



# Standard Test Method for Graphite Furnace Atomic Absorption Spectrometric Determination of Lead and Cadmium Extracted from Ceramic Foodware<sup>1</sup>

This standard is issued under the fixed designation C 1466; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers 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 to 0.020 µg/mL and cadmium concentrations greater than 0.0005 to 0.002 µg/mL, depending on instrument design.

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

1.3 Cleaning and other contamination control procedures are described in this test method. Users may modify contamination control procedures provided that the modifications produce acceptable results and are used for both sample and quality control analyses.

1.4 The values stated in SI (metric) units are to be regarded as the standard. The values given in parentheses are for information only.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

C 738 Test Method for Lead and Cadmium Extract from Glazed Ceramic Surfaces<sup>2</sup>

## 3. Terminology

### 3.1 Definitions of Terms Specific to This Standard:

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

3.1.2 *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 (that is, approximately 0.100 or 0.200 A-s). Characteristic mass is compared to manufacturer specifications to verify that the instrument is optimized.

3.1.3 *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.

3.1.4 *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 (gravimetric dilution),  $DF = W_T/W_1$  where:  $W_1$  is the weight of leach solution in test solution and  $W_T$  is the total weight of leach solution and diluent in the test solution.

3.1.5 *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.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee C-21 on Ceramic Whitewares and Related Products and is the direct responsibility of Subcommittee C21.03 on Test Methods for Whiteware Properties.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 15.02.

3.1.6 *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 (that is, both solutions contain 4 % acetic acid). Volumetric flasks must be used when the densities are different (that is, 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:

$$C_2 = C_1 \times W_1/W_2 \quad (1)$$

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; and

$W_2$  = weight of final solution, g.

3.1.7 *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.

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

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

3.1.10 *sample*—six test vessels of identical size, shape, color, and decorative pattern.

3.1.11 *sample concentration limit (SCL)*—a low concentration ( $\mu\text{g/mL}$ ) that can be reliably measured in leach solutions. In this test 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 this test method for two reasons; 0.050 A-s is ten 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 (ten times) greater than those in a true blank; and percent relative standard deviation of instrument response (relative variability as a result of 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 charac-

teristic mass increases and as the volume of solution deposited in the furnace decreases.

3.1.12 *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.

3.1.13 *subsample*—each of the six individual vessels which make up the sample.

3.1.14 *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.

3.1.15 *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 0.3500-0.400 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.

## 4. Summary of Test Method

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

## 5. Significance and Use

5.1 Toxic effects of lead and cadmium are well known and release of these elements from foodware is regulated by many countries. Regulatory decisions are based on results of 24-h leaching with acetic acid because results of this test method are precise and accurate and this test method is easy to use. Concentrations of lead and cadmium extracted by food may be different from results of this method, however, because acidity, contact time, and temperature typical of consumer use are different from those of this test method.

5.2 This test method is intended for application only in contamination-free settings and should be performed by well-qualified technical personnel. It is recognized that it is not a practical or appropriate method to use in a nonlaboratory environment for quality assurance and control of the ceramic process. Users are advised to use Test Method C 738 (flame AAS) for purposes of the latter.

## 6. Interferences

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

6.2 Concomitant elements in leach solutions 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.

6.3 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.

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

## 7. Apparatus

7.1 *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 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 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.

7.2 *Gas Supply for Furnace*, high purity (99.99 %) argon.

7.3 *Cooling Water for Furnace*—Use device that controls temperature and recirculates coolant.

7.4 *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.

7.5 *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 (8.7). Disposable labware that does not need precleaning is preferred.<sup>3</sup> When precleaning 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.

7.6 *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>4</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.

7.7 *Gloves, Powder-Free Vinyl*—Wear gloves when handling test vessels to prevent contamination.

7.8 *Polyethylene Bags, Self-Sealing*—Cover or wrap labware with new plastic bags of suitable size to prevent contamination from dust during drying and storage.

7.9 *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.

## 8. Reagents

8.1 *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.

8.2 *Reagent Water*—Ultrapure, deionized, resistance  $\geq 18$  megohm-cm.

8.3 *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. Do not use chemicals or detergents designed for cleaning labware because such detergents may damage the ware.

8.4 *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.

8.5 *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  $\mu$ L contains 8.3- $\mu$ g phosphate ion ( $\text{PO}_4^{-3}$ ).

8.5.1 *Optional Matrix Modifier Solution for Instruments with Zeeman Background Correction (1 %, w/v,  $\text{NH}_4\text{H}_2\text{PO}_4$  with 0.4 %, w/v, Mg)*—Dissolve 2.1-g magnesium nitrate hexahydrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) in 50 mL of phosphate modifier solution. One  $\mu$ L of optional modifier contains 8.3- $\mu$ g phosphate ion and 4.0- $\mu$ g magnesium ion.

8.6 *Stock Lead and Cadmium Solutions*—Use 1000- or 10 000- $\mu$ g/mL single-element stock solutions in 2 to 10 % nitric acid prepared specifically for spectrometric analysis. Do not

<sup>3</sup> The sole source of supply known to the committee at this time is Polypropylene centrifuge tubes with caps, 50-mL capacity (Item No. 2068, Becton Dickinson and Co., Franklin Lakes, NJ). If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

<sup>4</sup> The sole source of supply known to the committee at this time is Micro Cleaner, a trademark of International Products Corp., Burlington, NJ, (Catalogue No. 6731). If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.



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.

**8.7 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.

**8.8 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 to 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 1—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.

## 9. Sample Preparation and Leaching

**9.1** 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.

**9.2** Fill method blank and test vessels with 4 % acetic acid to within 6 to 7 mm ( $\frac{1}{4}$ in.) of the edge of the vessel measured along the surface. Record volume of extractant for each vessel.

**9.3** Immediately cover vessels to minimize evaporation<sup>5</sup>. Use opaque material or place vessel in dark location to prevent photo-oxidation of insoluble cadmium sulfide to soluble cadmium sulfate.

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

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

**9.6** Gently stir leach solutions with plastic device and transfer by pipet to plastic container. Do not pour. For best results, analyze within one 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.

**9.7** Precipitated matter, if present, may be removed from leach solutions by filtering with PTFE filters in natural (not colored) polypropylene housings<sup>6</sup> attached to polypropylene

syringes.<sup>7</sup> Acid clean filters and syringes with 4 % acetic acid immediately before use.

## 10. Instrument Optimization

**10.1** Optimize spectrometer settings, furnace program, and mass of chemical modifier for each element so that characteristic mass of lead and cadmium is within approximately  $\pm 20$  % of manufacturer specifications, precision of ten measurements is  $\leq 5$  % (preferably  $\leq 3$  %) relative standard deviation, and atomization peaks are symmetrically shaped and centered in a window of approximately 5 s. 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 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.

**10.2** 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 reoptimize furnace program and mass of chemical modifier so that percent recovery is 90 to 110 % (preferably 95 to 105 %) and the atomization peak obtained from leach solutions is properly shaped. Use reoptimized conditions to analyze all test (leach and calibration) solutions.

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

**11.1** Complete screening, calibration, and analysis (Sections 11, 12, and 13) for lead first. Then repeat Sections 11, 12, and 13 for cadmium. Hold test solutions in tightly sealed containers. Discard test solutions which have been held in unsealed autosampler cups for longer than 15 to 20 min.

**11.2** 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 to 0.400 A-s is found. Serial dilutions with  $DF = 1, 10, 100, 1000$ , and so forth are recommended. Calculate approximate concentration in each subsample leach

<sup>5</sup> The sole source of supply known to the committee at this time is polystyrene culture dishes (Item No. 25030-150, Corning Inc., Corning, NY and Item No. 4014, Nalgene Nunc International, Naperville, IL). If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

<sup>6</sup> The sole source of supply known to the committee at this time is Item No. 6159-06N, Lida Corp., Kenosha, WI. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

<sup>7</sup> The sole source of supply known to the committee at this time is Item No. 14-826-13, Fisher Scientific, Pittsburgh, Pa. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

solution from the instrument response and dilution factor of the dilution which produces a response in working range. Screening serves three 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.

11.3 For each sample, prepare one fortified leach solution and three test solutions (*a*, *b*, and *c*) to check for matrix interference. Use leach solution from the subsample 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*.

11.3.1 Prepare the fortified leach solution by adding a known amount of lead or cadmium to 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 to 110 % of the concentration caused by 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 two times the sample concentration limit.

11.3.2 Prepare two 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 to 0.400 A-s and so that instrument response of test solution *a* is approximately half that of test solution *b*; that is, test solution *a* produces 0.10 A-s and test solution *b* produces 0.200 A-s. For leach solutions that produce  $\leq 2$  times the sample concentration limit, place two undiluted portions ( $DF = 1$ ) in two different autosampler cups for analysis.

11.3.3 Prepare one test solution (*c*) from the fortified leach solution. If concentration added by fortification is approximately 90 to 110 % of the concentration as a result of the 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 11.3.1-11.3.3 are followed. If concentration added by fortification is equal to approximately two times the sample concentration limit, dilute fortified leach solution so that the dilution factor of the test solution *c* is 2.

11.3.4 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.

11.3.4.1 *Example 1*—If screening indicates that the highest concentration of lead is 0.5  $\mu\text{g/mL}$  from Subsample 1, fortify a portion of Subsample 1 leach solution by adding 0.5  $\mu\text{g/mL}$  (add 50  $\mu\text{L}$  of lead solution containing 50.0  $\mu\text{g/mL}$  to 5.0 mL of Subsample 1 leach solution). Dilute two portions of Subsample 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 one portion of fortified leach solution in an autosampler cup so that it produces 0.200 A-s (test solution *c*,  $DF = 50$ ).

11.3.4.2 *Example 2*—If screening indicates that the concen-

tration of all subsamples is  $\leq 2$  times the sample concentration limit ( $\leq 0.010 \mu\text{g/mL}$ ), fortify a portion of any subsample 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 two portions of undiluted leach solution both of which produce  $\leq 0.100$  A-s, in two different autosampler cups (test solutions *a* and *b*,  $DF = 1$ ). Dilute one 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*,  $DF = 2$ ).

11.4 For each of the five subsample leach solutions which were not used to check for matrix interference, prepare two 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 to 0.400 A-s. Dilution factors of two test solutions from the same subsample leach solution may be equal, but the two test solutions must be prepared independently of each other and analyzed from two different autosampler cups.

## 12. Calibration

12.1 The analytical sequence that demonstrates that the instrument operated properly during the time leach solutions were analyzed is given in Sections 12 (calibration) and 13 (analysis of check and test solutions). Do not vary the sequence. An example of the sequence is shown in Table 1 at the end of the method.

12.2 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 to 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.

12.3 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.

12.4 Proceed immediately to Section 13.

## 13. Analysis of Check and Test Solutions

13.1 Verify the calibration and absence of carryover and contamination by analyzing independent check solution and method blank leach solution. Absence of carryover 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 carryover 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 12-13.1. 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 12-13.1. If contamination is found in method blank leach solution (if instrument response of method blank is

**TABLE 1 Example of Analytical Sequence Described in Sections 12 and 13<sup>A</sup>**

Analysis	Test Solution	DF <sup>B</sup>	Purpose of Analysis
1	0.000 A-s (0-ng/mL) calibration solution	1	calibrate instrument and 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 to 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 carryover
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 analysis of leach solution
12	Sub 1 (test solution <i>c</i> , example 1)	50	check percent recovery from 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 carryover
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 carryover

<sup>A</sup>Analyses 10 through 12 are examples of analysis of test solutions prepared in 11.3 (Example 1).

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

greater than approximately 0.005 A-s), eliminate source of contamination, obtain six additional subsamples, and repeat Sections 9-13.1.

13.2 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 percent recovery is acceptable (is approximately 90 to 110 % recovery), interference is absent. If interference is indicated, eliminate the problem and repeat Sections 12-13.2.

13.3 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 subsample 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 13.3 for the new test solutions.

13.4 After all test solutions have been successfully analyzed, verify absence of carryover and reverify calibration by analyzing check solutions that produce 0.000 and approximately 0.100 (or 0.200 to 0.300) A-s. Calibration and absence of carryover 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 carryover 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 carryover check. Eliminate source of error, repeat Section 12 (recalibrate instrument), and repeat Section 13 for remaining test solutions.

## 14. Calculation

14.1 Record and use three significant figures for all calculated values of concentration and mass in Section 14.

14.2 *Concentration in Test Solution ( $C_{ts}$ )*—Use slope and intercept determined in 12.3 and instrument response in Section 13 to calculate concentration in test solution, ng/mL, as follows:

$$C_{ts} = (A_{ts} - b)/m \quad (2)$$

where:

$A_{ts}$  = instrument response of test solution, A-s;

$b$  = intercept determined by least squares regression in 12.3, A-s; and

$m$  = slope determined by least squares regression in 12.3, (A-s)/(ng/mL).

Alternatively, instrument software may be used to calculate  $C_{ts}$  if it meets requirements in 12.3.

14.3 *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:

$$C_{ls} = (C_{ts-ls} \times DF \times 0.001) - (C_{ts-mb} \times 0.001) \quad (3)$$

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); and

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

14.4 *Percent Recovery from Fortified Leach Solution*



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

$$\% \text{ Rec} = 100 \times A/B \quad (4)$$

where:

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

$B$  =  $\mu\text{g/mL}$  added to fortified leach solution.

Calculate  $A$  and  $B$  as:

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

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

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; and

$G$  = concentration of fortification solution used to fortify leach solution;  $\mu\text{g/mL}$ .

**14.5 Leach Solution Concentration Calculated from Results of Two Test Solutions (Subsample Concentration,  $C_{\text{sub}}$ )**—Use leach solution concentrations calculated from results of single test solutions to calculate average concentration for each subsample leach solution,  $\mu\text{g/mL}$ .

$$C_{\text{sub}} = (C_{\text{ls-1}} + C_{\text{ls-2}})/2 \quad (5)$$

where:

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

$C_{\text{ls-2}}$  = leach solution concentration calculated from the other test solution of the subsample,  $\mu\text{g/mL}$ .

**14.5.1 Example**— $C_{\text{ls-1}}$  and  $C_{\text{ls-2}}$  are calculated from test solutions  $a$  and  $b$  for Subsample 1, from test solutions  $d$  and  $e$  for Subsample 2, and from test solutions  $f$  and  $g$  for Subsample 3.

**14.6 Mass Extracted from Food-Contact Surface ( $\mu\text{g}$ )**—Multiply concentration in subsample leach solution by volume of leach solution to obtain mass extracted as follows:

$$\text{mass extracted} = C_{\text{sub}} \times V \quad (6)$$

where:

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

$V$  = volume of subsample leach solution, mL.

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

$$\text{SCL} = (0.050/\text{slope}) \times 0.001 \quad (7)$$

where:

0.050 = definition of sample concentration limit, A-s;

slope = slope of calibration curve determined by least squares regression in 12.3, (A-s)/(ng/mL); and  
0.001 = factor that converts ng/mL to  $\mu\text{g/mL}$ , ( $\mu\text{g/mL}$ )/(ng/mL).

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

$$\text{SML} = \text{SCL} \times V \quad (8)$$

where:

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

$V$  = volume of subsample leach solution, mL.

## 15. Report

**15.1** For each subsample, 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 ( $C_{\text{sub}}$ ),  $\mu\text{g/mL}$ , and masses of lead and cadmium extracted ( $\mu\text{g}_{\text{sub}}$ ),  $\mu\text{g}$ .

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

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

**15.4** Report sample concentration and mass limits for lead and cadmium; that is,  $\text{SCL}_{\text{Pb}} = 0.020 \mu\text{g/mL}$  and  $\text{SML}_{\text{Pb}} = (0.020 \mu\text{g/mL}) \times 300 \text{ mL} = 6 \mu\text{g}$ .

## 16. Precision and Bias

**16.1** Precision and bias of GFAAS determinations of lead and cadmium in leach solutions were estimated by collaborative study. Seven laboratories analyzed blind duplicate portions of leach solutions containing the following concentrations: lead at 0.0195, 0.403, and 3.73  $\mu\text{g/mL}$  and cadmium at 0.002 36, 0.0456, and 0.544  $\mu\text{g/mL}$ . Repeatability was 0.87 to 6.7 % relative standard deviation (RSD) for lead and 3.7 to 11 % RSD for cadmium. Reproducibility was 4.5 to 12 % RSD for lead and 7.0 to 11 % RSD for cadmium. Accuracy of collaborator results (calculated as  $100 \times [\text{overall collaborator average}/\text{reference lab average}]$ ) was 97 to 98 % for lead and 94 to 101 % for cadmium.

**16.2** Variability of lead and cadmium release between individual subsamples (test vessels) is greater than the variability of lead and cadmium determinations by GFAAS. Analysis of large numbers of test vessels has shown that lead and cadmium release data conform to a Pearson III distribution with a coefficient of variation between 30 and 140 %, typically 60 %.<sup>8</sup>

## 17. Keywords

17.1 cadmium release; ceramicware; foodware; graphite furnace atomic absorption spectrometry; lead release

<sup>8</sup> Moore, F., *Transactions and Journal of the British Ceramic Society*, Vol 76, No 3, 1977, pp. 52–57.

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