AOAC Official Method 999.17
Lead and Cadmium Extracted from Ceramic Foodware

Graphite Furnace Atomic Absorption Spectrometric (GFAAS) Method
First Action 1999

[Method is suitable for use on 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 μg/mL and cadmium concentrations greater than 0.0005–0.002 μg/mL, depending on instrument design. *See* Table **999.17A** for the results of the interlaboratory supporting the accetance of the method.]

Caution: Maintain safe distance from furnaces equipped with Zeeman background correction when the magnet is on. Consult manufacturer's instructions to determine safe distance, which varies for different instruments. *See* Appendix B, Laboratory Safety, for safe use of compressed gases, inorganic acids, and atomic absorption spectrometer.

A. Principle

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 (¼ in) of overflowing and leaching for 24 h at 20–24°C (68–75°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.

Quality control procedures check for contamination and matrix interference and a specific analytical sequence of measurements demonstrates proper instrument operation during the time period in which test solutions are analyzed.

B. Definitions of Terms Used in This Method

(**a**) *Sample*.—Six test vessels of identical size, shape, color, and decorative pattern.

(**b**) *Subsample*.—Each of the 6 individual vessels which make up the sample.

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

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

(**e**) *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.

(**f**) *Dilution factor (DF)*.—Factor by which concentration in test solution is multiplied to obtain concentration in original leach solution. For test solutions prepared by mixing pipet-measured portions of leach solution and diluent, $DF = (V_1 + V_2)/V_1$ where V_1 and V_2 are volumes of leach solution and diluent in test solution, respectively. For test solutions prepared by mixing weighed portions of leach solution and diluent (gravimetric dilution), $DF = W_T/W_1$ 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.

Table 999.17A Interlaboratory study results for the determination of lead and cadmium in ceramicware leach solutions by graphite furnace atomic absorption spectroscopy[a]

	Lead			Cadmium		
Statistic	Solution A[b]	Solution B	Solution C	Solution A[c]	Solution B	Solution C
No. of labs in statistical evaluation	6	7	7	7	7	7
No. of labs excluded from statistical evaluation	1	0	0	0	0	0
Collaborative average, μg/mL	0.0196	0.403	3.73	0.00236	0.0456	0.544
Reference laboratory average, μg/mL	0.0202	0.410	3.82	0.00234	0.0478	0.582
Accuracy[d], %	97	98	98	101	95	93
Repeatability						
s_r, μg/mL	0.0013	0.0035	0.16	0.000088	0.0032	0.060
RSD_r, %	6.7	0.87	4.3	3.7	7.0	11
r value ($2.8 \times s_r$), μg/mL	0.0036	0.010	0.45	0.00025	0.0090	0.17
Reproducibility						
s_R, μg/mL	0.0023	0.018	0.260	0.00022	0.0032	0.060
RSD_R, %	12	4.5	7.0	9.3	7.0	11
R value ($2.8 \times s_R$), μg/mL	0.0064	0.050	0.73	0.0062	0.0090	0.17

[a] Interlaboratory study results statistics are calculated for results obtained by each collaborator analyzing a portion of leach solution prepared from a single test vessel. Variability of results from multiple test vessels is greater than the variability of the graphite furnace determination. Average and range of variability of results of multiple test vessels is typically 60 and 30–140% relative standard deviation, respectively.

[b] Values were calculated excluding results from laboratory 3.

[c] Values were calculated including Cochran outliers. When Cochran outliers were excluded, statistics were: number of laboratories in evaluation, 6; number of laboratories excluded, 1; collaborator average, 0.002317 μg/mL; accuracy, 99%; s_r, 0.000031 μg/mL; RSD_r, 1.4%; r value, 0.000087 μg/mL; s_R, 0.00019 μg/mL; RSD_R, 8.1%; R value, 0.00053 μg/mL.

[d] Accuracy was calculated as 100 × collaborator average/reference laboratory average.

(**g**) *Calibration solutions*.—4% Acetic acid solutions containing known amounts of lead or cadmium which are used to calibrate the instrument.

(**h**) *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 test 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 test 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.

(**i**) *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.

(**j**) *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.

(**k**) *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.

(**l**) *Working range*.—Range of instrument response that may be described as a linear function of the mass of analyte. The linear range of graphite furnace peak area measurements is approximately 0.050 to 0.350–0.400 A-s. The range of linear response depends on the element and operating conditions and must be verified by analyzing calibration solutions each time the instrument is used. The linear range of instrument response was chosen as the working range of this method because responses in the linear range are well below those at which roll-over and self-reversal adversely affect Pb and Cd instrument responses obtained using Zeeman and Smith-Hieftje background correction, respectively.

(**m**) *Analyte concentration limit (ACL)*.—A low concentration (μg/mL) that can be reliably measured in leach solutions. In this method, the analyte concentration limit is the concentration of Pb or Cd that produces 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 test solutions are significantly (10 times) greater than those in a true blank; and percent relative standard deviation of instrument response (relative variability due to instrument precision) is better for 0.050 A-s than for lower values. The analyte 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.

(**n**) *Analyte mass limit (AML)*.—A low mass (μg) of extractable Pb or Cd that can be reliably measured by this method. The analyte mass limit is the product of the concentration limit times the volume of leach solutions.

(**o**) *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:

$$C_2 = C_1 \times \frac{\quad}{\quad}$$

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.

C. Apparatus

(**a**) *Atomic absorption spectrometer*.—Capable of displaying and recording fast, transient signals, measuring peak area, and having sensitivity (m_0 based on peak area) ≤ to 30 pg Pb and 1.3 pg Cd when wavelengths 283.3 and 228.8 nm are used for Pb and Cd determinations, respectively; equipped with light sources (hollow cathode or electrodeless discharge lamps) specific for Pb and Cd, 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 Pb and Cd, 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.

(**b**) *Gas supply for furnace*.—High purity (99.99%) argon.

(**c**) *Cooling water for furnace*.—Use device that controls temperature and recirculates coolant.

(**d**) *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. Do not use glass pipets.

(**e**) *Plastic labware*.—Use plastic labware (graduated cylinders, beakers, stirrers, containers, pipette tips, autosampler cups) for all procedures except preparation of intermediate Pb and Cd in **D**(**g**). Disposable labware that does not need pre-cleaning is preferred. Test before using. If pre-cleaning is needed to eliminate contamination, rinse plastic labware with 10% (1 + 9) HNO_3 followed by rins-

ing with copious quantities of reagent water. Air-dry the ware in a dust-free environment.

(**f**) *Filtration device*.—Use PTFE filters in natural (not colored) polypropylene housings attached to polypropylene syringes to remove particulate matter from leach solutions. Acid-clean filters and syringes with 4% acetic acid immediately before use.

(**g**) *Glassware*.—Use volumetric flasks dedicated for use with only this method to prepare intermediate calibration solutions. Do not use flasks used for other laboratory operations because potential for contamination is too great. Wash new flasks with warm tap water and laboratory detergent (Micro Cleaner, a trademark of International Products Corp., Burlington, NJ 08016 USA, Cat. No. 6731, is suitable to clean laboratory glassware) followed by soaking overnight in 10% (1 + 9) HNO_3 and rinsing with copious quantities of reagent water. Air-dry in dust-free environment. Dedicated volumetric flasks may be reused after rinsing with copious quantities of reagent water and repeating the acid-cleaning procedure.

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

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

(**j**) *Polystyrene culture dishes*.—Cover test vessels with plastic during leaching to prevent evaporation. Culture dishes, item No. 25030-150, Corning, Inc., Corning, NY 14830 USA, and item No. 4014, Nalgene Nunc International, 200 North Aurora Rd, Naperville, IL 60563 USA, are suitable for this purpose.

(**k**) *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.

D. Reagents

Check reagents for contamination before use in this method.

(**a**) *Reagent water*.—Ultrapure, deionized, resistance ≥18 megohm-cm.

(**b**) *Detergent solution for cleaning test vessels (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 test vessels.

(**c**) *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.

(**d**) *Matrix modifier solution (1%, w/v, $NH_4H_2PO_4$)*.—Dissolve 0.5 g $NH_4H_2PO_4$, in 50 mL reagent water. One microliter contains 8.3 µg phosphate ion (PO_4^{3-}). *Optional matrix modifier solution [1%, w/v, $NH_4H_2PO_4$ with 4.2%, w/v, $Mg(NO_3)_2 \cdot 6H_2O$]*.—Dissolve 2.1 g $Mg(NO_3)_2 \cdot 6H_2O$ in 50 mL phosphate modifier solution. One µL of optional modifier contains 8.3 µg phosphate ion and 4.0 µg magnesium ion.

(**e**) *Stock lead and cadmium solutions*.—Use 1000 or 10 000 µg/mL single-element stock solutions in 2–10% HNO_3 prepared specifically for spectrometric analysis. Do not use solutions containing HCl, H_2SO_4, or H_3PO_4. Multi-element solutions may be used to prepare independent check solutions. Commercially prepared stock solutions are recommended.

(**f**) *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.

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

(*Note*: Daily preparation of intermediate, independent check, and calibration solutions is recommended. Solutions may be held 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.)

E. Sample Preparation and Leaching

(**a**) 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.

(**b**) Fill method blank and test vessels with 4% acetic acid to within 6–7 mm (¼ in) of the edge of the vessel measured along the surface. Use a contamination-free measuring device (i.e., graduated cylinder or measuring pipet) to dispense extractant into vessel. Record volume of extractant for each vessel.

(**c**) 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.

(**d**) Leach vessels for 24 h at 22 ± 2°C.

(**e**) 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. Use a contamination-free device to add extractant to vessel. Proceed immediately to next section.

(**f**) 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.

(**g**) Particulate matter, if present, may be removed from leach solutions by filtering with acid-cleaned PTFE filters in natural (not colored) polypropylene housings attached to acid-cleaned, contamination-free polypropylene syringes.

F. Instrument Optimization

(**a**) Optimize spectrometer settings, furnace program, and mass of chemical modifier for each element so that characteristic mass of Pb and Cd is within approximately ±20% of manufacturer specifications, precision of 10 measurements is ≤5% (preferably ≤3%) relative standard deviation, and atomization peaks are symmetrically shaped and centered in a window of approximately 5 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 µL Pb calibration solution (10 µL Cd 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.

(**b**) Concomitant elements in leach solutions may alter the atomization process and instrument response. Verify that the furnace program, mass of chemical modifier, and test solution dilution factors are optimum for leach solution analysis by analyzing a leach solution fortified with the analyte of interest. If necessary, further dilute the leach solution and re-optimize furnace program and mass of chemical modifier so that percent 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.

G. Screening of Leach Solutions and Preparation of Test Solutions

(**a**) Complete screening, calibration, and analysis, **G–I**, for Pb first. Then repeat sections **G–I** for Cd. Hold test solutions in tightly sealed containers. Discard test solutions which have been held in unsealed autosampler cups for longer than 15–20 min.

(**b**) 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 subsample leach solution from the instrument response and dilution factor of the dilution which produces a response in working range. Screening serves 3 purposes: (*1*) It saves time by determining appropriate dilutions for test solutions systematically rather than by trial-and-error; (*2*) it determines appropriate fortification level; and (*3*) it conditions the graphite with the leach solutions to be analyzed. Do not report results of screening.

(**c**) 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 subsample which produced the highest concentration of Pb or Cd found by screening. If no Pb or Cd was found by screening, use any leach solution to prepare test solutions a, b, and c.

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

(*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 instrument response of test solution a is approximately half that of test solution b; i.e., test solution a produces 0.100 A-s and test solution b produces 0.200 A-s. For leach solutions that produce ≤2 times the analyte concentration limit, place 2 undiluted portions (DF = 1) in 2 different autosampler cups for analysis.

(*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 (*1*)–(*3*) are followed. If concentration added by fortification is equal to approximately 2 times the analyte concentration limit, dilute fortified leach solution so that the dilution factor of test solution c is 2.

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

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

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

(**e**) For each of the 5 subsample 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 subsample leach solution may be equal but the 2 test solutions must be prepared independently of each other and analyzed from 2 different autosampler cups.

H. Calibration

(**a**) The analytical sequence which demonstrates that the instrument operated properly during the time leach solutions were analyzed is given in **H** (*Calibration)* and **I** (*Analysis of Check and Test Solutions*). Do not vary the sequence. An example of the sequence is shown in Table **999.17B**.

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

(**c**) 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.

(**d**) Proceed immediately to **I**.

I. Analysis of Check and Test Solutions

(**a**) Verify the calibration and absence of carry-over and contamination by analyzing independent check solution and method blank leach solution. The method blank dilution factor must equal 1. Ab-

sence 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 **G**–**I**(**a**). If concentration found in independent check solution does not agree with the actual concentration within approximately ±5% relative difference, calibration or independent solutions, or both, have been prepared incorrectly. Determine source of error, prepare new solutions correctly, and repeat **G**–**I**(**a**). 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 **E**–**I**(**a**).

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

(**c**) 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 ±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 (**c**) for the new test solutions.

(**d**) 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

Table 999.17B Example of analytical sequence described in sections H and I[a]

Analysis	Test solution	DF[b]	Purpose of analysis
1	0.000 A-s (0 ng/mL) calibration solution	1	Calibrate instrument/check reagents for contamination
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)[c]	1	Document absence of carry-over
9	Method blank solution	1	Document absence of contamination
10	Sub 1 (test solution a, example 1)	50	Analyze leach solution
11	Sub 1 (test solution b, example 1)	25	Check analysis of leach solution
12	Sub 1 (test solution c, example 1)[d]	50	Check percent recovery from leach solution
13	Sub 2 (test solution d)	50	Analyze leach solution
14	Sub 2 (test solution e)	25	Check analysis of leach solution
15	Sub 3 (test solution f)	10	Analyze leach solution
16	0.200 A-s check solution (optional)[e]	1	Check calibration/instrument performance
17	0 ng/mL check solution (optional)	1	Check carry-over
18	Sub 3 (test solution g)	10	Check analysis of leach solution
19	Sub 4 (test solution h)	5	Analyze leach solution
20	Sub 4 (test solution i)	5	Check analysis of leach solution
21	Sub 5 (test solution j)	4	Analyze leach solution
22	Sub 5 (test solution k)	4	Check analysis of leach solution
23	Sub 6 (test solution l)	2	Analyze leach solution
24	Sub 6 (test solution m)	2	Check analysis of leach solution
25	0.200 A-s check solutione	1	Check calibration/instrument performance
26	0 ng/mL check solution	1	Document absence of carry-over

[a] Analyses 10–12 are examples of analysis of test solutions prepared in **G**(**d**; example 1).

[b] DF = dilution factor. DF of method blank, calibration, and all check solutions must equal 1.

[c] The 0.000 A-s calibration solution may be used.

[d] Test solution c is prepared from the fortified leach solution.

[e] The independent check solution or any nonzero calibration solution in the middle of the working range may be used.

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, repeat **H** (re-calibrate instrument), and repeat **I** for remaining test solutions.

J. Report

(**a**) 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 Pb and Cd in leach solution (C_{sub}), μg/mL, and masses of Pb and Cd extracted (μg_{sub}), μg.

(**b**) For the sample, report average of concentrations found in subsample leach solutions (C_{SPL}) and average of masses extracted (μg_{SPL}).

(**c**) For leach solutions with concentrations that are less than analyte limits, report <X and <Y, where X and Y are the numeric values of the analyte concentration and mass limits, respectively.

(**d**) Report analyte concentration and mass limits for Pb and Cd; i.e., $SCL_{Pb} = 0.020$ μg/mL and $SML_{Pb} = (0.020\ \mu g/mL) \times 300$ mL = 6 μg.

K. Calculations

(**a**) Record and use at least 3 significant figures for all calculated values of concentration and mass in **K**.

(**b**) *Concentration in test solution (C_{ts}).*—Use slope and intercept determined in **H**(**c**) and instrument response in **I** to calculate concentration in test solution, ng/mL, as follows:

$$C_{ts} = \text{———}$$

where A_{ts} = instrument response of test solution, A-s; b = intercept determined by least squares regression in **H**(**c**), A-s; m = slope determined by least squares regression in **H**(**c**), (A-s)/(ng/mL).

Alternatively, instrument software may be used to calculate C_{ts} if it meets requirements in **H**(**c**).

(**c**) *Leach solution concentration (C_{ls}) calculated from result of a single test solution.*—Use concentration found in test solution to calculate concentration in leach solution, μg/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 μg/mL, (μg/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}.

(**d**) *Percent recovery from fortified leach solution (% rec).*—Calculate percent recovery from fortified leach solution as follows:

$$\text{Recovery, \%} = \quad \times \text{—}$$

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

Calculate A and B as:

$$A = C - \frac{\times}{\text{———}}$$

$$B = \frac{\times}{\text{———}}$$

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

(**e**) *Leach solution concentration calculated from results of 2 test solutions (subsample concentration, C_{sub}).*—Use leach solution concentrations calculated from results of single test solutions to calculate average concentration for each subsample leach solution, μg/mL.

$$C_{sub} = \text{———————}$$

where C_{ls-1} = leach solution concentration calculated from one of the test solutions of a subsample, μg/mL; C_{ls-2} = leach solution concentration calculated from the other test solution of the subsample, μg/mL.

Example: C_{ls-1} and C_{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.

(**f**) *Mass extracted from food-contact surface (μg).*—Multiply concentration in subsample leach solution by volume of leach solution to obtain mass extracted as follows:

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

where C_{sub} = concentration in subsample leach solution, μg/mL; V = volume of subsample leach solution, mL.

(**g**) Calculate analyte concentration limit (ACL), μg/mL, from the slope of the calibration curve as:

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

where 0.050 = definition of analyte concentration limit, A-s; slope = slope of calibration curve determined by least squares regression in **H**(**c**), (A-s)/(ng/mL); 0.001 = factor that converts ng/mL to μg/mL, (μg/mL)/(ng/mL).

(**h**) Calculate sample mass limit (SML), μg, from the analyte concentration limit and the volume of leach solution as:

$$AML = SCL \times V$$

where ACL = analyte concentration limit, μg/mL; V= volume of subsample leach solution, mL.

Reference: *J. AOAC Int.* **83**, 1174(2000).

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