

## Graphite Furnace Atomic Absorption Spectrometric Determination of Lead and Cadmium Extracted from Ceramic Foodware

Susan C. Hight\*  
Center for Food Safety and Applied Nutrition (CFSAN)  
Elemental Research Branch

### INTRODUCTION

FDA is responsible for ensuring that foodware sold in the US does not release excessive amounts of lead and cadmium. These elements traditionally have been components of ceramic glazes, decorations, and lead crystal glass used to manufacture foodware and are known to migrate to food<sup>[1,2]</sup>. High concentrations of lead and cadmium released from silicate-based foodware can be determined by leaching for 24 hours with 4% acetic acid at room temperature and measuring lead and cadmium concentrations in the leach solutions using flame atomic absorption spectroscopy (AAS)<sup>[3,4]</sup>. To measure low concentrations, leach solutions must undergo time-consuming evaporative concentration before analysis by flame AAS<sup>[5]</sup>. Graphite furnace AAS is an extremely sensitive technique that can save time by eliminating the need for evaporative concentration when substituted for flame AAS in the 24-hour leaching procedure. Graphite furnace was recently shown to be effective in measuring a wide range of lead and cadmium concentrations in foodware leach solutions<sup>[6]</sup>. This LIB presents the method developed and used by CFSAN for determining low concentrations of lead and cadmium extracted from foodware. In this method, graphite furnace AAS is substituted for flame AAS to analyze leach solutions.

### METHOD

#### 1. Summary of Method

This test method describes procedures for using graphite furnace atomic absorption spectroscopy (GFAAS) 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 composed of silicate-based materials (earthenware, glazed ceramicware, decorated ceramicware, decorated glass, and lead crystal glass) and is capable of determining lead concentrations greater than 0.005–0.020  $\mu\text{g}/\text{mL}$  and cadmium concentrations greater than 0.0005–0.002  $\mu\text{g}/\text{mL}$ , depending on instrument design. 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 in) of overflowing and leaching them for 24 h at 20–24°C (68–75°F). Lead and cadmium are measured by GFAAS using phosphate modifier and instrumental background correction. Concentrations in leach solutions are calculated by using a calibration curve and linear least squares regression.

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\*For information about this LIB, contact Susan C. Hight, HFS-338, US Food and Drug Administration, 200 C Street SW, Washington, DC 20204 (e-mail: shight@bangate.fda.gov; phone: 202-205-4063)

## 2. Interferences

2.1 Non-specific absorption and scattering of light due to concomitant species in leach solutions may produce erroneously high results. Instrumental background correction must be used to compensate for this interference.

2.2 Concomitant elements in leach solutions may also 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 phosphate modifier and is monitored by calculating percent recovery from a portion of spiked (fortified) leach solution.

2.3 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.

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

## 3. Quality Control

3.1 This method describes specific quality control procedures to check for contamination and matrix interference during GFAAS analyses. The method also describes a specific sequence of analytical measurements that demonstrates proper instrument operation during the time period in which sample solutions are analyzed.

3.2 Cleaning and other procedures which have been shown to adequately control contamination are described in the method. Users may modify contamination control procedures provided that the modifications produce acceptable results and are used for both sample and quality control analyses.

## 4. Definition of Terms Specific to This Method

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

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

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

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

4.5 *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.

4.6 *Dilution factor (DF)*—factor by which concentration in test solution is multiplied to obtain concentration in original leach solution.  $DF = (V_1 + V_2) / V_1$  where  $V_1$  and  $V_2$  are volumes of leach solution and diluent in test solution, respectively.

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

4.8 *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.

4.9 *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. Independent check solutions must be used to verify calibrations until such time that a reference material certified for lead and cadmium leaching becomes available.

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

4.11 *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.

4.12 *Working range*—range of instrument response that may be described as a linear function of the mass of analyte. The linear region of graphite furnace peak area measurements is generally 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. Do not calculate and report concentrations from test solutions that produce <0.050 A-s or >0.350-0.400 when using this method. The linear region of instrument response was chosen as the working range of this method because responses in the linear region are well below those at which roll-over and self-reversal adversely affect lead and cadmium instrument responses obtained using Zeeman and Smith-Hieftje background correction, respectively.

4.13 *Sample concentration limit (SCL)*—a low concentration ( $\mu\text{g}/\text{mL}$ ) 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. Do not calculate and report concentrations from test solutions that produce <0.050 A-s. The value 0.050 A-s is chosen to establish the limit of the method for 2 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 % 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.

4.14 *Sample mass limit (SML)*—a low mass ( $\mu\text{g}$ ) 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.

4.15 *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 ( $\geq 1.0000$  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. Apparatus

5.1 *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 and appearance time that occur in leach and calibration solutions.

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

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

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

5.5 *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 (section 6.7). Disposable labware that does not need pre-cleaning is preferred<sup>1</sup>. 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.

5.6 *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<sup>2</sup> 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.

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

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

5.9 *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.

1. 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.
2. Micro Cleaner, a trademark of International Products Corp., Burlington, NJ, (catalogue number 6731) has been found suitable to clean laboratory glassware.

## 6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals may be used in all tests 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. At a minimum, all reagents must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society when such specifications are available.

6.2 *Reagent water*—Ultrapure, deionized, resistance  $\geq 18$  megohm-cm.

6.3 *Detergent solution for cleaning samples (0.02%, by volume)*—Mix 1 mL detergent with 5 L tap water. Use non-acidic, liquid detergent designed for washing household dishes by hand<sup>3</sup>. Do not use chemicals or detergents designed for cleaning labware because such detergents may damage the ware.

6.4 *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.

6.5 *Matrix modifier solution (1%, w/v,  $\text{NH}_4\text{H}_2\text{PO}_4$ )*—Dissolve 0.5 g ammonium dihydrogen phosphate in 50 mL reagent water. One  $\mu\text{L}$  contains 8.3  $\mu\text{g}$  phosphate ion ( $\text{PO}_4^{-3}$ ). Dilute with reagent water if less modifier is needed.

6.6 *Stock lead and cadmium solutions*—Use 1000 or 10,000  $\mu\text{g}/\text{mL}$  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.

6.7 *Intermediate lead and cadmium solutions*—Transfer by pipet  $\geq 1000$   $\mu\text{L}$  stock solution to acid-cleaned volumetric flask and dilute to  $\geq 100.0$  mL with 4% acetic acid.

6.8 *Calibration and independent check solutions*—Prepare calibration solutions that produce responses of 0.000 A-s (0 ng/mL) and approximately ( $\pm 20\%$ ) 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.

6.9 *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.

## 7. Sample Preparation and Leaching

7.1 Wash method blank and test vessels for 30 s by immersing in 0.02% detergent solution ( $\leq 40^\circ\text{C}$ ) and rubbing gently with soft cloth. Rinse with tap water ( $\leq 40^\circ\text{C}$ ) followed by copious quantities of reagent water. Air-dry in dust-free environment.

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

7.3 Immediately cover vessels to minimize evaporation<sup>4</sup>. Use opaque material or place vessel in dark location to prevent photo-oxidation of insoluble cadmium sulfide to soluble cadmium sulfate.

7.4 Leach vessels for 24 h at  $22 \pm 2^\circ\text{C}$ .

7.5 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 section.

7.6 Gently stir leach solutions with plastic device and transfer by pipet to plastic container.

3. Ajax or Joy, trademarks of Colgate-Palmolive Co., New York, NY and Proctor and Gamble Co., Cincinnati, OH, respectively, have been found suitable to clean test vessels.

4. 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 this purpose.

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.

7.7 Precipitated matter, if present, may be removed from leach solutions by filtering with PTFE filters in natural (not colored) polypropylene housings<sup>5</sup> attached to polypropylene syringes<sup>6</sup>. Acid-clean filters and syringes with 4% acetic acid immediately before use.

## 8. Instrument Optimization

8.1 Optimize spectrometer settings, furnace program, and mass of phosphate modifier for each element so that characteristic mass of lead and cadmium is  $\pm 20\%$  of manufacturer specifications, precision of 10 measurements is  $\leq 5\%$  (preferably  $\leq 3\%$ ) 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  $\mu\text{L}$  of a lead calibration solution (10  $\mu\text{L}$  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 reduce background absorbance of phosphate to zero. 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.

8.2 Concomitant elements in leach solutions may alter the atomization process and instrument response. Verify that the furnace program, mass of phosphate, and test solution dilutions 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 phosphate 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.

## 9. Screening of Leach Solutions and Preparation of Test Solutions

9.1 Complete screening, calibration, and analysis (sections 9, 10, and 11) for lead first. Then repeat sections 9, 10, and 11 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 minutes.

9.2 Screen leach solutions by serially diluting them with 4% acetic acid and analyzing the series until a dilution which produces 0.050 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.

9.3 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.

9.3.1 Prepare the fortified leach solution by adding a known amount of lead or cadmium to

5. Item no. 6159-06N, Lida Corp., Kenosha, WI, has been found suitable for this purpose.

6. Item no. 14-826-13, Fisher Scientific, Pittsburgh, PA, has been found suitable for this purpose.

a portion (preferably  $\geq 5$  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  $\leq 2$  times the sample concentration limit, fortify the leach solution so that the concentration added is approximately equal to 2 times the sample concentration limit.

9.3.2 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 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  $\leq 2$  times the sample concentration limit, place 2 undiluted portions ( $DF=1$ ) in 2 different autosampler cups for analysis.

9.3.3 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 instructions in sections 9.3.1 through 9.3.3 are followed. If concentration added by fortification is approximately equal to 2 times the sample concentration limit, dilute fortified leach solution so that the dilution factor of the test solution *c* is 2.

9.3.4 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  $0.5 \mu\text{g/mL}$  from sub-sample 1, fortify a portion of sub-sample 1 leach solution by adding  $0.5 \mu\text{g/mL}$  (add  $50 \mu\text{L}$  of a lead solution containing  $50.0 \mu\text{g/mL}$  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  $\leq 2$  times the sample concentration limit ( $\leq 0.010 \mu\text{g/mL}$ ), fortify a portion of any sub-sample leach solution by adding  $0.010 \mu\text{g/mL}$  (add  $50 \mu\text{L}$  of a lead solution containing  $1.0 \mu\text{g/mL}$  to 5.0 mL leach solution). Place 2 portions of undiluted leach solution, both of which produce  $\leq 0.100$  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  $\leq 0.100$  A-s (test solution *c*,  $DF=2$ ).

9.4 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.

## 10. Calibration

10.1 The analytical sequence which demonstrates that the instrument operated properly during the time leach solutions were analyzed is given in sections 10 (calibration) and 11 (analysis of check and test solutions). Do not vary the sequence.

10.2 Calibrate the instrument by analyzing calibration solutions that produce responses of 0.000 A-s (0 ng/mL) and approximately ( $\pm 20\%$ ) 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.

10.3 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.

10.4 Proceed immediately to section 11.

## 11. Analysis of Check and Test Solutions

11.1 Verify the calibration and absence of carry-over and contamination by analyzing independent check solution and method blank leach solution. 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 and repeating sections 10 through 11.1. If concentration found in independent check solution does not agree with the actual concentration within approximately  $\pm 5\%$  relative difference, calibration or independent solutions, or both, have been prepared incorrectly. Determine source of error, prepare new solutions correctly, and repeat sections 10 through 11.1. 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 sections 7 through 11.1.

11.2 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  $\pm 5\%$  relative difference and % recovery is acceptable (is approximately 90-110% recovery), interference is absent. If interference is indicated, eliminate the problem and repeat sections 10 through 11.2.

11.3 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  $\pm 5\%$  relative difference, test solutions have been diluted with acceptable precision and contamination is absent from autosampler cups. If concentrations do not agree, carefully prepare new test solutions and repeat section 11.3.

11.4 After all test solutions have been successfully analyzed, verify absence of carry-over and re-verify 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  $\pm 5\%$  relative difference), discard all results obtained after last acceptable calibration and carry-over check. Eliminate source of error, repeat section 10 (re-calibrate instrument), and repeat section 11 for remaining test solutions.

## 12. Report

12.1 For each sub-sample, report 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 ( $C_{sub}$ ),  $\mu\text{g/mL}$ , and masses of lead and cadmium extracted ( $\mu\text{g}_{sub}$ ),  $\mu\text{g}$ .

12.2 For the sample, report average of concentrations found in sub-sample leach solutions ( $C_{SPL}$ ) and average of masses extracted ( $\mu\text{g}_{SPL}$ ).

12.3 For sub-sample results calculated from test solutions that produce instrument response  $<0.050$  A-s, report  $<SCL$  and  $<SML$  where SCL is the sample concentration limit and SML is the sample mass limit.



**13. Calculations**

13.1 Concentration in test solution ( $C_{ts}$ )—Use slope and intercept determined in section 10.3 and instrument response in section 11 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 least squares regression in section 10.3, A-s

$m$  = slope determined by least squares regression in section 10.3, (A-s)/(ng/mL)

Alternatively, instrument software may be used to calculate  $C_{ts}$  if it meets requirements in section 10.3.

13.2 Leach solution concentration calculated from result of a single test solution ( $C_{ls}$ )—Use concentration found in test solution to calculate concentration in leach solution,  $\mu\text{g/mL}$ , as:

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

where

$C_{ts-ls}$  = concentration in test solution prepared from leach solution, ng/mL

DF = dilution factor of test solution

0.001 = factor that converts ng/mL to  $\mu\text{g/mL}$ , ( $\mu\text{g/mL}$ )/(ng/mL)

$C_{ts-mb}$  = 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  $C_{ts-mb}$ .

13.3 Percent recovery from fortified leach solution (%Rec)—Calculate % recovery from fortified leach solution as follows:

$$\% \text{Rec} = 100 \times A/B$$

where

A =  $\mu\text{g/mL}$  recovered from fortified leach solution

B =  $\mu\text{g/mL}$  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,  $\mu\text{g/mL}$

D = concentration found in unfortified leach solution,  $\mu\text{g/mL}$ . 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,  $\mu\text{g/mL}$

13.4 Leach solution concentration calculated from results of 2 test solutions (Sub-sample concentration,  $C_{sub}$ )—Use leach solution concentrations calculated from results of single test solutions to calculate average concentration for each sub-sample leach solution,  $\mu\text{g/mL}$ .

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

where

$C_{1s-1}$  = leach solution concentration calculated from 1 of the test solutions of a sub-sample,  $\mu\text{g/mL}$

$C_{1s-2}$  = leach solution concentration calculated from the other test solution of the sub-sample,  $\mu\text{g/mL}$

Example:  $C_{1s-1}$  and  $C_{1s-2}$  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.

13.5 Mass extracted from food-contact surface ( $\mu\text{g}$ )—Multiply concentration in sub-sample leach solution by volume of leach solution to obtain mass extracted as follows:

$$\text{mass extracted} = C_{\text{sub}} \times V$$

where

$C_{\text{sub}}$  = concentration in sub-sample leach solution,  $\mu\text{g/mL}$

$V$  = volume of sub-sample leach solution, mL

13.6 Calculate sample concentration limit (SCL),  $\mu\text{g/mL}$ , from the slope of the calibration curve as:

$$\text{SCL} = (0.050/\text{slope}) \times 0.001$$

where

0.050 = definition of sample concentration limit, A-s

slope = slope of calibration curve determined by least squares regression in section 10.3, (A-s)/(ng/mL)

0.001 = factor that converts ng/mL to  $\mu\text{g/mL}$ , ( $\mu\text{g/mL}$ )/(ng/mL)

13.7 Calculate sample mass limit (SML),  $\mu\text{g}$ , from the sample concentration limit and the volume of leach solution as:

$$\text{SML} = \text{SCL} \times V$$

where

SCL = sample concentration limit,  $\mu\text{g/mL}$

$V$  = volume of sub-sample leach solution, mL

#### METHOD VALIDATION

The 24-hour leaching procedure for ceramicware is officially recognized by the American Society for Testing and Materials<sup>[3]</sup> and AOAC International<sup>[4]</sup>. Use of GFAAS for analysis of leach solutions from decorated glass and ceramicware was validated by CFSAN<sup>[6]</sup>. In the validation study, leach solutions were obtained from 1 sub-sample of 9 different foodware articles. Foodware articles were chosen to represent various types of decorated glass and ceramicware that FDA generally encounters in its regulatory program. Results of the validation study were excellent and are summarized in Table 1. Examples of typical operating conditions and an analytical sequence are summarized in Tables 2 and 3. Examples of atomization profiles are shown in Figures 1 and 2. Note that precision of sample results is limited by the ability to obtain a representative sample of the statistical universe being sampled and may be worse than precision of GFAAS results for individual sub-samples. Analysis of large populations has shown that sample results for lead and cadmium release conform to a Pearson III distribution with a coefficient of variation between 30% and 140%, typically 60%<sup>[3]</sup>.

Table 1. Summary of results of method validation study<sup>(6)</sup>

Figure of Merit	Lead	Cadmium
Range of leach solution concentrations in study $\mu\text{g}/\text{mL}$	<0.006–19,200	<0.0005–0.086
Average (and range) of precision of GFAAS measurements (analysis of test solutions <i>a</i> and <i>b</i> ) % relative difference	2 (0.1–6)	3 (0–9)
Average (and range) of recovery %	102 (95–119)	98 (87–107)
Approximate fortification levels $\mu\text{g}/\text{mL}$	0.005–19,000	0.0005–0.085
Sample concentration limits $\mu\text{g}/\text{mL}$	0.006	0.0005
Characteristic mass (peak area), $m_0$ pg	9.6	0.45

Table 2. Example of operating conditions. Use furnace program as a guide. Optimum furnace program will vary.

## Furnace Program

Step	1	2	3	4	5	6
Temperature, °C	130 <sup>a</sup>	CT <sup>b</sup>	CT <sup>b</sup>	AT <sup>c</sup>	2700	130
Ramp time, s	0	16	0	0	0	12.9
Hold time, s	t <sup>d</sup>	5	2	5	2	2
Read signal	no	no	no	yes	no	no
Argon flow, L/min	3	3	0	0	3	3

<sup>a</sup> Step 1 preceded by injection (rate 2) of test solution onto 130°C platform.

<sup>b</sup> CT indicates char temperatures: Pb = 950°C, Cd = 950°C.

<sup>c</sup> AT indicates atomization temperatures: Pb = 1900°C, Cd = 1800°C.

<sup>d</sup> t indicates drying times: Pb = 80 s, Cd = 40 s.

Other operating conditions	Lead	Cadmium
Analytical wavelength, nm	283.3	228.8
Volume test solution in furnace, $\mu\text{L}$	20	10
Phosphate deposited in furnace, $\mu\text{g PO}_4^{-3}$	8.3	8.3
Lamp current, mA	5	4
	(same for lead and cadmium)	
Slit width, nm	0.5	
Slit height	normal	
Time constant	0.05	
Instrument mode	absorbance	
Measurement mode	peak area	
Replicates	1	
Background correction	Zeeman	
Lamp	hollow cathode	
Pyrolytic graphite-coated tubes	partitioned	
platforms	forked	
Instrument Manufacturer	Varian <sup>a</sup>	
Spectrometer	SpectrAA-300	
Furnace	GTA	
Autosampler	95PSD	

<sup>a</sup> Varian Associates, Sugarland, TX

Table 3. Example of Analytical Sequence<sup>a</sup>

Anal- ysis	Test solution	DF <sup>b</sup>	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 <i>a</i> , example 1)	50	analyze leach solution
11	sub 1 (test solution <i>b</i> , example 1)	25	check for interference in leach solution
12	sub 1 (test solution <i>c</i> , example 1)	50	check for interference in leach solution
13	sub 2 (test solution <i>d</i> )	50	analyze leach solution
14	sub 2 (test solution <i>e</i> )	25	check analysis of leach solution
15	sub 3 (test solution <i>f</i> )	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 <i>g</i> )	10	check analysis of leach solution
19	sub 4 (test solution <i>h</i> )	5	analyze leach solution
20	sub 4 (test solution <i>i</i> )	5	check analysis of leach solution
21	sub 5 (test solution <i>j</i> )	4	analyze leach solution
22	sub 5 (test solution <i>k</i> )	4	check analysis of leach solution
23	sub 6 (test solution <i>l</i> )	2	analyze leach solution
24	sub 6 (test solution <i>m</i> )	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

<sup>a</sup> Analyses 10-12 are examples of analysis of test solutions prepared in section 9.3 (example 1).

<sup>b</sup> DF indicates dilution factor.

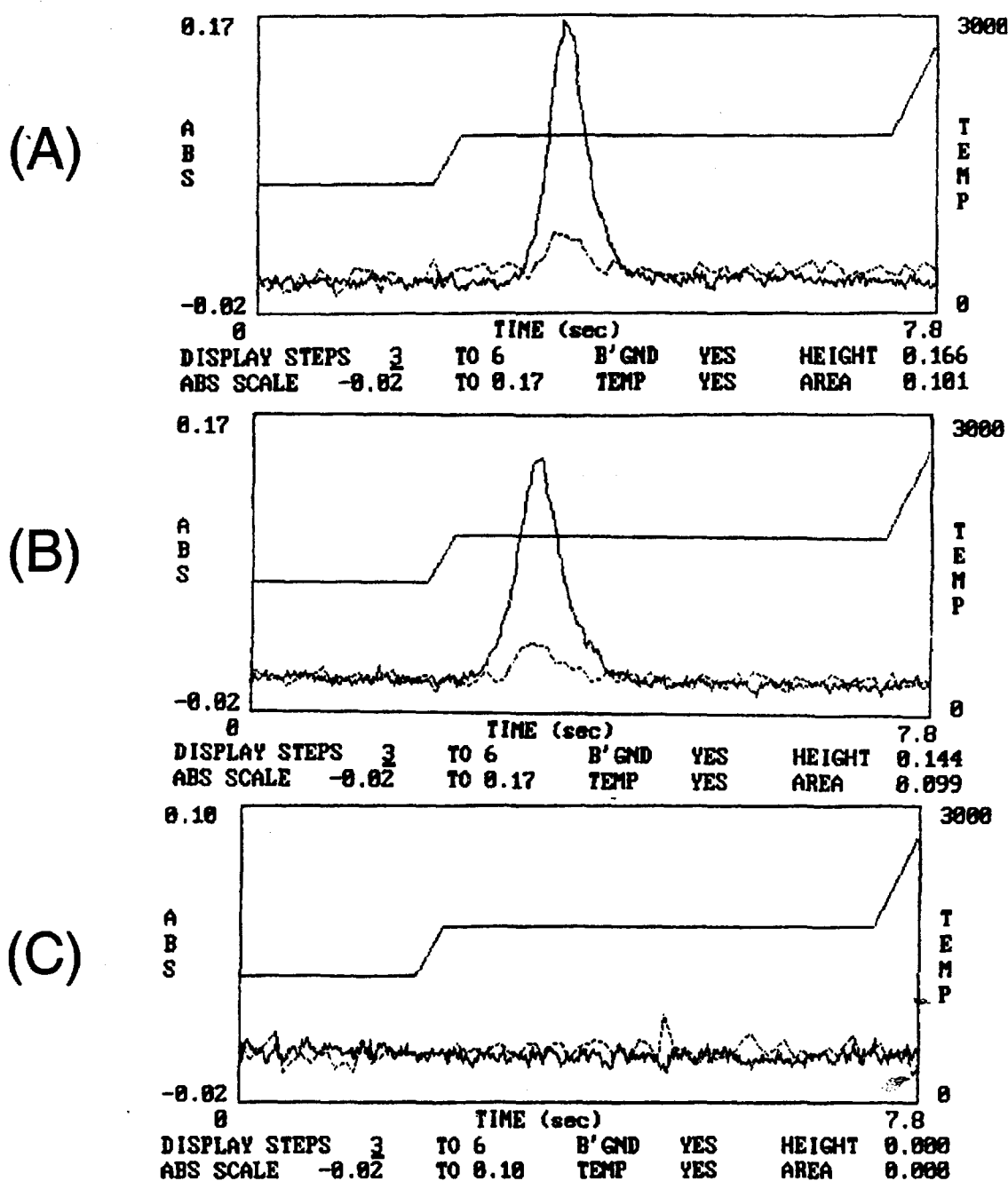


Figure 1. Atomization profiles for determination of lead using  $8.3 \mu\text{g}$  phosphate ion ( $\text{PO}_4^{3-}$ ) as modifier: (A) 200 pg Pb in  $20 \mu\text{L}$  test solution prepared from a ceramicware leach solution (vessel 271-1,  $\text{DF}=2$ ), (B) 200 pg Pb in  $20 \mu\text{L}$  10.0 ng/mL calibration solution ( $m_0=8.9 \text{ pg}$ ), (C) 0 pg Pb in  $20 \mu\text{L}$  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 segmented line in A, B, and C indicates temperature in program steps 3 and 4 and the ramp of step 5 (Table 2). Char and atomization temperatures of this analysis are  $1300^\circ\text{C}$  and  $1800^\circ\text{C}$ , respectively.

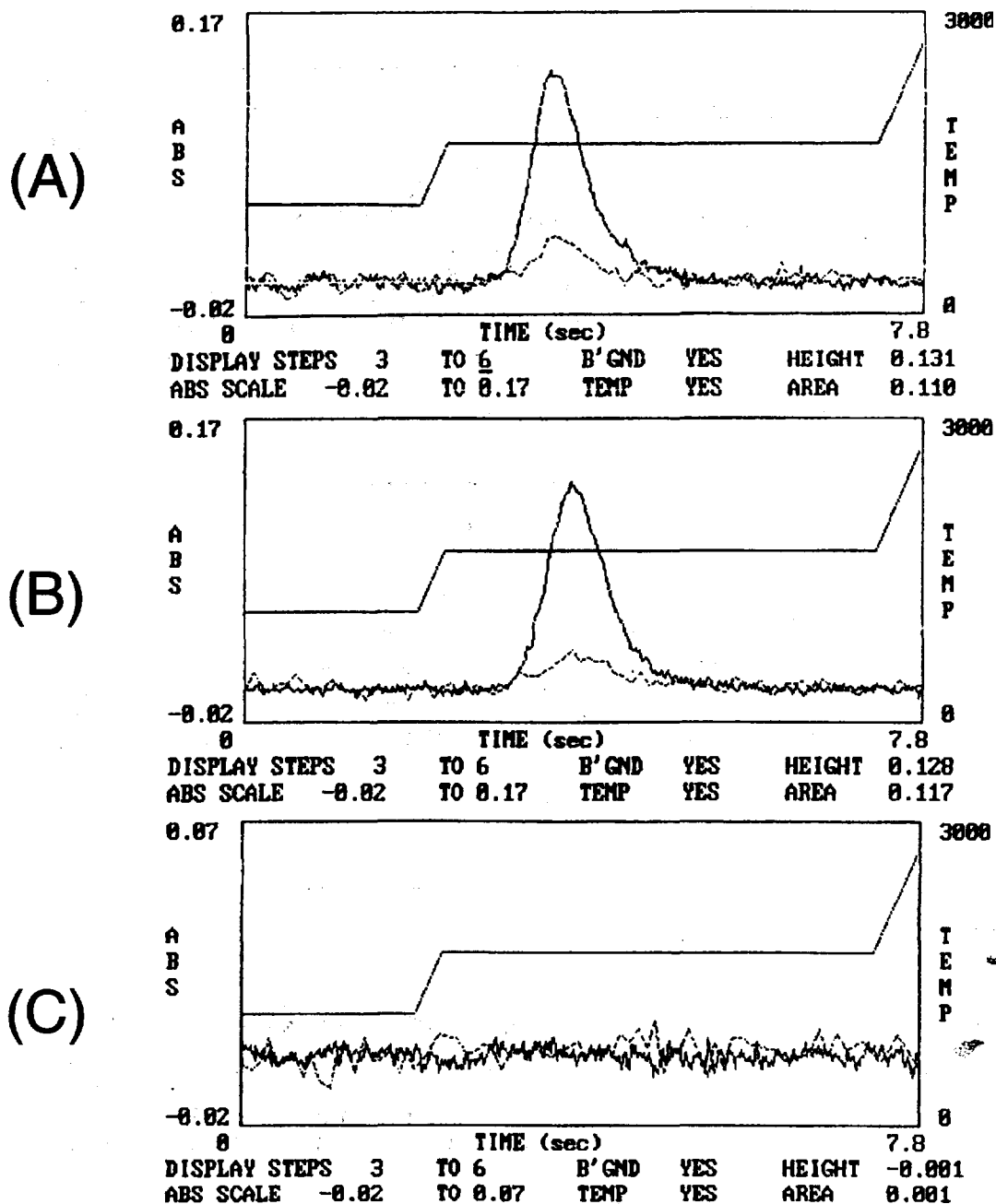


Figure 2. Atomization profiles for determination of cadmium using  $8.3 \mu\text{g}$  phosphate ion ( $\text{PO}_4^{-3}$ ) as modifier: (A)  $8.27 \mu\text{g}$  Cd in  $10 \mu\text{L}$  test solution prepared from a ceramicware leach solution (vessel 210-2,  $\text{DF}=4.17$ ), (B)  $8.76 \mu\text{g}$  Cd in  $10 \mu\text{L}$   $0.876 \text{ ng/mL}$  calibration solution ( $m_0=0.33 \mu\text{g}$ ), (C)  $0 \mu\text{g}$  Cd in  $10 \mu\text{L}$   $0.0 \text{ ng/mL}$  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 segmented line in A, B, and C indicates temperature in program steps 3 and 4 and the ramp of step 5 (Table 2). Char and atomization temperatures of this analysis are  $1100^\circ\text{C}$  and  $1700^\circ\text{C}$ , respectively.

**REFERENCES**

- [1] Hight, S. C., Gould, J. H., Mindak, W. R., Capar, S. G., 1995, *Ceramic Transactions Volume 61: Environmental and Waste Management Issues in the Ceramic and Nuclear Industries*, ed. V. Jain and R. Palmer (Westerville, OH, American Ceramic Society), pp. 11-22
- [2] Hight, S. C., *Food Additives and Contaminants*, 1996, vol. 13, no. 7, pp.747-765
- [3] American Society for Testing and Materials, *Annual Book of ASTM Standards, Volume 15.02, Glass; Ceramic Whitewares*, designation C738-94, ASTM, West Conshohocken, PA, 1997
- [4] *Official Methods of Analysis*, 1997, 16th Ed., 3rd Revision, Method 973.32, AOAC International, Arlington, VA
- [5] *Official Methods of Analysis*, 1997, 16th Ed., 3rd Revision, Method 973.82, AOAC International, Arlington, VA
- [6] Hight, S. C., *Standard Operating Procedure No. 108*, 1997, Elemental Research Branch, CFSAN, FDA