4.2 GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRIC DETERMINATION OF LEAD AND CADMIUM EXTRACTED FROM CERAMIC FOODWARE

1. Scope and Application

This method describes procedures for using graphite furnace atomic absorption spectroscopy (AAS) to quantitatively determine lead and cadmium extracted by acetic acid at room temperature from the food-contact surface of foodware. The method is applicable to food-contact surfaces of silicate-based materials (earthenware, glazed ceramicware, decorated ceramicware, decorated glass, and lead crystal glass) and is capable of determining lead concentrations greater than approximately 0.005–0.020 µg/mL and cadmium concentrations greater than approximately 0.0005–0.002 µg/mL, depending on instrument design. This method also describes quality control procedures to check for contamination and matrix interference and a specific analytical sequence of measurements that demonstrates proper instrument operation during the time period in which sample solutions are analyzed.

2. Summary of Method

Lead and cadmium are extracted from the food-contact surface of test vessels by filling them with 4% acetic acid to within 6-7 mm (1/4") of overflowing and leaching them for 24 h at 20-24° C (68-75° F). Lead and cadmium are determined by graphite furnace AAS using a chemical modifier and instrumental background correction. Concentrations in leach solutions are calculated using a calibration curve and linear least squares regression.

3. Safety

This method does not attempt to address all safety issues, if any, associated with its use. The user of this method must establish appropriate safety and health practices prior to use.

4. Definitions

Sample—six test vessels of identical size, shape, color, and decorative pattern.

Sub-sample—each of the 6 individual vessels which make up the sample.

Method blank—a contamination-free laboratory beaker or dish that is analyzed by the entire method including preparation, leaching, and solution analysis.

Leach solution—solution obtained by leaching a test vessel or method blank with 4% acetic acid for 24 h.

Test solution—solution deposited in the graphite furnace for analysis. Test solutions are prepared by diluting leach solutions with known amounts of 4% acetic acid. Test solutions also include portions of undiluted leach, check, and independent check solutions deposited in the furnace.

Dilution factor (DF)—factor by which concentration in test solution is multiplied to obtain

concentration in original leach solution. For test solutions prepared by mixing pipet-measured portions of leach solution and diluent, DF = $(V_1+V_2)/V_1$ where V_1 and V_2 are volumes of leach solution and diluent in test solution, respectively. For test solutions prepared by mixing weighed portions of leach solution and diluent (gravimetric dilution), DF = W_2/W_1 where W_1 is the weight of leach solution in test solution and W_2 is the total weight of leach solution and diluent in the test solution.

Calibration solutions—4% acetic acid solutions containing known amounts of lead or cadmium which are used to calibrate the instrument.

Check solutions—4% acetic acid solutions containing known amounts of lead or cadmium which are analyzed in the same time period and subjected to the same analytical conditions and calibration curve as sample solutions. Check solutions are analyzed to verify that carry-over did not occur and the instrument was operating correctly during the time period in which sample solutions were analyzed. Portions of calibration solutions analyzed as unknown test solutions (as opposed to analysis for calibrating the instrument) are used for this purpose.

Independent check solution—4% acetic acid solution containing a known amount of lead or cadmium which is from a starting material that is different from the starting material used to prepare calibration solutions. Starting materials with different lot numbers are acceptable, but starting materials from different manufacturers are preferable. The independent check solution is analyzed to verify that calibration solutions have been prepared correctly. An independent check solution must be used to verify calibration until such time that a reference material certified for lead and cadmium leaching becomes available.

Fortified leach solution—a portion of leach solution to which a known amount of lead or cadmium is added. A fortified leach solution is analyzed to calculate percent recovery and monitor matrix interference. Stock, intermediate, and calibration solutions are used to fortify leach solutions.

Characteristic mass (m_0)—mass (picograms, pg) of lead or cadmium that produces instrument response (peak area) of 0.0044 integrated absorbance (absorbance-seconds, A-s). Characteristic mass is a measure of instrument sensitivity and is a function of instrument design, operating conditions, and analyte-matrix-graphite interactions. Characteristic mass is calculated from the volume of solution in the furnace and the slope of the calibration curve or the concentration that gives an instrument response in the middle of the working range (*i.e.*, approximately 0.100 or 0.200 A-s). Characteristic mass is compared to manufacturer specifications to verify that the instrument is optimized.

Working range—range of instrument response that may be described as a linear function of the mass of analyte. The linear range of graphite furnace peak area measurements is approximately 0.050 to 0.350-0.400 A-s. The range of linear response depends on the element and operating conditions and must be verified by analyzing calibration solutions each time the instrument is used. The linear range of instrument response was chosen as the working range of this method because responses in the linear range are well below those at which roll-over adversely affects lead and cadmium instrument responses obtained using Zeeman background correction.

Sample concentration limit (SCL)—a low concentration (µg/mL) that can be reliably measured in leach solutions. In this method, the sample concentration limit is the concentration of lead or cadmium that produces 0.050 A-s. The value 0.050 A-s is chosen to establish the limit of the method for two reasons; 0.050 A-s is 10 times greater than the maximum response (0.005 A-s) typically expected from periodic, repeated analysis of a contamination-free, 0 ng/mL solution and thus guarantees that concentrations in sample solutions are significantly (10 times) greater than those in a true blank; and percent relative standard deviation of instrument response (relative variability due to instrument precision) is

better for 0.050 A-s than for lower values. The sample concentration limit depends on the characteristic mass of the instrument and volume of solution deposited in the furnace; the numerical value of the limit increases as characteristic mass increases and as the volume of solution deposited in the furnace decreases.

Sample mass limit (SML)—a low mass (μg) of extractable lead or cadmium that can be reliably measured by this method. The sample limit is the product of the concentration limit times the volume of leach solutions.

Gravimetric dilution—practice of quantitatively preparing dilute solutions from more concentrated ones by combining known weights of diluent and solution of known concentration. Gravimetric dilution using contamination-free, disposable plasticware is recommended whenever possible because glass volumetric flasks require time-consuming, acid-cleaning procedures to eliminate contamination. Gravimetric dilution may be used when densities and major components of the diluent and concentrated solution are the same (*i.e.*, both solutions contain 4% acetic acid). Volumetric flasks must be used when the densities are different (*i.e.*, as when diluent contains 4% acetic acid and stock standards contain 2% nitric acid). Gravimetric dilution is accomplished as follows: Weigh necessary amount (≥1.0000 g) of solution with known concentration to nearest 0.0001 g in a tared, plastic container. Add 4% acetic acid so that weight of final solution provides required concentration. Calculate concentration in final solution as:

$$C_2 = C_1 \times W_1 / W_2$$

where

C_2 = concentration in diluted (final) solution, ng/mL
C_1 = concentration in initial solution, ng/mL
W_1 = weight of initial solution, g
W_2 = weight of final solution, g

5. Interferences

Nonspecific absorption and scattering of light due to concomitant species in leach solutions may produce erroneously high results. Instrumental background correction is used to compensate for this interference.

Concomitant elements in leach solutions may alter the atomization process and thus degrade or enhance instrumental response. This problem, generally referred to as matrix interference, is controlled by diluting leach solutions and by using a chemical modifier and is monitored by calculating percent recovery from a fortified (spiked) portion of leach solution.

Contamination from laboratory glassware, supplies, and environmental particulate matter (dust) may cause erroneously high results. Contamination is minimized by keeping work areas and labware scrupulously clean, using plastic labware whenever possible, using acid-cleaning procedures when glass labware is required, and protecting samples and supplies from dust. Analysts must establish contamination control procedures before attempting sample analysis because correcting for lead and cadmium contamination that is sporadic (heterogeneous) by the practice of “blank subtraction” is not scientifically valid. Cleaning and other contamination control procedures are described in this method. Users may modify contamination control procedures provided that the modifications produce acceptable results and are used for both sample and quality control analyses.

Spectral interferences due to direct line overlap are extremely rare when hollow cathode lamps are used and are not expected from leach solutions.

6. Apparatus and Materials

Disclaimer: The use of trade names in this method constitutes neither endorsement nor recommendation by the Food and Drug Administration. Equivalent performance may be achievable using apparatus and materials other than those cited here.

Atomic Absorption spectrometer—capable of displaying and recording fast, transient signals, measuring peak area, and having sensitivity (m_0 based on peak area) less than or equal to 30 pg lead and 1.3 pg cadmium when wavelengths 283.3 nm and 228.8 nm are used for lead and cadmium determinations, respectively; equipped with light sources (hollow cathode or electrodeless discharge lamps) specific for lead and cadmium, instrumental background correction (deuterium arc, Zeeman, or pulsed techniques such as Smith-Hieftje), autosampler, and electrothermal atomizer (graphite furnace) with pyrolytically coated tubes and platforms. Use wavelengths of 283.3 nm and 228.8 nm for lead and cadmium, respectively. Record instrument response as peak area (A-s). Do not use peak height. Peak area compensates for small differences in peak shape an appearance time that occur in leach and calibration solutions.

Gas supply for furnace—high purity (99.99%) argon.

Cooling water for furnace—Use device that controls temperature and recirculates coolant.

Adjustable macro- and micropipettes—Manually operated pipets with disposable, colorless, plastic tips and with capacity ranging from 10 µL to 10 mL are acceptable. Motorized pipets capable of automatic dilution are preferred.

Plastic labware—Use plastic or Teflon labware (graduated cylinders, beakers, stirrers, containers, pipet tips, autosampler cups) for all procedures except preparation of intermediate lead and cadmium solutions. Disposable labware that does not need pre-cleaning is preferred. When pre-cleaning is necessary to eliminate contamination, rinse plastic labware with 10% (1+9) nitric acid followed by rinsing with copious quantities of reagent water. Air-dry the ware in a dust-free environment.

Note: Polypropylene centrifuge tubes with caps, 50 mL capacity (item no. 2068, Becton Dickinson and Co., Franklin Lakes, NJ) have been found suitable for holding solutions.

Glassware—Use new volumetric flasks dedicated for use with only this method to prepare intermediate calibration solutions. Do not use glassware used for other laboratory operations because potential for contamination is too great. Do not use glass pipets. Wash new glassware with warm tap water and laboratory detergent followed by soaking over night in 10% (1+9) nitric acid and rinsing with copious quantities of reagent water. Air-dry in dust-free environment. Dedicated glassware may be reused after rinsing with copious quantities of reagent water and repeating the acid-cleaning procedure.

Note: Micro Cleaner, a trademark of International Products Corp., Burlington, NJ, (catalogue number 6731) has been found suitable laboratory detergent to clean laboratory glassware.

Gloves, powder-free vinyl—Wear gloves when handling test vessels to prevent contamination.

Polyethylene bags, self-sealing—Cover or wrap labware with new plastic bags of suitable size to prevent contamination from dust during drying and storage.

Clean-air canopy—Laminar flow canopy equipped with high-efficiency particulate filters is recommended because it makes contamination control easier and analyses faster. Contamination can be controlled, however, without using a clean-air canopy if care is taken to prevent contamination from dust.

7. Reagents

Reagent grade chemicals may be used provided that they are of sufficiently high purity to permit their use without lessening the accuracy of the determination. The high sensitivity of graphite furnace may require reagents of higher purity than reagent grade.

Reagent water—Ultrapure, deionized, resistance ≥18 megohm-cm.

Detergent solution for cleaning samples (0.02%, by volume)—Mix 1 mL detergent with 5 L tap water. Use nonacidic, liquid detergent designed for washing household dishes by hand. Do not use chemicals or detergents designed for cleaning labware because such detergents may damage the ware.

Note: Ajax or Joy, trademarks of Colgate-Palmolive Co., New York, NY and Proctor and Gamble Co., Cincinnati, OH, respectively, have been found suitable for cleaning samples.

Acetic acid (4% by volume)— Mix 1 volume glacial acetic acid with 24 volumes reagent water. Prepare a quantity sufficient for leaching samples and preparing calibration and check solutions.

Matrix modifier solution (1%, w/v, $NH_4H_2PO_4$)—Dissolve 0.5 g ammonium dihydrogen phosphate in 50 mL reagent water. One µL contains 8.3 µg phosphate ion (PO_4^{-3}).

Optional matrix modifier solution for instruments with Zeeman background correction(1%, w/v, $NH_4H_2PO_4$ with 4.2%, w/v, $Mg(NO_3)_2 \cdot 6H_2O$)—Dissolve 2.1 g magnesium nitrate hexahydrate in 50 mL of phosphate modifier solution. One µL of optional modifier contains 8.3 µg phosphate ion and 4.0 µg magnesium ion.

Stock lead and cadmium solutions—Use 1000 or 10,000 µg/mL single-element stock solutions in 2-10% nitric acid prepared specifically for spectrometric analysis. Do not use solutions containing hydrochloric, sulfuric, or phosphoric acid. Multi-element solutions may be used to prepare independent check solutions. Commercially prepared stock solutions are recommended.

Intermediate lead and cadmium solutions—Transfer by pipet ≥1000 µL stock solution to acid-cleaned volumetric flask and dilute to ≥100.0 mL with 4% acetic acid.

Calibration and independent check solutions—Prepare calibration solutions that produce responses of 0.000 A-s (0 ng/mL) and approximately (±20%) 0.050, 0.100, 0.200, and 0.350-0.400 A-s. Prepare an independent check solution that produces approximately 0.300 A-s. Preparation of a calibration solution that produces approximately 0.300 A-s is optional. Use of gravimetric dilution or pipets with disposable, plastic tips is recommended. Do not use glass volumetric flasks.

Note: Daily preparation of intermediate, independent check, and calibration solutions is recommended. Solutions may be stored for longer periods however, if stored in clean, plastic containers with tightly sealed caps. Calibration solutions alternatively may be prepared by instrument autosampler immediately before analysis of test solutions.

8. Sample Preparation and Leaching

Wash method blank and test vessels for 30 s by immersing in 0.02% detergent solution (≤40° C) and rubbing gently with soft cloth. Rinse with tap water (≤40° C) followed by copious quantities of reagent water. Air-dry in dust-free environment.

Fill method blank and test vessels with 4% acetic acid to within 6-7 mm (1/4") of the edge of the vessel measured along the surface. Record volume of extractant for each vessel.

Immediately cover vessels to minimize evaporation. Use opaque material or place vessel in dark location to prevent photo-oxidation of insoluble cadmium sulfide to soluble cadmium sulfate.

Note: Polystyrene culture dishes (item no. 25030-150, Corning Inc., Corning, NY and item no. 4014, Nalgene Nunc International, Naperville, IL) have been found suitable for covering test vessels.

Leach vessels for 24 h at 22±2° C.

At 24 h, visually observe level of leach solutions. If evaporative losses have occurred, add 4% acetic acid to within 6-7 mm of the edge of vessel. Proceed immediately to next step.

Gently stir leach solutions with plastic device and transfer by pipet to plastic container. Do not pour. For best results, analyze within 1 day. Leach solutions with no precipitate may be held longer if stored in clean containers with tightly sealed caps. Store in total darkness until analysis.

Precipitated matter, if present, may be removed from leach solutions by filtering with PTFE filters in natural (not colored) polypropylene housings attached to polypropylene syringes. Acid-clean filters and syringes with 4% acetic acid immediately before use.

Note: Item no. 6159-06N, Lida Corp., Kenosha, WI, has been found suitable for filtering and item no. 14-826-13, Fisher Scientific, Pittsburgh, PA, has been found a suitable polypropylene syringe.

9. Instrument Optimization

Examples of instrument operating conditions are listed in Table 1. Optimum furnace programs will vary. Examples of optimized atomization profiles obtained on longitudinally heated graphite tubes are in Figures 1 and 2. Atomization profiles obtained on transversely heated tubes will appear slightly less symmetrical and earlier during the “read” segment of the program.

Optimize spectrometer settings, furnace program, and mass of chemical modifier for each element so that characteristic mass of lead and cadmium is within approximately ±20% of manufacturer specifications, precision of 10 measurements is ≤5% (preferably ≤3%) relative standard deviation, and atomization peaks are symmetrically shaped and centered in a window of approximately 5 seconds. Instruments with multi-element capability may be optimized for one element and used with compromised conditions for determination of the other element if quality control measurements are acceptable. Begin the optimization process by using 20 µL of a lead calibration solution (10 µL of a cadmium calibration solution) that produces approximately 0.100 or 0.200 A-s and furnace program recommended by manufacturer. Optimize dry, char, atomization, and clean steps of the furnace program as follows. Dry: determine highest temperature and shortest time required to evaporate solution without

spattering. Char: determine highest temperature at which no loss of atomic absorbance (peak area) occurs and shortest time required to minimize background absorbance of chemical modifier. Atomization: determine lowest temperature which gives maximum atomic absorbance, complete volatilization of analyte (atomic absorbance returns to baseline), and a properly shaped atomization peak. Clean: determine lowest temperature and shortest time required to eliminate carry-over from previous solution.

Concomitant elements in leach solutions may alter the atomization process and instrument response. Verify that the furnace program, mass of chemical modifier, and test solution dilution factors are optimum for leach solution analysis by analyzing a leach solution fortified with the analyte of interest. If necessary, further dilute the leach solution and re-optimize furnace program and mass of chemical modifier so that per cent recovery is 90–110% (preferably 95–105%) and the atomization peak obtained from leach solutions is properly shaped. Use re-optimized conditions to analyze all test (leach and calibration) solutions.

10. Screening of Leach Solutions and Preparation of Test Solutions

Complete screening, calibration, and analysis (Sections 10, 11, and 12) for lead first. Then repeat Sections 10, 11, and 12 for cadmium. Hold test solutions in tightly sealed containers. Discard test solutions which have been held in unsealed autosampler cups for longer than 15-20 min.

Screening

Screen leach solutions by serially diluting them with 4% acetic acid and analyzing the series until a dilution which produces 0.050 A-s to 0.350-0.400 A-s is found. Serial dilutions with DF=1, 10, 100, 1000, etc. are recommended. Calculate approximate concentration in each sub-sample leach solution from the instrument response and dilution factor of the dilution which produces a response in working range. Screening serves 3 purposes: it saves time by determining appropriate dilutions for test solutions systematically rather than by trial-and-error; it determines appropriate fortification level; and it conditions the graphite with the leach solutions to be analyzed. Do not report results of screening.

Preparation of Fortified Leach and Test Solutions

For each sample, prepare 1 fortified leach solution and 3 test solutions (*a*, *b*, and *c*) to check for matrix interference. Use leach solution from the sub-sample which produced the highest concentration of lead or cadmium found by screening. If no lead or cadmium was found by screening, use any leach solution to prepare test solutions *a*, *b*, and *c*.

- Prepare the fortified leach solution by adding a known amount of lead or cadmium to a portion (preferably ≥5 mL) of the leach solution. If concentration in the leach solution is >2 times the sample concentration limit, fortify the leach solution so that the concentration added by fortification is approximately 90-110% of the concentration due to test vessel. If concentration in the leach solution is ≤2 times the sample concentration limit, fortify the leach solution so that the concentration added is approximately equal to 2 times the sample concentration limit.

- Prepare 2 test solutions (*a* and *b*) from portions of unfortified leach solution by diluting with 4% acetic acid so that the test solutions produce 0.050 A-s to 0.350-0.400 A-s and so that instrument response of test solution *a* is approximately half that of test solution *b*; *i.e.*, test solution *a* produces 0.100 A-s and test solution *b* produces 0.200 A-s. For leach solutions that produce ≤2 times the sample concentration limit, place 2 undiluted portions (DF=1) in 2 different autosampler cups for analysis.

- Prepare 1 test solution (*c*) from the fortified leach solution. If concentration added by fortification is approximately 90-110% of the concentration due to test vessel, dilute with 4% acetic acid so that test solution *c* produces an instrument response approximately equal to that of test solution *b*. Dilution factors of test solution *c* and test solution *a* will be equal if these fortification recovery instructions are followed. If concentration added by fortification is equal to approximately 2 times the sample concentration limit, dilute fortified leach solution so that the dilution factor of the test solution *c* is 2.

- See examples below for of preparation of test solutions *a*, *b*, and *c*. Instrument responses, dilution factors, and sample concentration limits in the examples are applicable to instruments for which lead sensitivity (m_0) is 10 pg.

Example 1: If screening indicates that the highest concentration of lead is 0.5 µg/mL from sub-sample 1, fortify a portion of sub-sample 1 leach solution by adding 0.5 µg/mL (add 50 µL of a lead solution containing 50.0 µg/mL to 5.0 mL of sub-sample 1 leach solution). Dilute 2 portions of sub-sample 1 leach solution so that test solution *a* produces 0.100 A-s (DF = 50) and test solution *b* produces 0.200 A-s (DF = 25). Dilute 1 portion of fortified leach solution in an autosampler cup so that it produces 0.200 A-s (test solution *c*, DF = 50).

Example 2: If screening indicates that the concentration of all sub-samples is ≤2 times the sample concentration limit (≤0.010 µg/mL), fortify a portion of any sub-sample leach solution by adding 0.010 µg/mL (add 50 µL of a lead solution containing 1.0 µg/mL to 5.0 mL leach solution). Place 2 portions of undiluted leach solution, both of which produce ≤0.100 A-s, in 2 different autosampler cups (test solutions *a* and *b*, DF=1). Dilute 1 portion of fortified leach solution in an autosampler cup with an equal volume of 4% acetic acid so that it produces ≤0.100 A-s (test solution *c*, DF=2).

Preparation of Remaining Test Solutions

For each of the 5 sub-sample leach solutions which were not used to check for matrix interference, prepare 2 test solutions (test solutions *d* and *e*, *f* and *g*, ... *l* and *m*) to check for precision of the dilution process and absence of contamination in autosampler cups. Dilute leach solutions with 4% acetic acid so that the test solutions produce 0.050 to 0.350-0.400 A-s. Dilution factors of the 2 test solutions from the same sub-sample leach solution may be equal but the 2 test solutions must be prepared independently of each other and analyzed from 2 different autosampler cups.

11. Calibration

The analytical sequence which demonstrates that the instrument operated properly during the time leach solutions were analyzed is given in this Calibration section and the following section on Analysis of Check and Test Solutions. Do not vary the sequence. An example of the sequence is shown in Table 2.

Calibrate the instrument by analyzing calibration solutions that produce responses of 0.000 A-s (0 ng/mL) and approximately (±20%) 0.050, 0.100, 0.200, and 0.350-0.400 A-s. Analysis of a calibration solution which produces approximately 0.300 A-s is optional. Evaluate calibration curve. If errors in preparation of calibration solutions, deviations from linearity, or contamination are observed, correctly prepare new solutions and repeat calibration with new solutions.

Use least squares regression to calculate slope (m) and intercept (b) of the linear equation (y=mx+b) that best fits data from calibration solutions. Do not force equation through zero; use instrument response obtained from 0 ng/mL calibration solution. Instrument software may be used if it satisfies requirements of this section. Proceed immediately to analysis of check and test solutions.

12. Analysis of Check and Test Solutions

Verify the calibration and absence of carry-over and contamination by analyzing independent check solution and method blank leach solution. The dilution factor of the method blank must equal 1. Absence of carry-over may also be demonstrated by analyzing a 0 ng/mL check solution in addition to, but not as a substitute for, the method blank leach solution. If carry-over is indicated (if instrument response of method blank or 0 ng/mL check solution is >0.005 A-s), eliminate it by re-optimizing furnace program, re-calibrate instrument and analyze test solutions. If concentration found in independent check solution does not agree with the actual concentration within approximately ±5% relative difference, calibration or independent solutions, or both, have been prepared incorrectly. Determine source of error, prepare new solutions correctly, re-calibrate instrument and analyze test solutions. If contamination is found in method blank leach solution (if instrument response of method blank is greater than approximately 0.005 A-s), eliminate source of contamination, obtain 6 additional sub-samples, and repeat analysis beginning with sample preparation.

Check for matrix interference by analyzing test solutions *a*, *b*, and *c*. Calculate concentrations in unfortified and fortified leach solutions. If leach solution concentrations calculated from test solutions *a* and *b* agree within approximately ±5% relative difference and % recovery is acceptable (is approximately 90-110% recovery), interference is absent. If interference is indicated, eliminate the problem, re-calibrate instrument and re-analyze test solutions.

Analyze test solutions *d* through *m*. Calculate leach solution concentrations from results of single test solutions. If leach solution concentrations calculated from results of test solutions from the same sub-sample agree within approximately ±5% relative difference, test solutions have been diluted with acceptable precision and contamination is absent from autosampler cups. If concentrations do not agree, carefully prepare and analyze new test solutions.

After all test solutions have been successfully analyzed, verify absence of carry-over and reverify calibration by analyzing check solutions that produce 0.000 and approximately 0.100 (or 0.200-0.300) A-s. Calibration and absence of carry-over may be verified periodically during the time test solutions are analyzed in addition to, but not as a substitute for, verification at the end of the analytical sequence. If carry-over is indicated (if instrument response of 0 ng/mL check solution is >0.005 A-s) or calibration is no longer valid (if concentration found in check solution does not agree within approximately ±5% relative difference), discard all results obtained after last acceptable calibration and carry-over check. Eliminate source of error, re-calibrate instrument, and analyze remaining test solutions.

13. Report

For each sub-sample report the presence or absence of a spout or handle, internal height of vessel (length of a perpendicular line from lowest internal point to the plane defined by the top edge), mm, volume of leach solution, mL, concentrations of lead and cadmium in leach solution (C_{sub}), µg/mL, and masses of lead and cadmium extracted (M_{sub}), µg.

For the sample, report average of concentrations found in sub-sample leach solutions (C_{SPL}) and average of masses extracted (M_{SPL}).

For leach solutions with concentrations that are less than the limits, report <X and <Y, where X and Y are the numeric values of the sample concentration limit and sample mass limit, respectively.

Report sample concentration and mass limits for lead and cadmium; *i.e.*, SCL_{Pb} = 0.020 µg/mL and SML_{Pb} = 0.020 µg/mL) x 300 mL = 6 µg.

14. Calculations

Record and use 3 significant figures for all calculated values of analyte concentration and mass.

Concentration in Test Solution (C_{ts}), ng/mL

Use slope and intercept determined from calibration data and instrument response from test solution to calculate concentration in test solution, ng/mL, as follows:

$$C_{ts} = (A_{ts} - b)/m$$

where

A_{ts} = instrument response of test solution, A-s
b = intercept determined by linear least squares regression of calibration data, A-s
m = slope determined by linear least squares regression of calibration data, (A-s)/(ng/mL)

Alternatively, instrument software may be used to calculate C_{ts} if it meets requirements in Calibration section.

Concentration in Leach Solution Calculated from Result of Single Test Solution (C_{ls}), µg/mL

Use concentration found in test solution to calculate concentration in leach solution, µg/mL, as:

$$C_{ls} = (C_{ts\text{-}ls} \times DF \times 0.001) - (C_{ts\text{-}mb} \times 0.001)$$

where

$C_{ts\text{-}ls}$ = concentration in test solution prepared from leach solution, ng/mL
DF = dilution factor of test solution
0.001 = factor that converts ng/mL to µg/mL, (µg/mL)/(ng/mL)
$C_{ts\text{-}mb}$ = concentration in method blank test solution, ng/mL. DF_{mb} must = 1. If the absolute value of instrument response of method blank is less than approximately 0.005 A-s, zero (0) may be substituted for $C_{ts\text{-}mb}$.

Concentration in Sub-Sample Leach Solution (C_{sub}), µg/mL

Use concentrations calculated from results of single test solutions to calculate average concentration in leach solution, µg/mL.

$$C_{sub} = (C_{ls-1} + C_{ls-2})/2$$

where

$C_{ls\text{-}1}$ = leach solution concentration calculated from 1 of the test solutions of a sub-sample, µg/mL
$C_{ls\text{-}2}$ = leach solution concentration calculated from the other test solution of the sub-sample, µg/mL

Example: C_{ls-1} and C_{ls-2} are calculated from test solutions *a* and *b* for sub-sample 1, from test solutions *d* and *e* for sub-sample 2, and from test solutions *f* and *g* for sub-sample 3, etc.

Sample Concentration (C_{SPL}), µg/mL

Use sub-sample concentrations to calculate average concentration released from sample as:

$$C_{SPL} = (C_1 + C_2 + C_3 + C_4 + C_5 + C_6)/6$$

where

C_1-C_6 = are sub-sample concentrations (C_{sub}), µg/mL. For sub-sample concentrations <SCL, use C_{sub}=SCL/2, where SCL is the sample concentration limit calculated for lead and cadmium in 4% acetic acid.

Recovery of Fortified Analyte (Rec), %

Calculate percent recovery from fortified leach solution as follows:

$$Rec = 100 \times A/B$$

where

A = µg/mL recovered from fortified leach solution
B = µg/mL added to fortified leach solution

Calculate A and B as:

$$A = C - [(D \times E)/(E + F)]$$

$$B = (G \times F)/(E + F)$$

where

C = concentration found in fortified leach solution, µg/mL
D = concentration found in unfortified leach solution, µg/mL. When using percent recovery to check for matrix interference, calculate D from results of test solution *a* only. After matrix interference has been shown to be absent, calculate D from the average of results from test solutions *a* and *b*.
E = volume of leach solution in fortified leach solution, mL
F = volume of fortification solution in the fortified leach solution, mL
G = concentration of fortification solution used to fortify leach solution, µg/mL

Mass of Analyte Extracted from Food-Contact Surface (M), µg

Multiply concentration in sub-sample leach solution by volume of leach solution to obtain mass extracted as follows:

$$M = C_{sub} \times V$$

where

C_{sub} = concentration in sub-sample leach solution, µg/mL
V = volume of sub-sample leach solution, mL

Sample Concentration Limit (SCL), µg/mL

Calculate from the slope of the calibration curve as:

$$SCL = (0.050/m) \times 0.001$$

where

0.050 = definition of sample concentration limit, A-s
m = slope of calibration curve determined by least squares regression of calibration data, (A-s)/(ng/mL)
0.001 = factor that converts ng/mL to µg/mL, (µg/mL)/(ng/mL)

Sample Mass Limit (SML), μg

Calculate from the sample concentration limit and the volume of leach solution as:

$$SML = SCL \times V$$

where

SCL = sample concentration limit, μg/mL
V = volume of sub-sample leach solution, mL

15. Method Validation

The 24-hour leaching procedure for ceramicware is officially recognized by the American Society for Testing and Materials (Reference 1) and AOAC International (Reference 2). The method (Reference 3) successfully completed an interlaboratory trial (Reference 4). Precision and bias of graphite furnace AAS determinations of lead and cadmium in leach solutions were estimated by collaborative study (Reference 5) and are reported in Table 3. Quality control results obtained in the collaborative study are presented in Table 4. Sample concentration limits obtained in the collaborative study are presented in Table 5.

16. References

(1) American Society for Testing and Materials (1997) Standard Test Method for Lead and Cadmium Extracted from Glazed Ceramic Surfaces. *Annual Book of ASTM Standards, Volume 15.02, Glass; Ceramic Whitewares*, Standard Designation C738-94. ASTM, West Conshohocken, PA.

(2) AOAC International (1997) Lead and Cadmium Extracted from Ceramicware. *Official Methods of Analysis of AOAC International*, 16th Ed., 3rd Revision, Method 973.32. AOAC International, Gaithersburg, MD.

(3) Hight, S. C. (1998) Graphite Furnace Atomic Absorption Spectrometric Determination of Lead and Cadmium Extracted from Ceramic Foodware. *FDA Laboratory Information Bulletin No. 4123*, Food and Drug Administration, Division of Field Science, Rockville, MD.

(4) Hight, S. C. (1998) Interlaboratory Trial: Graphite Furnace Atomic Absorption Spectrometric Determination of Lead and Cadmium Extracted from Ceramic Foodware. *FDA Laboratory Information Bulletin No. 4124*, Food and Drug Administration, Division of Field Science, Rockville, MD.

(5) Hight, S. C. (1999) (*submitted to AOAC International*)

Table 1. Example of Operating Conditions Used for Determination of Pb and Cd in 4% Acetic Acid Leach Solutions[a]

Lab	Spectrometer Model	Furnace Model	Background Correction	Char & Atomization Temperatures, °C Pb	Cd	Matrix Modifier µg PO_4–µg Mg[b]	No. of Firings[c]	Characteristic Mass, pg Pb–Cd[d]	Volume of Test Solution, µL Pb–Cd[e]
Perkin Elmer Corp. (Norwalk, CT) Instrumentation									
1	4110–ZL	THGA	Zeeman	850–1750	800–2100	41–5	2	32–1.6[f]	20–10
2	5100–PC	HGA–600	Zeeman	850–1800	850–650	66–0 Pb, 66–4 Cd[g]	1	13–0.55[h]	20–10
5	2100	HGA–700	Deuterium	800–1200	600–100	8.3–0	2	11–0.45[i]	20–10
6	3300	HGA–600	Deuterium	not reported		41–0	2	15–0.63[i]	20–20
7	5100–ZL	THGA	Zeeman	850–1350	550–1300	41–0	3	25–0.90[f]	20–20
Varian Corp. (Sugarland, TX) Instrumentation									
3	AA–880Z	GTA–100	Zeeman	550–1850	500–1700	14–0 Pb, 7.2–0 Cd[j]	1	16–0.62[k]	10–16
4	AA–100	GTA–100	Zeeman	800–1900	750–1800	8.3–0	1	12–0.60[k]	20–10
R[l]	AA–300	GTA–96	Zeeman	1200–1800	1100–1700	8.3–0	1	9.6–0.38[k]	20–10

[a] From collaborative study reported in Reference 5.

[b] One matrix modifier was used for both Pb and Cd analyses except where noted. The sources of phosphate (PO_4) and magnesium (Mg) were $NH_4H_2PO_4$ and $Mg(NO_3)_2$, respectively.

[c] Indicates number of times furnace was cycled through the program to obtain each reading.

[d] Characteristic mass (m_o) was calculated as follows: $m_o = [1/S] \times V \times 0.0044$, where S is slope of the calibration curve ([A-s]/[ng/mL]), V is volume of test solution in furnace (µL), and 0.0044 is the defining instrument response (A-s) for characteristic mass.

[e] Indicates volume of test solution pipetted into furnace for analysis.

[f] Manufacturer specifications of characteristic mass for Pb and Cd on this furnace model using combination phosphate/magnesium are 30 and 1.3 pg, respectively.

[g] Phosphate modifier was used for Pb analysis. Combination phosphate/magnesium modifier was used for Cd.

[h] Manufacturer specifications of characteristic mass for Pb and Cd on this furnace model using combination phosphate/magnesium modifier are 12 and 0.5 pg, respectively.

[i] Manufacturer specifications of characteristic mass for Pb and Cd on this furnace model using phosphate modifier are 10 and 0.5 pg, respectively.

[j] Different amounts of phosphate were used for Pb and Cd analyses. No magnesium was used.

[k] Manufacturer specifications of characteristic mass for Pb and Cd on this furnace model using phosphate modifier are 16 and 0.6 pg, respectively.

[l] R indicates reference lab.

Table 2. Example of Analytical Sequence[a]

Anal-ysis	Test solution	DF[b]	Purpose of analysis
1	0.000 A-s (0 ng/mL) calibration solution	1	calibrate instrument & check for contamination in reagents
2	0.050 A-s calibration solution	1	calibrate instrument
3	0.100 A-s calibration solution	1	calibrate instrument
4	0.200 A-s calibration solution	1	calibrate instrument
5	0.300 A-s calibration solution (optional)	1	calibrate instrument
6	0.350-0.400 A-s calibration solution	1	calibrate instrument
7	independent check solution	1	verify calibration solutions
8	0 ng/mL check solution (optional)	1	document absence of carry-over
9	method blank solution	1	document absence of contamination
10	sub 1 (test solution *a*, example 1)	50	analyze leach solution
11	sub 1 (test solution *b*, example 1)	25	check analysis of leach solution
12	sub 1 (test solution *c*, example 1)	50	check % recovery from leach solution
13	sub 2 (test solution *d*)	50	analyze leach solution
14	sub 2 (test solution *e*)	25	check analysis of leach solution
15	sub 3 (test solution *f)*	10	analyze leach solution
16	0.200 A-s check solution (optional)	1	check calibration/instrument performance
17	0 ng/mL check solution (optional)	1	check carry-over
18	sub 3 (test solution *g*)	10	check analysis of leach solution
19	sub 4 (test solution *h*)	5	analyze leach solution
20	sub 4 (test solution *i*)	5	check analysis of leach solution
21	sub 5 (test solution *j*)	4	analyze leach solution
22	sub 5 (test solution *k*)	4	check analysis of leach solution
23	sub 6 (test solution *l*)	2	analyze leach solution
24	sub 6 (test solution *m*)	2	check analysis of leach solution
25	0.200 A-s check solution	1	check calibration/instrument performance
26	0.000 A-s (0 ng/mL) check solution	1	document absence of carry-over

[a]Analyses 10-12 are of test solutions prepared as in Fortification Recovery Example 1.
[b]DF indicates dilution factor.

Table 3. Precision, Bias and Collaborative Data for Determination of Lead and Cadmium by Graphite Furnace AAS in Blind Duplicate Portions of Ceramicware Leach Solutions[a]

	Lead, µg/mL			Cadmium, µg/mL		
Laboratory	Solution A	Solution B	Solution C	Solution A	Solution B	Solution C
1	0.0181	0.366	3.30	0.00210	0.0423	0.514
	0.0187	0.373	3.42	0.02210	0.0441	0.525
2	0.0201	0.409	3.87	0.00224	0.0464	0.640
	0.0206	0.416	3.86	0.00226	0.0450	0.529
3	0.0196[b]	0.402	3.68	0.00221	0.0444	0.417
	0.0266[c]	0.400	3.72	0.00224	0.0450	0.563
4	0.0213	0.402	3.70	0.00278[d]	0.0416	0.497
	0.0255	0.406	3.64	0.00247[d]	0.0516	0.597
5	0.0186	0.410	3.42	0.00266	0.0455	0.545
	0.0177	0.404	3.74	0.00256	0.0514	0.560
6	0.0173	0.400	3.88	0.00246	0.0457	0.522
	0.0186	0.404	3.89	0.00248	0.0457	0.600
7	0.0191	0.426	3.84	0.00225	0.0453	0.560
	0.0192	0.428	4.32	0.00224	0.0450	0.558
Statistical Evaluation						
Collaborator average, µg/mL	0.01957	0.4033	3.734	0.002361	0.04564	0.5448
Reference lab average, µg/mL	0.02015	0.4100	3.821	0.002337	0.04779	0.5818
Accuracy[e]*, %*	97	98	98	101	96	94
Repeatability						
s_r, µg/mL	0.00132	0.00353	0.159	0.000088	0.00317	0.0598
RSD_r, %	6.7	0.87	4.3	3.7	6.9	11
Reproducibility						
s_R, µg/mL	0.00227	0.0175	0.260	0.000216	0.00317	0.0598
RSD_R, %	12	4.4	7.0	9.1	6.9	11

[a] From Reference 5.

[b] Value was removed from data set to maintain balanced design for statistical evaluation (see footnote c).

[c] Value was removed from data set because quality control measurements on this solution were unacceptable when compared to quality control measurements of the other laboratories on this solution.

[d] This pair of values was a Cochran outlier (had significantly larger variance than variances of data pairs from other labs) but was retained in the data set for statistical evaluation because it was a statistical artifact of the extremely small variances (good precision) of the other values.

[e] Accuracy was calculated as 100 x [collaborator average/reference lab average].

Table 4. Average (and Range) of Quality Control (QC) Results Obtained During Collaborative Study of the Method[a]

Result	Analyte	Reference Laboratory	Collaborative Laboratories
QC duplicates (%RD)[b]	Pb	2 (0 to 5)	2 (0 to 7)[c]
	Cd	3 (0 to 6)	4 (0 to 11)
Independent check solutions (%RD)[d]	Pb	2 (1 to 6)	2 (0 to 4)
	Cd	5 (3 to 8)	7 (1 to 14)
Fortified leach solutions (percent Recovery)[e]	Pb	101 (94 to 105)	103 (96 to 118)
	Cd	101 (94 to 109)	99 (92 to 110)
Instrument sensitivity[f]	Pb	60 (58 to 61)	105 (75 to 150)
(percent of manufacturer specifications)	Cd	63 (60 to 65)	103 (69 to 126)
Carry-over and contamination check solutions			
(peak area, integrated atomic absorbance, A-s)	Pb	0.000 (-0.005 to 0.003)	0.002 (-0.002 to 0.013)
	Cd	-0.001 (-0.005 to 0.001)	0.001 (-0.002 to 0.011)
(approximate concentration, ng/mL)	Pb	-0.3 (-0.9 to 0.0)	-0.6 (-2.2 to 0.8)
	Cd	-0.04 (-0.07 to -0.01)	0.01 (-1.4 to 1.5)

[a] From Reference 5.

[b] Results of QC duplicates (test solutions *a* and *b*) are expressed as percent relative difference (%RD) of concentrations found.

[c] Values in table were calculated excluding outliers.

[d] Results are expressed as %RD of calculated and measured concentrations.

[e] Lead and cadmium concentrations added to fortified leach solutions were approximately 3.7 and 0.54 µg/mL, respectively. Lead and cadmium concentrations were approximately 3.7 and 0.54 µg/mL, respectively, in the unfortified leach solutions.

[f] Instrument sensitivity is described by characteristic mass and expressed in this table as a percent of manufacturer specifications. Values <100% indicate sensitivity that is better than manufacturer specifications. Values >100% indicate sensitivity that is not as good as manufacturer specifications. Values from 80 to 120% of manufacturer specifications are generally recommended.

Table 5. Sample Concentration Limits (SCL) Obtained During Collaborative Study of the Method[a]

Lab	SCL_{Pb}	SCL_{Cd}
1	0.018	0.0019
2	0.008	0.0006
3	0.019	0.0004
4	0.007	0.0007
5	0.006	0.0005
6	0.008	0.0004
7	0.014	0.0005
Reference	0.005	0.0004

[a] From Reference 5.

Figure 1.
Atomization profiles for determination of lead using 8.3 µg phosphate ion (PO_4^{-3}) as modifier: (A) 200 pg Pb in 20 µL test solution prepared from a ceramicware leach solution (vessel 271-1, DF=2), (B) 200 pg Pb in 20 µL 10.0 ng/mL calibration solution (m_0=8.9 pg), (C) 0 pg Pb in 20 µL 0.0 ng/mL calibration solution. Large peaks in A and B are atomic absorbance signals. Small peaks in A and B are background signals due to a portion of atomic absorbance included in the measurement by the spectrometer. (Background signals in A and B are not due to light scattering or molecular absorption and therefore are not illustrative of non-specific "background" absorbance.) Atomic and background absorbances are coincident and equal to zero in C. The horizontal portions of the segmented line in A, B, and C indicate relative temperature of the char and atomization steps of the furnace program. Char and atomization temperatures of this analysis are 1300°C and 1800°C, respectively.

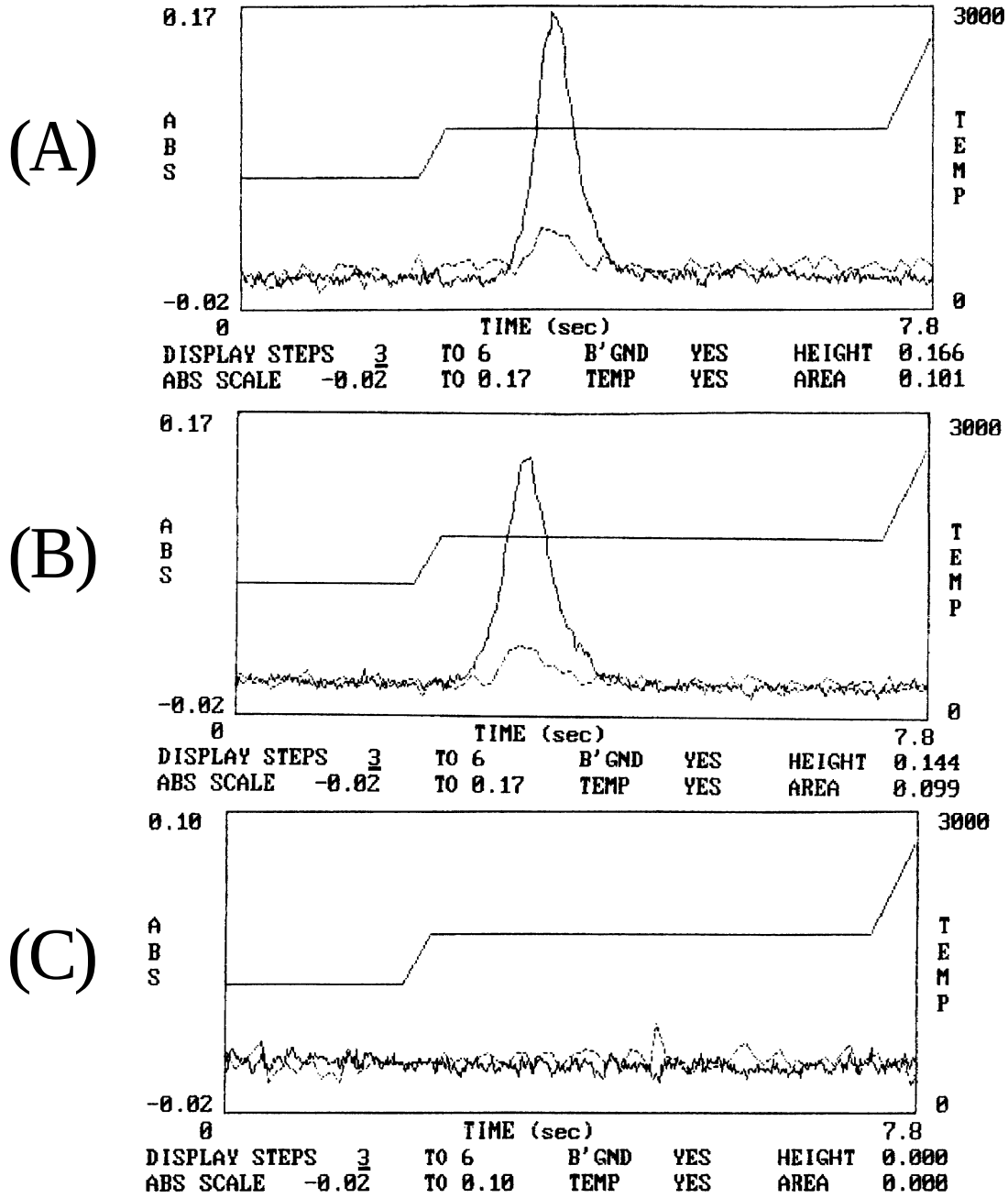
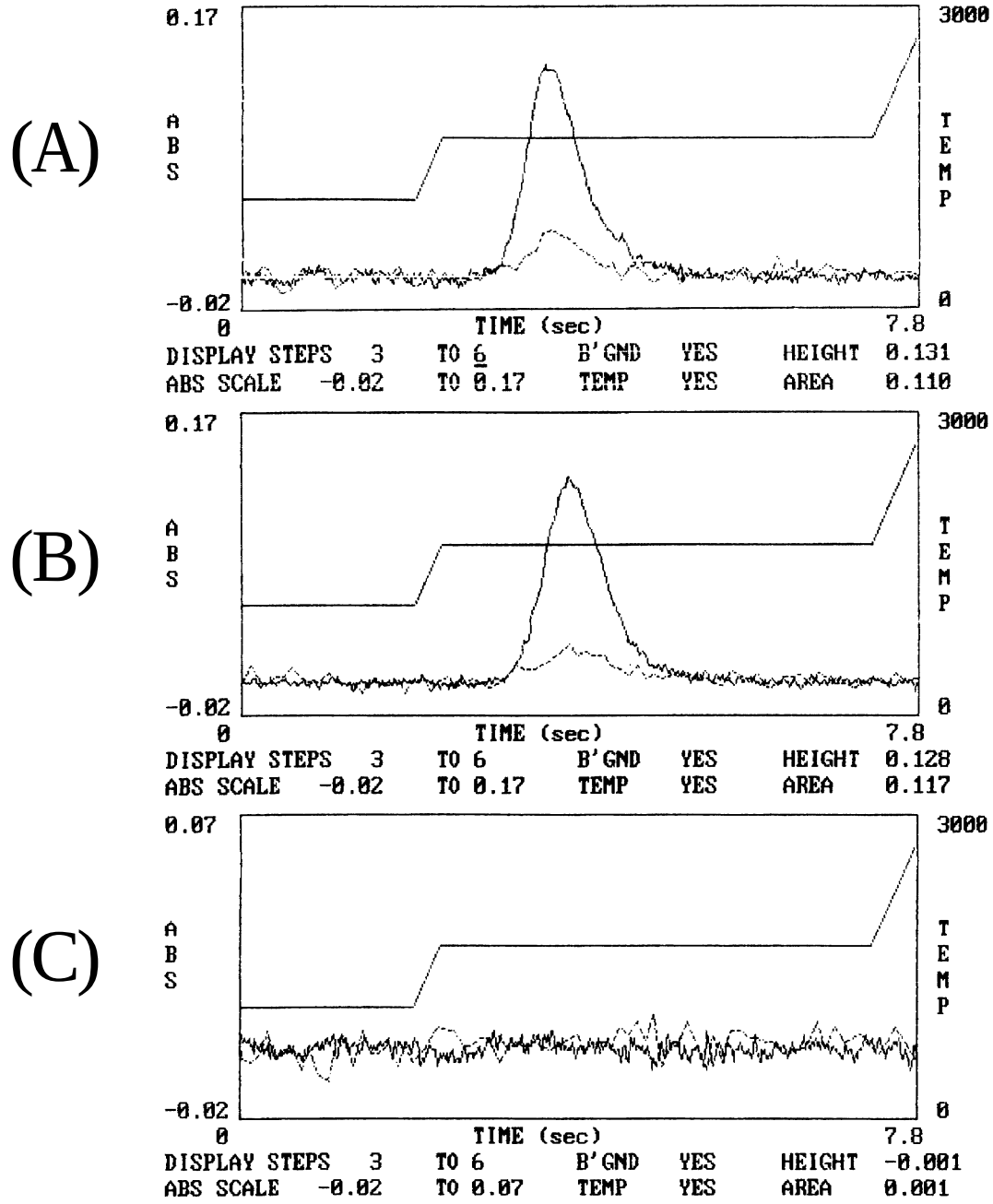


Figure 2.
Atomization profiles for determination of cadmium using 8.3 µg phosphate ion (PO_4^{-3}) as modifier: (A) 8.27 pg Cd in 10 µL test solution prepared from a ceramicware leach solution (vessel 210-2, DF=4.17), (B) 8.76 pg Cd in 10 µL 0.876 ng/mL calibration solution (m_0=0.33 pg), (C) 0 pg Cd in 10 µL 0.0 ng/mL calibration solution. Large peaks in A and B are atomic absorbance signals. Small peaks in A and B are background signals due to a portion of atomic absorbance included in the measurement by the spectrometer. (Background signals in A and B are not due to light scattering or molecular absorption and therefore are not illustrative of non-specific "background" absorbance.) Atomic and background absorbances are coincident and equal to zero in C. The horizontal portions of the segmented line in A, B, and C indicate relative temperature of the char and atomization steps of the furnace program. Char and atomization temperatures of this analysis are 1100°C and 1700°C, respectively.



Revision History

Revision 1 – Issued April, 2000

Definitions: Deleted reference to Smith-Hieftje background correction under working range.

Reagents: Corrected instructions for preparation of optional matrix modifier solution.

Table 1: Corrected matrix modifier values.

Revision 0 – Issued January, 2000