0.10	84 80 83	n = 3. mean = 82.3. std dev = 2.08. CV = 0.025.
0.20	161 161 158	n = 3. mean = 160.0. std dev = 1.73. CV = 0.011.
0.50	391 389 393	n = 3. mean = 391.0. std dev = 2.00. CV = 0.005.
1.00	760 748 752	n = 3. mean = 753.3. std dev = 6.11. CV = 0.008.
2.00	1416 1426 1401	n = 3. mean = 1414.3. std dev = 12.6. CV = 0.009.

Table III - Cd Detection Limit Study

[AAS-HGA Analysis]

STD (ng/mL)	Peak area readings $\times 10^3$ at 228.8 nm	Statistical analysis
Reagent blank	0 0 0 1 0 0	n = 6. mean = 0.167. std dev = 0.41. CV = 2.45.
0.1	8 6 5 7 13 7	n = 6. mean = 7.7. std dev = 2.8. CV = 0.366.

STD (ng/mL)	Peak area readings × 10³ at 228.8 nm	Statistical analysis
0.2	11 13 11 12 12 12	n = 6. mean = 11.8. std dev = 0.75. CV = 0.064.
0.5	28 33 26 28 28 30	n = 6. mean = 28.8. std dev = 2.4. CV = 0.083.
1.0	52 55 56 58 54 54	n = 6. mean = 54.8. std dev = 2.0. CV = 0.037.
2.0	101 112 110 110 110 110	n = 6. mean = 108.8. std dev = 3.9. CV = 0.036.

Table IV - Cd Standard Working Range Study

[AAS-HGA Analysis]

STD (ng/mL)	Peak area readings × 10³ at 228.8 nm	Statistical analysis
0.2	11 13 11 12 12 12	n = 6. mean = 11.8. std dev = 0.75. CV = 0.064.
0.5	28 33 26 28 28 30	n = 6. mean = 28.8. std dev = 2.4. CV = 0.083.
1.0	52 55 56 58 54 54	n = 6. mean = 54.8. std dev = 2.0. CV = 0.037.

STD (ng/mL)	Peak area readings × 10³ at 228.8 nm	Statistical analysis
2.0	101 112 110 110 110 110	n = 6. mean = 108.8. std dev = 3.9. CV = 0.036.
5.0	247 265 268 275 259 279	n = 6. mean = 265.5. std dev = 11.5. CV = 0.044.
10.0	495 520 523 513 516 533	n = 6. mean = 516.7. std dev = 12.7. CV = 0.025.
20.0	950 953 951 958 949 890	n = 6. mean = 941.8. std dev = 25.6. CV = 0.027.
30.0	1269 1291 1303 1307 1295 1290	n = 6. mean = 1293. std dev = 13.3. CV = 0.010.
40.0	1505 1567 1535 1567 1566 1572	n = 6. mean = 1552. std dev = 26.6. CV = 0.017.

Table V - Analytical Method Recovery

[Flame AAS Analysis]

Test level	0.5 ×	Percent rec.	µg taken	1.0 ×	Percent rec.	µg taken	2.0 ×	Percent rec.
	µg found			µg found			µg found	
µg taken	µg found	rec.	taken	found	rec.	taken	found	rec.

Test level	0.5 ×	Percent rec.	µg taken	1.0 ×	Percent rec.	µg taken	2.0 ×	Percent rec.
	µg found			µg found			µg found	
1.00	1.0715	107.2	2.00	2.0688	103.4	4.00	4.1504	103.8
1.00	1.0842	108.4	2.00	2.0174	100.9	4.00	4.1108	102.8
1.00	1.0842	108.4	2.00	2.0431	102.2	4.00	4.0581	101.5
1.00	*1.0081	*100.8	2.00	2.0431	102.2	4.00	4.0844	102.1
1.00	1.0715	107.2	2.00	2.0174	100.9	4.00	4.1504	103.8
1.00	1.0842	108.4	2.00	2.0045	100.2	4.00	4.1899	104.7

n=		5			6			6
mean =		107.9			101.6			103.1
std dev =		0.657			1.174			1.199
CV ₁ =		0.006			0.011			0.012
CV ₁ (pooled) = 0.010								

* Rejected as an outlier - this value did not pass the outlier T-test at the 99% confidence level.

Test level	0.1 ×	Percent rec.	
	µg found		
0.200		0.2509	125.5
0.200		0.2509	125.5
0.200		0.2761	138.1
0.200		0.2258	112.9
0.200		0.2258	112.9
0.200		0.1881	94.1

n=		6
mean =		118.2

std dev =			15.1
CV ₁ =			0.128

Table VI - Analytical Method Recovery

[AAS-HGA Analysis]

Test level	0.5 ×	Percent rec.	ng taken	1.0 ×	Percent rec.	ng taken	2.0 ×	Percent rec.
	ng found			ng found			ng found	
75	71.23	95.0	150	138.00	92.0	300	258.43	86.1
75	71.47	95.3	150	138.29	92.2	300	258.46	86.2
75	70.02	93.4	150	136.30	90.9	300	280.55	93.5
75	77.34	103.1	150	146.62	97.7	300	288.34	96.1
75	78.32	104.4	150	145.17	96.8	300	261.74	87.2
75	71.96	95.9	150	144.88	96.6	300	277.22	92.4

n=			6			6		6
mean =			97.9			94.4		90.3
std dev =			4.66			2.98		4.30
CV ₁ =			0.048			0.032		0.048
CV ₁ (pooled) = 0.043								

Attachment 1**Instrumental Parameters for Flame AAS Analysis**

Atomic Absorption Spectrophotometer (Perkin-Elmer Model 603)

Flame: Air/Acetylene - lean, blue

Oxidant Flow: 55

Fuel Flow: 32

Wavelength: 228.8 nm

Slit: 4 (0.7 nm)

Range: UV

Signal: Concentration (4 exp)

Integration Time: 3 sec

Attachment 2

Instrumental Parameters for HGA Analysis

Atomic Absorption Spectrophotometer (Perkin-Elmer Model 5100)

Signal Type: Zeeman AA

Slitwidth: 0.7 nm

Wavelength: 228.8 nm

Measurement: Peak Area

Integration Time: 6.0 sec

BOC Time: 5 sec

BOC = Background Offset Correction.

Zeeman Graphite Furnace (Perkin-Elmer Model HGA-600)

Step	Ramp time (sec)	Hold time (sec)	Temp. (°C)	Argon flow (mL/min)	Read (sec)
1) Predry	5	10	90	300	
2) Dry	30	10	140	300	
3) Char	10	20	900	300	
4) Cool Down	1	8	30	300	
5) Atomize	0	5	1600	0	-1
6) Burnout	1	8	2500	300	

[57 FR 42389, Sept. 14, 1992, as amended at 58 FR 21782, Apr. 23, 1993]

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