4.1 FLAME ATOMIC ABSORPTION SPECTROMETRIC DETERMINATION OF LEAD AND CADMIUM EXTRACTED FROM CERAMIC FOODWARE

1. Scope and Application

This method describes procedures for using flame atomic absorption spectrometry (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 1.0 µg/mL and cadmium concentrations greater than approximately 0.1 µg/mL. This method also describes contamination control procedures which ensure that leach solutions are not contaminated and are suitable for subsequent analysis by graphite furnace AAS if lead and cadmium concentrations are too low to be determined by flame AAS (are less than 1.0 and 0.1 µg/mL, respectively.) This method describes a specific analytical sequence of measurements which demonstrates proper instrument operation during the time period in which test 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 flame AAS using instrumental background correction. Concentrations in leach solutions are calculated by 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 aspirated into the flame 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 aspirated into the flame.

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 measured portions of leach solutions 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 in volumetric flasks, DF = V_2/V_1 where V_1 and V_2 are volumes of leach solution in volumetric flask and total volume of test solutions (volume of volumetric flask), respectively.

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. Independent check solutions must be used to verify calibrations 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. Fortified leach solutions are analyzed to calculate percent recovery. Stock, intermediate, and calibration solutions are used to fortify leach solutions.

Characteristic concentration (c_0)—concentration ($\mu g/mL$) of lead or cadmium that produces instrument response (peak area) of 0.0044 absorbance. Characteristic concentration is a measure of instrument sensitivity and is a function of instrument and nebulizer design and operating conditions. Characteristic concentration is calculated from the response of a solution that gives instrument response in the middle of the working range (*i.e.,* approximately 0.100 or 0.200 Abs) or from the slope of the calibration curve. Characteristic concentration 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 concentration. The linear region of flame AAS measurements is generally 0.050 to 0.350-0.400 Abs. 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.

Sample concentration limit (SCL)—a low concentration ($\mu g/mL$) 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 Abs. The value 0.050 Abs is chosen to establish the limit of the method for two reasons; 0.050 Abs is 10 times greater than the maximum response (0.005 Abs) typically expected from periodic, repeated analysis of a contamination-free, 0 $\mu g/mL$ 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 Abs than for lower values. The sample concentration limit depends on the characteristic concentration of the instrument; the numerical value of the limit increases as characteristic concentration increases.

Sample mass limit (SML)—a low mass (μg) of extractable lead or cadmium that can be reliably measured by this method. The sample mass 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, μg/mL
C_1 = concentration in initial solution, μg/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 must be used to compensate for this interference.

Contamination from laboratory glassware, supplies, and environmental particulate matter (dust) may cause erroneously high results for solutions that require subsequent analysis by graphite furnace AAS. Contamination must therefore be 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.

Note: 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.

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—equipped with light sources (hollow cathode or electrodeless discharge lamps) specific for lead and cadmium and instrumental background correction. To determine lead, use wavelength 283.3 nm for solutions containing high

concentrations and 217.0 nm for those containing either low or high concentrations. Use 228.8 nm for cadmium analyses. Record instrument response as absorbance (Abs).

Gas supply for flame—breathing quality air and welding or atomic absorption grade acetylene

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 calibration solutions and diluting leach solutions with high concentrations. 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 volumetric flasks dedicated for use with only this method to prepare calibration solutions and test solutions. Do not use glassware used for other laboratory operations because potential for contamination is too great. Do not use glass pipets. Wash glassware with warm tap water and laboratory detergent followed by soaking over with 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 AAS may require regents 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.

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 Abs (0 μg/mL) and approximately (±20%) 0.050, 0.100, 0.200, and 0.350-0.400 Abs. Prepare an independent check solution that produces approximately 0.300 Abs. Preparation of a calibration solution that produces approximately 0.300 Abs is optional.

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

Optimize spectrometer settings and nebulizer controls for each element so that characteristic concentration of lead and cadmium is ±20% of manufacturer specifications, precision of 10 measurements is ≤5% (preferably ≤2%) relative standard deviation. Use a calibration solution that produces approximately 0.100 or 0.200 Abs for the optimization process.

10. Screening of Leach Solutions and Preparation of Test Solutions

To prevent cross-contamination of bulk leach solutions by the nebulizer uptake tube, transfer a portion of leach solution to a 15 mL plastic container for flame AAS procedures. This contamination control precaution is essential if graphite furnace AAS procedures will be used for subsequent analysis of leach solutions that contain concentrations that are too low for measurement by flame AAS. Complete screening, calibration, and analysis procedures for lead first. Then repeat these procedures for cadmium. Hold test solutions in tightly sealed containers. Discard test solutions which have been held in unsealed containers for longer than 15-20 min.

Screening

Screen leach solutions as follows. Analyze undiluted and diluted (with 4% acetic acid) leach solutions until a test solution which produces instrument response in the working range (0.050 to 0.350-0.400 Abs) is found. Use this response and the dilution factor to calculate approximate concentration in each sub-sample leach solution. If undiluted leach solutions produce instrument response <0.050 Abs or have lead or cadmium concentrations <1.0 or <0.1 μg/mL, respectively, do not complete the analyses using flame AAS. Instead, use graphite furnace AAS procedures in EAM Method 4.2 to analyze the remainder of the bulk leach solutions. Do not skip the screening step because it serves 2 purposes; (a) it determines appropriate dilutions for test solutions for the final analytical run and (b) it determines appropriate fortification levels. Do not report results of screening because the instrument (a) is not properly calibrated and (b) requires 20-30 min warm-up after igniting the flame.

Preparation of Fortified Leach and Test Solutions

For each sample, prepare 1 fortified leach solution and appropriate test solutions to check for recovery and dilution error (test solutions *a*, *b*, and *c*). Use leach solution from the sub-sample which produced the highest concentration of lead or cadmium found by screening.

- Prepare the fortified leach solution by adding a known amount of lead or cadmium to a portion (preferably ≥5 mL) of the leach solution. 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 test solution(s) from the unfortified leach solution. If the leach solution produces instrument response >0.350-0.400 Abs, prepare 2 test solutions (*a* and *b*) from portions of unfortified leach solution by diluting with 4% acetic acid so that test solutions produce 0.050 to 0.350-0.400 Abs 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 Abs and test solution *b* produces 0.200 Abs. If the leach solution produces instrument response <0.350-0.400 Abs, analyze the undiluted leach solution as is (test solution *a*, DF = 1).

- 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 solutions *c* and *a* will be equal if these fortification recovery instructions are followed. If concentration added by fortification is approximately 2 times the sample concentration limit, analyze the fortified leach solution as is (test solution *c*, DF = 1).

The following are examples 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 (c_0) is 0.07 µg/mL.

Example 1: If screening indicates that the highest concentration of lead is 30 µg/mL from sub-sample 1, fortify a portion of sub-sample 1 leach solution by adding 30 µg/mL (add 150 µL of a lead solution containing 1000 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 Abs (DF = 20) and test solution *b* produces 0.200 Abs (DF = 10). Dilute 1 portion of fortified leach solution so that it produces 0.200 Abs (test solution *c*, DF = 20).

Example 2: If screening indicates that the concentration of all sub-samples is ≤2 times the sample concentration limit (≤1.2 µg/mL), fortify a portion of any sub-sample leach solution by adding 1.2 µg/mL (add 60 µL of a lead solution containing 100 µg/mL to 5.0 mL leach solution). Analyze test solutions *a* and *c* as is (DF=1).

Preparation of Remaining Test Solutions

For each of the 5 sub-sample leach solutions not used to prepare fortification recovery test solutions, prepare 1 test solution (test solutions *d* through *h*) that produces instrument response in the working range (0.050 through 0.350-0.400 Abs) by diluting leach solutions with 4% acetic acid when necessary.

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 1.

Calibrate the instrument by analyzing calibration solutions that produce responses of 0.000 Abs (0 µg/mL) and approximately (±20%) 0.050, 0.100, 0.200, and 0.350-0.400 Abs. Analysis of a calibration solution which produces approximately 0.300 Abs 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 μg/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 solution must equal 1. Absence of carry-over may also be demonstrated by analyzing a 0 μg/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 μg/mL check solution is >0.005 Abs), eliminate it and 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 check 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 Abs), eliminate source of contamination, obtain 6 additional sub-samples, and repeat analysis beginning with sample preparation.

Check for dilution error and recovery 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 approximately 90-110%, solutions have been diluted with good precision and recovery is acceptable. If results do not meet this criteria, test solutions have been prepared incorrectly or an interference, possibly precipitate, is present. Filter leach solutions, prepare test solutions again with greater care, re-calibrate instrument and re-analyze test solutions.

Analyze remaining test solutions (*d* through *h*).

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) Abs. 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 μg/mL check solution is >0.005 Abs) 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.

Figures 1 and 2 give examples of analytical data obtained for lead and cadmium, respectively, using the analytical sequence and flame AAS.

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 (μg_{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; *e.g.*, SCL_{Pb} = 0.020 $\mu g/mL$ and SML_{Pb} = (0.020 $\mu g/mL$) × 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}), $\mu g/mL$

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

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

where

A_{ts} = instrument response of test solution, Abs
b = intercept determined by linear least squares regression of calibration data, Abs
m = slope determined by linear least squares regression of calibration data, (Abs)/($\mu g/mL$)

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 a Single Test Solution (C_{ls}), $\mu g/mL$

Use concentration found in test solution to calculate concentration in leach solution, $\mu g/mL$, as:

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

where

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

Concentration in Leach Solution Calculated from Results of 2 Test Solutions (C_{ls-ab}), $\mu g/mL$

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

$$C_{ls-ab} = (C_{ls-a} + C_{ls-b})/2$$

where

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

Example: C_{ls-a} and C_{ls-b} are calculated from test solutions *a* and *b.*

Concentration in Sub-sample Leach Solution (C_{sub}), $\mu g/mL$

For the leach solution used to prepare test solutions *a* and *b*,
$$C_{sub} = C_{ls\text{-}ab}$$
For leach solutions used to prepare test solutions *d* through *h*,
$$C_{sub} = C_{ls}$$

Sample Concentration (C_{SPL}), $\mu g/mL$

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}), $\mu g/mL$. For sub-sample concentrations <SCL, use C_{sub}=SCL/2, where SCL is the sample concentration limit calculated for lead or 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 = $\mu g/mL$ recovered from fortified leach solution
B = $\mu g/mL$ 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, $\mu g/mL$
D = concentration found in unfortified leach solution, $\mu g/mL$. When using percent recovery to check for dilution error, calculate D from results of test solution *a* only. After dilution error 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, $\mu g/mL$

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, $\mu g/mL$
V = volume of sub-sample leach solution, mL

Sample Concentration Limit (SCL), μg/mL

Calculate from the slope of the calibration curve as:
$$SCL = 0.050/m$$
where

0.050 = definition of sample concentration limit, Abs
m = slope of calibration curve determined by least squares regression of calibration data, $(Abs)/(μg/mL)$

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). Collaborative study results showed that interlaboratory precision was approximately 5% and 11% relative standard deviation for lead concentrations 4.5-83 μg/mL and 1-2 μg/mL, respectively (References 3 and 4). 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 repeated flame AAS analysis of a single solution. 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% (Reference 5). Contamination and quality control procedures were taken from Reference 6.

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) Krinitz, B. and Franco, V. (1973) Collaborative Study of an Atomic Absorption Method for the Determination of Lead and Cadmium Extracted from Glazed Ceramic Surfaces. *J. Assoc. Off. Anal. Chem.* **56**, 869-875.

(4) Krinitz, B. and Holak, W. (1976) Collaborative Study of Effect of Light on Cadmium and Lead Leaching from Ceramic Glazes. *J. Assoc. Off. Anal. Chem.* **59**, 158-161.

(5) Moore, F. (1977) Some Statistical Aspects of Metal Release Regulations. *J. Br. Ceramic. Soc.* **76**, 52-57.

(6) Hight, S. C. (1998) Flame Atomic Absorption Spectrometric Determination of Lead and Cadmium Extracted from Ceramic Foodware. *FDA Laboratory Information Bulletin No. 4126*, Food and Drug Administration, Division of Field Science, Rockville, MD.

Table 1. Example of Analytical Sequence[a]

Analysis	Test solution	DF[b]	Purpose of analysis
1	0.000 Abs (0 µg/mL) calibration solution	1	calibrate instrument & check for contamination in reagents
2	0.050 Abs calibration solution	1	calibrate instrument
3	0.100 Abs calibration solution	1	calibrate instrument
4	0.200 Abs calibration solution	1	calibrate instrument
5	0.300 Abs calibration solution (opt'l)	1	calibrate instrument
6	0.350-0.400 Abs calibration solution	1	calibrate instrument
7	independent check solution	1	verify calibration solutions
8	0 µg/mL check solution (optional)	1	document absence of carry-over
9	method blank solution	1	document absence of contamination
10	spl 1 sub 1 (test solution *a*, example 1)	20	analyze leach solution
11	spl 1 sub 1 (test solution *b*, example 1)	10	check for dilution error
12	spl 1 sub 1 (test solution *c*, example 1)	20	check for recovery
13	spl 1 sub 2 (test solution *d*)	50	analyze leach solution
14	spl 1 sub 3 (test solution *e*)	25	analyze leach solution
15	spl 1 sub 4 (test solution *f*)	10	analyze leach solution
16	spl 1 sub 5 (test solution *g*)	10	analyze leach solution
17	spl 1 sub 6 (test solution *h*)	5	analyze leach solution
18	0.200 Abs check solution (optional)	1	check calibration/instrument performance
19	0 µg/mL check solution (optional)	1	check carry-over
20	spl 2 sub 1 (test solution *a*, example 2)	1	analyze leach solution
21	spl 2 sub 1 (test solution *b*, example 2)	1	check for dilution error
22	spl 2 sub 1 (test solution *c*, example 2)	1	check for recovery
23	spl 2 sub 2 (test solution *d*)	1	analyze leach solution
24	spl 2 sub 3 (test solution *e*)	1	analyze leach solution
25	spl 2 sub 4 (test solution *f*)	1	analyze leach solution
26	spl 2 sub 5 (test solution *g*)	1	analyze leach solution
27	spl 2 sub 6 (test solution *h*)	1	analyze leach solution
28	0.200 Abs check solution	1	check calibration/instrument performance
29	0.000 Abs (0 µg/mL) check solution	1	document absence of carry-over

[a]Analyses 10-12 and 20-22 are of test solutions prepared as in Fortification Recovery Examples 1 and 2, respectively.
[b]DF indicates dilution factor.

Figure 1. Examples of analytical data obtained for lead using flame AAS.

    Fig. 1A—calibration, linearity check, instrument operating conditions.

    Fig. 1B—analysis of test and check solutions, calculations of results.

    Fig. 1C—percent recovery and relative difference of results calculated from test solutions a, b and c.

Figure 1A.

Flame Atomic Absorption Spectrometry				Date	11/20/96		
Element:	Lead (Pb)			Analyst	S. Hight, K. Cook		
Matrix:	4% acetic acid leach solutions			Instrument	PE5000 Room 1056 FDA#1005083		
Sample:	ceramicware			Wavelength	217		
Method:	ASTM 738-94			HCL current	10 mAmps		
SOP:	109			Slit	0.7 nm (H)		
Comment:	sample IDs	259-1		Bkg corr'n	D2 on		
		247-1		Mode	abs (AA-BG)		
		271-1		Integration	3 sec		
		210-2		Signal	HOLD, AVG (2 integrations), CV		
		275-1		Nebulizer	PE high efficiency part# B050-5590		
		197-2		Flame	PE burner contrl box FDA#1005087		
		250-1		Air	rotam. 40 (30#/sq in.)		
		272-1		Acetylene	rotam. 20 (80#/sq in.)		
		108-1		PMT check	volts		
	instrument zeroed on H_2O			Energy check	52		
				AA-BG check	50-45		

Analysis of Calibration Solutions							
Data				Calculations - Linearity check		Rel. Dif. Conc.	
Concentration	Atomic			Actual Conc.	Calc'd Conc.	check, %	
µg/mL	Absorbance			µg/mL	µg/mL	calc-act/act	
0.00	0.005			0.00	-0.05		
0.50	0.040			0.50	0.49	-2	
1.00	0.073			1.00	1.00	0	
2.00	0.142			2.00	2.05	3	
3.00	0.207			3.00	3.05	2	
6.00	0.397			6.00	5.96	-1	

	Slope	Intercept	
	abs/ppm	atom. abs.	
	0.0653	0.0080	
Coefficient of determination (r squared)			1.000
Characterisitc concentration, µg/mL			
		this analysis	0.07
		manufacturer specification	<0.08
Sensitivity check, ppm/0.200 abs			
		this analysis	2.9
		manufacturer specification	<4
Sample conc. limit, ppm/0.050 abs			0.6

Plot of atomic absorbance vs. µg/mL (y-axis: atomic absorbance 0.000–0.500; x-axis: µg/mL 0.00–8.00).
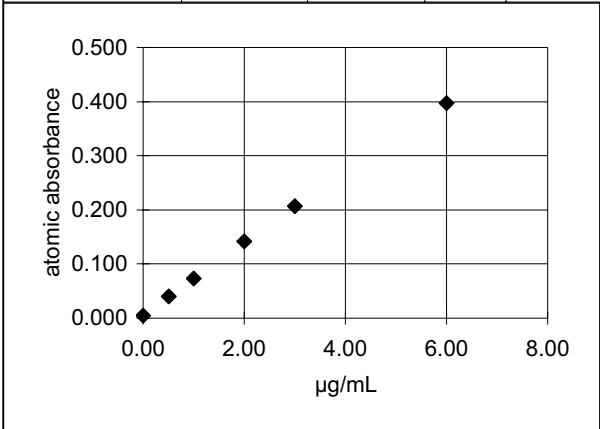
Figure 1B.

Flame Atomic Absorption Spectrometry					Date	11/20/96		
Element:	Lead (Pb)				Analyst	S. Hight, K. Cook		
Analaysis of Check and Test Solutions								
Data			Calculations			Actual Conc.		
			Calculated Concentration			of Check	Rel. Dif. Conc.	
	Dilution	Atomic	Test Soln	Leach Soln		Soln	check, %	
Test solution ID	Factor	Abs.	µg/mL	µg/mL		µg/mL	calc-act/act	Comment
independent chec	1	0.435	6.54	6.54		6.54	0	
check 0 ppm	1	0.005	-0.05	-0.05				
mb 210-2	1	0.004	-0.06	-0.06				<SCL
mb 197-2	1	0.004	-0.06	-0.06				<SCL
mb 250-1	1	0.004	-0.06	-0.06				<SCL
mb 272-1	1	0.004	-0.06	-0.06				<SCL
mb 108-1	1	0.004	-0.06	-0.06				<SCL
check 1 ppm	1	0.073	1.00	1.00		1.00	0	
check 2 ppm	1	0.140	2.02	2.02		2.00	1	
check 0 ppm	1	0.004	-0.06	-0.06				
259-1	1	0.004	-0.06	-0.06				<SCL
247-1	1	0.005	-0.05	-0.05				<SCL
271-1	1	0.005	-0.05	-0.05				<SCL
check 0 ppm	1	0.004	-0.06	-0.06				
210-2	1	0.032	0.37	0.37				<SCL
275-1	1	0.200	2.94	2.94				
197-2	1	0.466	7.02	7.02				
197-2	2	0.248	3.68	7.35				
250-1	100	0.380	5.70	569.93				
250-1	200	0.202	2.97	594.40				
check 2 ppm	1	0.140	2.02	2.02		2.00	1	
check 0 ppm	1	0.004	-0.06	-0.06				
272-1	1000	0.299	4.46	4,458.20				
272-1	2000	0.157	2.28	4,565.03				
108-1	4000	0.265	3.94	15,749.05				
108-1	8000	0.139	2.01	16,053.80				
check 2 ppm	1	0.140	2.02	2.02		2.00	1	
check 0 ppm	1	0.003	-0.08	-0.08				
275-1 spike	2	0.197	2.90	5.79				
197-2 spike	2	0.432	6.50	12.99				
197-2 spike	4	0.227	3.36	13.42				
250-1 spike	201	0.361	5.41	1,087.04				
250-1 spike	402	0.191	2.80	1,126.99				
272-1 spike	1000	0.418	6.28	6,281.49				
272-1 spike	2000	0.222	3.28	6,556.86				
108-1 spike	2857	0.310	4.63	13,218.60				
108-1 spike	5714	0.160	2.33	13,304.94				
check 3 ppm	1	0.205	3.02	3.02		3.00	1	
check 2 ppm	1	0.138	1.99	1.99		2.00	0	
check 1 ppm	1	0.071	0.96	0.96		1.00	-4	
check 0.5 ppm	1	0.036	0.43	0.43		0.50	-14	
check 0.25 ppm	1	0.019	0.17	0.17		0.25	-33	
check 0 ppm	1	0.002	-0.09	-0.09				

Figure 1C.

Flame Atomic Absorption Spectrometry				Date	11/20/96		
Element:	Lead (Pb)			Analyst	S. Hight, K. Cook		
Calculation of percent relative difference of leach solution concentrations							
derived from test solutions a and b							
	Leach Solution Concentration				Rel. Dif. Conc.		
	high	low		average		check, %	
Solution ID	µg/mL	µg/mL		µg/mL	100*(high-low)/low		
197-2	7.35	7.02		7.19	5		
250-1	594	570		582.16	4		
272-1	4,565	4,458		4511.62	2		
108-1	16,054	15,749		15901.42	2		
197-2 spike	13.4	13.0		13.21	3		
250-1 spike	1,127	1,087		1107.01	4		
272-1 spike	6,557	6,281		6419.17	4		
108-1 spike	13,305	13,219		13261.77	1		
Calculation of percent recovery							
Solution ID	C	D	E	F	G	µg/mL added	% Recovery
275-1 spike	5.79	2.94	5.00	0.150	100	2.91	101
197-2 spike	13.21	7.19	10.00	0.700	100	6.54	99
250-1 spike	1,107	582	1.000	0.060	10,000	566	99
272-1 spike	6,419	4,512	1.000	0.500	10,000	3,333	102
108-1 spike	13,262	15,901	0.500	0.500	10,000	5,000	106
% Recovery = 100 x A/B							
where							
A =	µg/mL recovered from spiked leach solution						
B =	µg/mL added to spiked leach solution						
Calculate A and B as:							
A =	C - [(D x E)/(E + F)]						
B =	(G x F)/(E + F)						
where							
C =	concentration found in spiked leach solution, µg/mL						
D =	concentration found in unspiked leach solution						
E =	volume of leach solution in spiked leach solution, mL						
F =	volume of spiking solution in spiked leach solution, mL						
G =	concentration of spiking solution, µg/mL						

Figures 2. Examples of analytical data obtained for cadmium using flame AAS.

    Fig. 2A—calibration, linearity check, instrument operating conditions.

    Fig. 2B—analysis of test and check solutions, calculations of results.

    Fig. 2C—percent recovery and relative difference of results calculated from test solutions *a*, *b* and *c* .

Figure 2A.

Flame Atomic Absorption Spectrometry				Date	11/21/96		
Element:	Cadmium (Cd)			Analyst	S. Hight, K. Cook		
Matrix:	4% acetic acid leach solutions			Instrument	PE5000 Room 1056 FDA#1005083		
Sample:	ceramicware			Wavelength	228.8		
Method:	ASTM 738-94			HCL current	4 mAmps		
SOP:	109			Slit	0.7 nm (H)		
Comment:	sample IDs	259-1		Bkg corr'n	D2 on		
		247-1		Mode	abs (AA-BG)		
		271-1		Integration	3 sec		
		210-2		Signal	HOLD, AVG (2 integrations), CV		
		275-1		Nebulizer	PE high efficiency part# B050-5590		
		197-2		Flame	PE burner contrl box FDA#1005087		
		250-1		Air	rotam. 40 (30#/sq in.)		
		272-1		Acetylene	rotam. 20 (80#/sq in.)		
		108-1		PMT check	volts		
	instrument zeroed on H_2O			Energy check	54		
				AA-BG check	50-50		

Analysis of Calibration Solutions							
Data				Calculations - Linearity check		Rel. Dif. Conc.	
Concentration	Atomic			Actual Conc.	Calc'd Conc.	check, %	
µg/mL	Absorbance			µg/mL	µg/mL	calc-act/act	
0.000	0.000			0.000	-0.007		
0.100	0.047			0.100	0.098	-2	
0.200	0.095			0.200	0.205	3	
0.300	0.140			0.300	0.306	2	
0.500	0.228			0.500	0.502	0	
0.600	0.273			0.600	0.603	0	
0.700	0.313						

			Slope	Intercept	
			abs/ppm	atom. abs.	
			0.4479	0.0030	
			Coefficient of determination (r squared)		1.000
			Characterisitc concentration, µg/mL		
				this analysis	0.01
				manufacturer specification	<0.02
			Sensitivity check, ppm/0.200 abs		
				this analysis	0.4
				manufacturer specification	<0.8
			Sample conc. limit, ppm/0.050 abs		0.1

Figure 2B.

Flame Atomic Absorption Spectrometry				Date	11/21/96		
Element:	Cadmium (Cd)			Analyst	S. Hight, K. Cook		
Analaysis of Check and Test Solutions							
Data			Calculations		Actual Conc.		
			Calculated Concentration		of Check	Rel. Dif. Conc.	
	Dilution	Atomic	Test Soln	Leach Soln	Soln	check, %	
Test solution ID	Factor	Abs.	µg/mL	µg/mL	µg/mL	calc-act/act	Comment
independent chec	1	0.317	0.701	0.701	0.695	1	
check 0 ppm	1	-0.001	-0.009	-0.009			
mb 275-1	1	-0.002	-0.011	-0.011			<SCL
mb 210-2	1	-0.002	-0.011	-0.011			<SCL
mb 250-1	1	-0.002	-0.011	-0.011			<SCL
mb 197-2	1	-0.002	-0.011	-0.011			<SCL
mb 108-1	1	-0.002	-0.011	-0.011			<SCL
check 0.1 ppm	1	0.046	0.096	0.096	0.100	-4	
check 0.2 ppm	1	0.093	0.201	0.201	0.200	0	
check 0 ppm	1	-0.002	-0.011	-0.011			
275-1	1	-0.002	-0.011	-0.011			<SCL
247-1	1	-0.001	-0.009	-0.009			<SCL
272-1	1	-0.001	-0.009	-0.009			<SCL
210-2	1	0.000	-0.007	-0.007			<SCL
250-1	1	-0.001	-0.009	-0.009			<SCL
check 0.1 ppm	1	0.046	0.096	0.096	0.100	-4	
check 0.2 ppm	1	0.094	0.203	0.203	0.200	2	
check 0 ppm	1	-0.002	-0.011	-0.011			
259-1	1	0.008	0.011	0.011			<SCL
271-1	1	0.038	0.078	0.078			<SCL
197-2	1	0.052	0.109	0.109			
108-1	1	0.218	0.480	0.480			
check 0.3	1	0.140	0.306	0.306	0.300	2	
check 0.5	1	0.230	0.507	0.507	0.500	1	
check 0 ppm	1	-0.002	-0.011	-0.011			
check 0.5 ppm	1	0.228	0.502	0.502	0.500	0	
check 0 ppm	1	-0.002	-0.011	-0.011			
197-2 spike	1	0.437	0.969	0.969			discard data; over range
197-2 spike	2	0.234	0.516	1.031			
108-1 spike	1	0.415	0.920	0.920			discard data; over range
108-1 spike	2	0.222	0.489	0.978			
check 0 ppm	1	-0.003	-0.013	-0.013			
check .1 ppm	1	0.046	0.096	0.096	0.100	-4	
check 0.2 ppm	1	0.093	0.201	0.201	0.200	0	
check 0.5	1	0.228	0.502	0.502	0.500	0	
197-2	1	0.052	0.109	0.109			
check 0.7 ppm	1	0.312	0.690	0.690	0.700	-1	
197-2	1	0.052	0.109	0.109			
check 0.7	1	0.312	0.690	0.690	0.700	-1	
197-2	1	0.052	0.109	0.109			
check 0.7 ppm	1	0.313	0.692	0.692	0.700	-1	
check 0.5 ppm	1	0.230	0.507	0.507	0.500	1	
108-1	1	0.218	0.480	0.480			
check 0 ppm	1	-0.003	-0.013	-0.013			
check 0.5 ppm	1	0.229	0.505	0.505	0.500	1	

Figure 2C.

Flame Atomic Absorption Spectrometry				Date	11/21/96		
Element: Cadmium (Cd)				Analyst	S. Hight, K. Cook		
Calculation of percent relative difference of leach solution concentrations							
derived from test solutions a and b							
	Leach Solution Concentration			Rel. Dif. Conc.			
	high	low		average	check, %		
Solution ID	µg/mL	µg/mL		µg/mL	100*(high-low)/low		
none analyzed				#DIV/0!		#DIV/0!	
Calculation of percent recovery							
Solution ID	C	D	E	F	G	µg/mL added	% Recovery
108-1 spike	0.978	0.480	10.00	0.050	100	0.498	101
197-2 spike	1.031	0.109	10.00	2.00	5.50	0.917	103
% Recovery = 100 x A/B							
where							
A = µg/mL recovered from spiked leach solution							
B = µg/mL added to spiked leach solution							
Calculate A and B as:							
A = C - [(D x E)/(E + F)]							
B = (G x F)/(E + F)							
where							
C = concentration found in spiked leach solution, µg/mL							
D = concentration found in unspiked leach solution							
E = volume of leach solution in spiked leach solution, mL							
F = volume of spiking solution in spiked leach solution, mL							
G = concentration of spiking solution, µg/mL							