EMBAJADA DE ESPAÑA
OFICINA ECONOMICA Y COMERCIAL

2375 Pennsylvania Avenue, N.W.
Washington, DC - 20037
Telef.: 202 728 2368 Fax: 202 466 7385
E-mail: buzon.oficial@washington.ofcomes.mcx.es

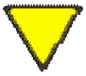
NOTA INFORMATIVA:

Normativa para la exportación a EE UU y al Estado de California de cerámica de uso alimentario con relación a la migración de metales pesados (cadmio y plomo).

La Food and Drug Administration FDA es la agencia federal responsable del control de las importaciones de estos productos en todo el territorio de los EE UU. Uno de los parámetros que vigila cuidadosamente es el cumplimiento de los límites establecidos en la legislación federal para la migración de cadmio y plomo a los alimentos. Para ello utiliza procedimientos de análisis estandarizados.

El poder legislativo del estado de California consideró que sus ciudadanos precisaban de una mayor protección respecto al nivel establecido desde el punto de vista federal, por lo que ha establecido unos límites más exigentes.

La legislación de California es bastante más exigente que la Federal y presenta una particularidad: por un lado su ley general fija unos límites idénticos a los federales, pero una ley posterior, conocida como Proposition 65, fija unos más estrictos para los niveles de ***plomo***. Cuando el contenido de este metal se encuentre entre los límites admitidos por la legislación estatal (no deberá exceder de 0.0226 ppm para objetos planos ni de 0.1 ppm en los demás) y la Federal, los artículos podrán venderse en California, pero el establecimiento que los comercialice está obligado a colocar un aviso estandarizado (ver imagen a continuación) indicando que estos exponen al consumidor a la ingestión de plomo. Dependerá entonces de éste la decisión de comprar o no las piezas de cerámica. No hay necesidad del aviso si el nivel de plomo es igual o menor a 0.100 ppm.



Los niveles de ***cadmio*** de la legislación californiana son los mismos que los admitidos por la Federal.

En la tabla siguiente se indican los límites.

	California			*Federal*	
Tipo de objeto	**Plomo***	**Plomo**	**Cadmio**	**Plomo**	**Cadmio**
Planos	0.226	3	0.5	3	0.5
Huecos :					
- Grandes (1)	0.1	1	0.25	1	0.25
- Pequeños (2)	0.1	2	0.5	2	0.5
- Copas y Tazas	0.1	0.5	0.5	0.5	0.5
- Jarras	0.1	0.5	0.5	0.5	0.5

Unidades: ppm = µg/ml (microgramos por mililitro) de solución de lixiviación
(1): Capacidad igual o mayor de 1.1 litro
(2): Capacidad menor de 1.1 litro
*: California Proposition 65.

La legislación Federal indica que la muestra a analizar se compondrá de seis piezas.

La Secretaría de Estado de Comercio, dependiente del Ministerio de Economía, tiene establecido un acuerdo con la FDA para el reconocimiento de certificaciones analíticas en objetos de cerámica de uso alimentario. El mencionado acuerdo permite a las partidas de cerámica que van a ser exportadas a EE UU realizar los análisis de contenidos en metales a través de la red de laboratorios del SOIVRE, dependientes de la Secretaría en España. Estos certificados de análisis son aceptados por la FDA en el momento de la importación, evitándose demoras en el despacho aduanero. Las empresas interesadas en obtener estos certificados pueden contactar con la Subdirección General que se indica a continuación, la cual coordina la red nacional de oficinas y laboratorios del SOIVRE.

SUBDIRECCIÓN GENERAL DE INSPECCIÓN, CERTIFICACIÓN Y ASISTENCIA TÉCNICA DEL COMERCIO EXTERIOR (SOIVRE)
Paseo de la Castellana, 162 Pta. 6
Madrid 28046
Teléf.: 913.49.37.70
Fax: 913.49.37.40
E-mail: Buzon.Oficial@SGSOIVRE.SECGCOMEX.SSCC.MCX.ES

RED OFICINAS DEL SOIVRE:
http://www.mcx.es/sgcomex/soivre/Orgcatices.htm

En los anexos se incluye la legislación federal y del estado de California, así como los métodos de análisis oficiales.

Washington, DC a 28 de mayo de 2.003

Fco Guerra

Francisco Guerra Sarabia
Consejero Comercial

Fuentes de información complementarias:

- Ley Federal: Compliance Policy Guide 7117.06 y 7117.07
  http://www.fda.gov/ora/compliance_ref/cpg/cpgfod/default.htm#sc545

- California Tableware Education and Enforcement Program
  California Public Health Foundation
  2001 Addison, Ste. 210
  Berkeley, CA 94704
  http://www.childlead.com/tableware/twhome.html

- Proposition 65: Safe Drinking Water And Toxic Enforcement Act Of 1986
  (Chapter 6.6 added by Proposition 65, 1986 General Election)
  http://www.oehha.ca.gov/prop65/law/p65.html#download

CODE OF FEDERAL REGULATIONS

21 CFR - CHAPTER I - PART 109

§ 109.16 Ornamental and decorative ceramicware.

(a) Lead is a toxic metal that is used as a component of glazes and decorative decals on ceramics, including some ornamental and decorative ceramicware. The use of ornamental or decorative ceramicware to prepare, serve, or hold food may result in the leaching of lead from the glaze or decoration into the food. The provisions of paragraph (b) of this section are necessary to ensure that ornamental or decorative ceramicware bear adequate indications that they are not to be used for food-handling purposes.

(b) Ornamental or decorative ceramicware initially introduced or initially delivered for introduction into interstate commerce on or after July 13, 1994 appears to be suitable for food use will be considered to be for food use unless:

(1) It bears:

(i) A conspicuous stick-on label on a surface clearly visible to consumers that states in legible script in letters at least 3.2 millimeters (0.125 inch) in height one of the following messages: "Not for Food Use. May Poison Food," "Not for Food Use. Glaze contains lead. Food Use May Result in Lead Poisoning," and "Not for Food Use -- Food Consumed from this Vessel May be Harmful," and

(ii) A conspicuous and legible permanent statement of the message selected from paragraph (b)(1)(i) of this section molded or fired onto the exterior surface of the base or, when the ceramicware is not fired after decoration, permanently painted onto the exterior surface of the base. This permanent statement shall be in letters at least 3.2 millimeters (0.125 inch) in height, except that if insufficient space exists for the permanent statement in letters of such height, the statement shall be in the largest letters that will allow it to fit on the base of the piece, provided that the letters are at least 1.6 millimeters (0.062 inch) in height; or

(2) A hole is bored through the potential food-contact surface.

(c) In addition to steps required under paragraphs (b)(1) and (b)(2) of this section, the following optional information may be provided on the ware:

(1) A further explanatory statement concerning the decorative nature of the piece, such as "Decorative" or "For Decorative Purposes Only," may be used; however, such additional statement shall be placed after the required statement.

(2) A symbol may be used to advise that a piece of ornamental or decorative ceramicware is not to be used with food, as illustrated below.

View or Download PDF

http://www.access.gpo.gov/ecfr/graphics/pdfs/er01ja93.368.pdf

The circle of the above symbol should be at least 2.54 centimeters (1 inch) in diameter. The symbol may be used on the temporary label or applied to the base of the piece in the same manner as the permanent statement.

[59 FR 1641, Jan. 12, 1994]

FDA - Compliance Policy Guides Manual

(CPG 7117.06)

Sec. 545.400
Pottery (Ceramics); Imported and Domestic - Cadmium Contamination

BACKGROUND:
Imported and domestic ceramic ware has been found to have significant quantities of extractable cadmium. The metal is extractable by acid foods and could cause chronic cadmium poisoning under continued food use.
REGULATORY ACTION GUIDANCE:
The following criteria should be considered when deciding to recommend legal action or to detain imports to CFSAN/Office of Field Programs/Division of Enforcement (HFS-605):
The article:
1. Is suitable to be used for liquid foods,
and
2. Contains *upon examination of 6 units a level of cadmium per mL of leaching solution exceeding the guideline for the category specified as examined by *the current editions of ASTM method C738 (volume 15.02, Annual Book of ASTM Standards, American Society for Testing and Materials), AOAC methods 973.32 and 973.82 (Official Methods of Analysis, AOAC International), or FDA Laboratory Information Bulletin Numbers 4123 and 4126 (US Food and Drug Administration, Division of Filed Science, HFC-140, Rockville, MD 20857).*
Guidelines
Category *Criteria* micrograms/mL
Flatware Average of 6 units 0.5
Small Hollowware any one of 6 units 0.5
Large Hollowware any one of 6 units 0.25
The categories of ceramic articles, flatware and hollowware used in the preparation, serving or storage of food, are defined as follows:
Flatware: ceramic articles which have an internal depth, as measured from the lowest point to the horizontal plane passing through the upper rim, that does not exceed 25 mm.
Hollowware: ceramic articles having an internal depth, as measured from the lowest point to the horizontal plane passing through the upper rim, greater than 25 mm.
Small hollowware: a capacity of less than 1.1 liter.
Large hollowware: a capacity of 1.1 liter or more.
NOTE: The article may be considered unsuitable for food use if:
1. It is rendered unsuitable by some method such as boring holes through the potential food contact surface;
or
2. A label, incapable of obliteration, is permanently affixed to the back or base of the article; and such label states: "Not for Food Use - Article May Poison Food."
SPECIMEN CHARGE:
*Article (Flatware)(Hollowware) adulterated (when introduced into and while in interstate commerce)(while held for sale after shipment in interstate commerce), within meaning of Section 402(a)(2)(C) of the Federal Food, Drug and Cosmetic Act in that it contains a food additive, namely cadmium, which is unsafe within the meaning of

Section 409(a) because its use and intended use are not in conformity with a regulation or exemption established pursuant to Section 409.*

REMARKS:
If all lots in an entry were sampled using an invoice on a line by line basis, detain only those lots meeting the above criteria.
If *only one lot (line item) was sampled* and meets the above criteria, the entire entry may be detained without further analysis.
RELEASE OF IMPORT DETENTIONS:
Upon analysis or other examination by the importer to demonstrate suitability for release, the articles may be released on a lot by lot basis with checks by the district laboratory to determine compliance.
Release may be based on labeling of the article as for other than food use *when:*
1. The article is rendered unsuitable for food use;
or
2. A label is permanently affixed to the back or base of the article that is incapable of obliteration or removal and states: "Not for Food Use - Article May Poison Food."
Release based on any other labeling conditions must have prior clearance of the CFSAN/Office of Field Programs/Division of Enforcement (HFS-605).
EXEMPTION:
Non-food service plates will not be required to meet the guideline for dinnerware. These include, but are not necessarily limited to, the following types of plates manufactured solely for ornamental display purposes: commemorative plates, souvenir plates, hand-painted plates, and other highly decorated plates, provided that they do not come in place settings for the table and provided further that there is a permanent label on the back *or base* of the plate stating, *"Not for Food Use - Article May Poison Food," or a hole is bored through the food contact surface.*
Material between asterisks is new or revised.
Issued: 10/1/80
Revised: 6/27/88, 3/95, 12/12/95 (60 FR 63721)

FDA - Compliance Policy Guides Manual

(CPG 7117.06)

Sec. 545.450
Pottery (Ceramics); Imported and Domestic - Lead Contamination

BACKGROUND:
Some ceramic foodwares have been found to leach significant quantities of lead from potential food contact surfaces. The metal is extractable by foods and can cause a wide variety of adverse health effects including the traditional effects of chronic lead poisoning under continued food use.
REGULATORY ACTION GUIDANCE:
The following represents the criteria that should be considered in deciding whether to recommend legal action or to detain imports to the CFSAN/Division of Enforcement (HFS-605):
The article:
1. Is suitable for use with foods,
and
2. Contains upon examination of 6 units *a level of lead per mL of leaching solution exceeding the guideline by category specified, as examined by *the current editions of ASTM method C738 (volume 15.02, Annual Book of ASTM Standards, American Society for Testing and Materials), AOAC methods 973.32 and 973.82 (Official Methods of Analysis, AOAC International), or FDA Laboratory Information Bulletin Numbers 4123 and 4126 (US Food and Drug Administration, Division of Field Science, HFC-140, Rockville, MD 20857).*
Guidelines
Category Criteria micrograms/mL
Flatware average of 6 units 3.0
Small hollowware any one of 6 units 2.0
other than cups and mugs
Cups/mugs any one of 6 units 0.5
Large hollowware any one of 6 units 1.0
other than pitchers
Pitchers any one of 6 units 0.5

The categories of ceramic articles used in the preparation, serving or storage of food, are defined as follows:
Flatware: ceramic articles which have an internal depth as measured from the lowest point to the horizontal plane passing through the upper rim, that does not exceed 25mm.
Hollowware: ceramic articles which have an internal depth measured from the lowest point to the horizontal plane passing through the upper rim, greater than 25 mm.
Small hollowware: a capacity of less than 1.1 liter.
Large hollowware: a capacity of 1.1 liter or more.
Cups and mugs: small ceramic hollowware vessels commonly used for consumption of beverages, for example, coffee or tea at above room temperature. Cups and mugs normally, but not exclusively, have a capacity of about 240 mL or 8 fl. oz. and are manufactured with a handle. Cups normally have a base and curved sides while a mug has cylindrical sides.

Pitchers: large ceramic hollowware vessels (sometimes known as jugs) commonly used for the storage and dispensing of fruit and vegetable juices or other acidic beverages at or below room temperature which are normally manufactured without a lid but with a handle and lip spout. For the purpose of this guideline, creamers, coffeepots, and teapots are not considered to be pitchers. Depending on capacity, creamers, coffeepots and teapots will be considered small or large hollowware.

NOTE: *In accordance with 21 CFR 109.16(b),* the article will be considered unsuitable for food use if:

1. *It bears:

a. A conspicuous stick-on label on a surface clearly visible to consumers that states in legible script in letters at least 3.2 mm (0.125 inches) in height one of the following messages: "Not for Food Use. May Poison Food," "Not for Food-Use. Glaze contains lead. Food Use May Result in Lead Poisoning," or "Not for Food Use -Food Consumed from this Vessel [Plate] May be Harmful," and

b.A conspicuous and legible permanent statement of the message selected from the above paragraph molded or fired onto the exterior surface of the base or, when the ceramicware is not fired after decoration, permanently painted onto the exterior surface of the base. This permanent statement is in letters at least 3.2 mm (0.125 inches) in height; or

2. A hole is bored through the potential food-contact surface.*

SPECIMEN CHARGE:

Article (Flatware) (Hollowware) (Cups and Mugs) (Pitchers) adulterated (when introduced into and while in interstate commerce)(while held for sale after shipment in interstate commerce), within meaning of Section 402(a)(2)(C) of the Federal Food, Drug and Cosmetic Act, in that it contains a food additive, namely lead, which is unsafe within the meaning of Section 409(a), because its use and intended use are not in conformity with a regulation or exemption established pursuant to Section 409.

*REMARKS:

If all lots in an entry were sampled using an invoice on a line by line basis, detain only those lots meeting the above criteria. If only one lot (line item) was sampled and meets the above criteria, the entire entry may be detained without further analysis.*

RELEASE OF IMPORT DETENTIONS:

Upon analysis or other examination by the importer to demonstrate suitability for release, the articles may be released on a lot by lot basis with checks by the District laboratory to determine compliance.

Release may be based on labeling the article for other than food use *in compliance with 21 CFR 109.16(b).*

Release based on any other labeling conditions must have prior clearance of the CFSAN/Office of Field Programs/Division of Enforcement (HFS-605).

EXEMPTION:

Non-food service plates will not be required to meet the guidelines for dinnerware. These include, but are not necessarily limited to, the following types of articles manufactured solely for ornamental display purposes: commemorative plates, souvenir plates, hand-painted plates, and other highly decorated plates, provided *the article is in compliance with 21 CFR 109.16(b).*

*Material between asterisks is new or revised *

Issued: 10/1/80

Revised: 4/16/92, 12/12/95 (60 FR 63721)

CALIFORNIA HEALTH AND SAFETY CODE

http://www.leginfo.ca.gov/cgi-bin/calawquery?codesection=hsc&codebody=&hits=20

CHAPTER 9. CONTROL OF LEAD RELEASE FROM TABLEWARE

Article 1. Definitions

SECTION 108850-108855

108850. The Legislature finds and declares all of the following:
(a) The program maintained by the United States Food and Drug Administration to regulate the amount of lead and cadmium released from ceramic, metal, and other dishware and tableware is inadequate to protect Californians from the importation and sale of unsafe tableware in this state.
(b) Recent inspection and sampling conducted by local and state health departments in California has demonstrated that significant amounts of unsafe tableware are in fact being imported and sold in California.
(c) The standards established by the federal government for acceptable lead and cadmium release are likely inadequate to fully protect public health and may be inconsistent with requirements that already exist in California law governing exposure to lead and cadmium.
(d) It is the intent of the Legislature that the department, first, establish its own program to protect the public from unsafe tableware and, second, develop standards for lead and cadmium release from tableware that are consistent with existing state law.

108855. For purposes of this chapter the following definitions shall apply:
(a) "Director" means the Director of Health Services.
(b) "Department" means the State Department of Health Services.
(c) "Distributor" means any person who brings tableware into California from another state for sale.
(d) "Importer" means any person who brings tableware into California from another country for sale.
(e) "Manufacturer" means any person who makes tableware sold in California.
(f) "Small business" means any manufacturer, importer, or distributor whose gross annual revenue for the sale of tableware is thirty thousand dollars ($30,000) or less.
(g) "Tableware" means any glazed ceramic, enamel metalware, or pewter article, container, or utensil that may be used in the preparation, serving, or storage of food or drink.

Article 2. Standards

SECTION 108860-108870

108860. It is unlawful to manufacture, process, import, sell, deliver, hold for sale, supply, or offer for sale in this state any tableware that releases a level of lead or cadmium in violation of the standards contained in the Compliance Policy Guides 7117.06 and 7117.07 as described in 54 Federal Register 23485 or any subsequent, more stringent standards adopted by the United States Food and Drug

Administration, as determined by the director.

108865. On or before January 1, 1993, the department shall evaluate the standards specified in Section 108860 to determine whether they are adequate to protect the public health, including, but not limited to, the health of children and other sensitive groups of the population, and shall report the results of this evaluation to the Legislature. The evaluation and report shall specifically include recommendations regarding standards governing the release of lead and cadmium from tableware that would be necessary to adequately protect the public health and shall include comparisons with other public health standards governing exposure to lead and cadmium. The report shall also identify any additional studies necessary to adequately evaluate the public health impacts of exposures to lead and cadmium.

108870. (a) Except as provided in subdivisions (c) and (d), each piece of tableware sold, or offered for sale, in this state shall be permanently and indelibly marked with the name of the manufacturer or importer responsible for the sale of the tableware in California.

(b) For the purposes of this section, permanently and indelibly marked means fired or manufactured into the glazed tableware.

(c) This section shall not apply to any tableware that is manufactured without lead or cadmium as an intentionally added ingredient or as an unintentional contaminant.

(d) This section shall not apply to any tableware product that is of a peculiar structure or too small to accommodate the name of the manufacturer or importer in accordance with subdivision (a), provided that the product either (1) is permanently and indelibly marked with a registered trademark that is on file with the department, or is described and depicted in a certificate of registration that is on file with the department, or (2) is part of a tableware set or pattern, one or more pieces that are marked in accordance with subdivision (a).

Article 3. Enforcement

SECTION 108875-108915

108875. The department is responsible for the administration and enforcement of this chapter. The department, upon request, shall report to the Legislature concerning the number and findings of inspections performed and samples taken to determine compliance with this chapter.

108880. (a) For fiscal years 1991-92 and 1992-93, the department shall levy a fee of five hundred dollars ($500) for each manufacturer, importer, and distributor of tableware sold in this state to be used for the implementation of this chapter, except that the department shall levy a fee of one hundred fifty dollars ($150) for small businesses. A penalty of 10 percent per month shall be added to any fee that is not paid when due. The fee shall not exceed the costs of administering and enforcing this chapter for the 1991-92 and 1992-93 fiscal years.

No later than July 1993, the department shall establish and implement a fee schedule that assesses an annual fee upon manufacturers, importers, and distributors of tableware sold in California. The fees shall be based on the reasonable anticipated costs that will be incurred by the department, and by local health officers if an agreement is executed pursuant to Section 108885, to implement and enforce this chapter. In calculating the necessary fees, the department shall include any civil penalties generated pursuant to Section 100425. Commencing in fiscal year 1993-94, the fee established pursuant to this subdivision shall be adjusted pursuant to Section 100425 and shall further be adjusted annually by reducing the fee by an amount equal to the total amount of civil penalties collected pursuant to Section 108900 during the previous calendar year, divided by the total number of manufacturers, importers, and distributors having paid fees during the previous calendar year. The fee collected pursuant to subdivision (a) shall terminate upon implementation of the fee schedule developed pursuant to this subdivision. The fee schedule shall provide for the recovery of all costs of implementing this chapter, including the cost of establishing the fee schedule as prescribed in this section. In the event that the department's reasonable costs in any one fiscal year exceed the available fees for that year, the department shall, as necessary, delay any activities in administering this chapter that will incur costs exceeding available fees until the following year. All moneys collected as fees pursuant to this section shall be expended in carrying out this chapter.

108885. The department and a health officer, as defined in Section 111015, may enter into an agreement designating the local health department of a city, county, city and county, or local health district as the department's authorized agent for the purposes of enforcing this chapter. If an agreement is executed pursuant to this section, the department shall make fee revenues available to the health officer for performing duties relating to enforcing this chapter.

108890. (a) For the purposes of enforcing this chapter, any authorized agent of the department may, upon presenting credentials showing that he or she is an authorized agent of the department and at a reasonable time, do any of the following:

(1) Enter any factory, warehouse, or establishment in which any tableware is manufactured, held, distributed, used, or sold.

(2) Enter any vehicle that is being used to transport or hold tableware.

(3) Enter any place where any tableware is suspected of being held or sold in violation of this chapter.

(4) Inspect any factory, warehouse, establishment, vehicle, or place in which any tableware is manufactured, held, transported, distributed, used, or sold, and all equipment, raw materials, finished and unfinished materials, containers, and tableware therein.

The inspection shall include any record, file, paper, process, control, and facility that has a bearing on whether the tableware complies with this chapter.

(5) Secure any sample or specimen of any tableware or of any release of lead or cadmium from tableware. If the agent obtains any

samples prior to leaving the premises, he or she shall leave a receipt describing any sample obtained. The department shall secure only the quantity of tableware that is reasonably necessary to conduct the tests to determine the release of lead or cadmium as determined appropriate by the department.

(6) Have access to all records of carriers in commerce relating to the movement in commerce of any tableware, or the holding for sale of the tableware, and the quantity, shipper, and consignee.

(b) It is unlawful for any person to refuse to permit entry or inspection, the taking of samples or other evidence, including photographs, or access to copying of any record as authorized by this chapter, or to conceal the samples or evidence, or withhold evidence concerning them.

108895. The department may publish or publicly distribute any information regarding tableware, including results of tests and investigations, after assuring the accuracy of those tests and investigations, as the department considers necessary for the protection of public health and safety of the consumer or for the protection of the consumer from fraud.

108900. (a) The department may impose a civil penalty payable to the department upon any person who violates this chapter or any regulation adopted pursuant to this chapter in the amount of not more than five thousand dollars ($5,000) per day. Each day a violation continues shall be considered a separate violation.

(b) If, after examination of a possible violation and the facts surrounding that possible violation, the department concludes that a violation has occurred, the department may issue a complaint to the person charged with the violation. The complaint shall allege the acts or failures to act that constitute the basis for the violation and the amount of the penalty. The complaint shall be served by personal service or by certified mail and shall inform the person so served of the right to a hearing.

(c) Any person served with a complaint pursuant to subdivision (c) may, within 20 days after service of the complaint, request a hearing by filing with the department a notice of defense. A notice of defense is deemed to have been filed within the 20-day period if it is postmarked within the 20-day period. If a hearing is requested by the person, it shall be conducted within 90 days after the receipt by the department of the notice of defense. If no notice of defense is filed within 20 days after service of the complaint, the department shall issue an order setting the penalty as proposed in the complaint unless the department and the person have entered into a settlement agreement, in that case the department shall issue an order setting the penalty in the amount specified in the settlement agreement. When the person has not filed a notice of defense or where the department and the person have entered into a settlement agreement, the order shall not be subject to review by any court or agency.

(d) Any hearing required under this section shall be conducted pursuant to Section 100171, except to the extent that the procedures specified in Section 100171 are inconsistent with this section.

(e) Orders setting civil penalties under this section shall become effective and final upon issuance thereof, and payment shall be made within 30 days of issuance. A copy of the order shall be served by personal service or by certified mail upon the person served with the complaint.

(f) Within 30 days after service of a copy of a decision issued by the director after a hearing, any person so served may file with the superior court a petition for writ of mandate for review of the decision. Any person who fails to file the petition within this 30-day period may not challenge the reasonableness or validity of the decision or order of the director in any judicial proceeding brought to enforce the decision or order or for other remedies. Section 1094.5 of the Code of Civil Procedure shall govern any proceedings conducted pursuant to this subdivision. In all proceedings pursuant to this subdivision, the court shall uphold the decision of the director if the decision is based upon substantial evidence in the whole record. The filing of a petition for writ of mandate shall not stay any corrective action required pursuant to this chapter or the accrual of any penalties assessed pursuant to this section. This subdivision does not prohibit the court from granting any appropriate relief within its jurisdiction.

(g) The remedies under this section are in addition to, and do not supersede or limit, any and all other remedies, civil or criminal.

(h) If the violation is committed after a previous imposition of a penalty under this section that has become final, if the violation is committed with intent to mislead or defraud, or if the violation concerns tableware primarily used by children or marketed for children, the person shall be subject to imprisonment for not more than one year in the county jail or imprisonment in state prison, by a fine of not more than ten thousand dollars ($10,000), or by both the imprisonment and fine.

108905. (a) Whenever an authorized agent of the department finds, or has probable cause to believe, that any tableware has the potential to release amounts of lead or cadmium in violation of this chapter, he or she shall affix to the tableware a detention tag, embargo tag, or other similar marking, as determined appropriate by the authorized agent. The tag or other marking shall give notice that the tableware is suspected of releasing amounts of lead or cadmium in violation of this chapter and that no person shall remove or dispose of the tableware by sale or otherwise until permission for removal or disposal is given by an authorized agent of the department or the court.

(b) For the purposes of this section, an authorized agent has probable cause to believe that tableware has the potential to release amounts of lead or cadmium in violation of this chapter when, but not limited to instances when, the tableware tests positive for lead or cadmium release using the field test described in the document published by the United States Food and Drug Administration entitled Analytical Letters Vol. 21, 1988, pages 2145 to 2154, inclusive, or any other test for lead release subsequently approved for field use by the United States Food and Drug Administration and determined by the department to be at least as effective a test for lead or cadmium release as the test described in this subdivision.

(c) If a field test conducted pursuant to subdivision (b) tests positive for lead release, the department shall use the Association of Official Analytical Chemists/American Society for Testing and Material 24-hour test method, or any other test subsequently approved by the federal Food and Drug Administration determined by the department to be at least as effective a test for lead or cadmium release as the test described in this subdivision. The department shall conduct or obtain those tests within a reasonable time after embargoing affected tableware, and shall release any tableware found not to violate the standards of this chapter within a reasonable time after the laboratory test has been completed. For any food establishment, as defined in Section 113780, the department shall conduct or obtain those tests within a reasonable time, not to exceed 10 days, after embargoing affected tableware, and shall release any tableware found not to violate the standards of this chapter within 96 hours after the laboratory test has been conducted.

(d) If an item of tableware is found to violate this chapter, the manufacturer, importer, retailer, and distributor shall, at the option of the holder of the tableware, either provide the holder of the tableware with comparable replacement tableware acceptable to the holder or be liable to the holder of the tableware for the cost of purchasing comparable replacement tableware.

(e) No person shall remove, sell, or dispose of detained or embargoed tableware without permission of an authorized agent of the department or a court.

108910. Any tableware that violates this chapter shall also be governed by the procedures set forth in Sections 111875, 111880, 111885, 111895, 111900, 111910, and 111915. Except for use of the procedures set forth in those sections, nothing in this section shall be interpreted as making this chapter part of Part 5 (commencing with Section 109875).

108915. This chapter shall become operative on July 1, 1991.

The California Tableware Safety Law

The California Tableware Safety Law (Assembly Bill 3659) came into effect on July 1, 1991. It prohibits the sale in California of tableware that leaches lead or cadmium in excess of levels specified in FDA guidelines for tableware (see table below). This law applies to more types of tableware than the FDA regulations. It includes any glazed ceramicware, enameled metalware, or pewter products that may come into contact with food or drink. Unlike the FDA regulations, it also covers tableware that is made in California.

Marking requirements

The Tableware Safety Law requires manufacturers or importers of tableware into California to permanently mark each piece containing lead or cadmium with their company names or trademarks. They must also file a copy of the name or trademark with the Food and Drug Branch of the Department of Health Services. This allows the Food and Drug Branch to track the origin of suspect tableware.

Enforcement

The Tableware Safety Law is enforced by the California Department of Health Services Food and Drug Branch. Tableware sold or offered for sale in California with lead levels that exceed FDA standards, or tableware that is not marked in accordance with the Tableware Safety Law, is subject to enforcement action. Actions may include embargo of unsafe tableware, as well as civil, criminal, or administrative action against the persons responsible for the violations.

The standards below are based on the amount of lead that can leach out of tableware and potentially into food. If the amount is greater than that listed below, the tableware is considered potentially hazardous.

Type of tableware	FDA/ California Dept. of Health Services Tableware exceeding these levels cannot legally be sold in the USA.	California Proposition 65* Tableware exceeding these levels must carry a warning when sold in California.
Flatware (plates)	3.0 ppm	0.226 ppm
Small hollowware (bowls)	2.0 ppm	0.1 ppm
Large hollowware (serving dishes)	1.0 ppm	0.1 ppm
Cups or mugs	0.5 ppm	0.1 ppm
Large pitchers, jugs	0.5 ppm	0.1 ppm

ppm = parts per million

California Proposition 65

Proposition 65, the Safe Drinking Water and Toxic Enforcement Act of 1986, was enacted as a ballot initiative in November 1986. The Proposition was intended by its authors to protect California citizens and the State's drinking water sources from chemicals known to cause cancer, birth defects or other reproductive harm, and to inform citizens about exposures to such chemicals.
Proposition 65 requires the Governor to publish, at least annually, a list of chemicals known to the state to cause cancer or reproductive toxicity.

Proposition 65, also known as the Safe Drinking Water and Toxic Enforcement Act, was passed by California voters in 1986. It requires businesses to inform people when they are exposed to chemicals (including lead) known to cause cancer, birth defects, or reproductive harm. Proposition 65 requires makers of ceramic tableware that contains lead glazes, paints, or enamels to warn consumers if significant amounts of lead leach from the tableware into foods or beverages placed in it. Proposition 65 also applies to glassware for food use, particularly crystal. The standards established by Proposition 65 are significantly stricter than those of the FDA.

Warning requirements
Proposition 65 does not ban any tableware from sale. However, it does require that a warning be provided if lead leaches from the food surface in amounts greater than Proposition 65 levels (see table below). A yellow triangle like a "Yield" sign ▼ must be placed on or next to these dishes when they are sold or displayed for sale. In addition, a sign must be displayed in retail stores explaining that dishes with the triangle will expose users to lead. Proposition 65 warnings for mail order purchases must be posted in the catalogue or on the packing invoice. The manufacturer must tell retailers that its products require a warning and provide the necessary warning signs and stickers. Businesses with fewer than 10 employees are exempt from these warning requirements, so the consumer must be cautious when buying unmarked tableware in small stores.

Enforcement
There is no system of inspections to monitor compliance with Proposition 65. Lawsuits are the primary means of enforcement. Lawsuits to enforce Proposition 65 may be brought by the State Attorney General and local District Attorneys. Private citizens may sue if they notify public prosecutors and the potential defendant(s) of a violation, and the public prosecutors do not sue within 60 days.

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

1. Scope and Application

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

2. Summary of Method

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

3. Safety

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

4. Definitions

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

where

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

5. Interferences

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

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

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

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

6. Apparatus and Materials

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

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

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

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

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

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

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

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

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

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

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

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

7. Reagents

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

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

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

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

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

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

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

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

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

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

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

8. Sample Preparation and Leaching

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

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

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

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

Leach vessels for 24 h at 22±2° C.

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

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

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

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

9. Instrument Optimization

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

Optimize spectrometer settings, furnace program, and mass of chemical modifier for each element so that characteristic mass of lead and cadmium is within approximately ±20% of manufacturer specifications, precision of 10 measurements is ≤5% (preferably ≤3%) relative standard deviation, and atomization peaks are symmetrically shaped and centered in a window of approximately 5 seconds. Instruments with multi-element capability may be optimized for one element and used with compromised conditions for determination of the other element if quality control measurements are acceptable. Begin the optimization process by using 20 µL of a lead calibration solution (10 µL of a cadmium calibration solution) that produces approximately 0.100 or 0.200 A-s and furnace program recommended by manufacturer. Optimize dry, char, atomization, and clean steps of the furnace program as follows. Dry: determine highest temperature and shortest time required to evaporate solution without spattering. Char: determine highest temperature at which no loss of atomic absorbance (peak area) occurs and shortest time required to minimize background absorbance of chemical modifier. Atomization: determine lowest temperature which gives maximum atomic absorbance, complete volatilization of analyte (atomic absorbance returns to baseline), and a properly shaped atomization peak. Clean: determine lowest temperature and shortest time required to eliminate carry-over from previous solution.

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

10. Screening of Leach Solutions and Preparation of Test Solutions

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

Screening

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

Preparation of Fortified Leach and Test Solutions

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

- Prepare the fortified leach solution by adding a known amount of lead or cadmium to a portion (preferably ≥5 mL) of the leach solution. If concentration in the leach solution is >2 times the sample concentration limit, fortify the leach solution so that the concentration added by fortification is approximately 90-110% of the concentration due to test vessel. If concentration in the leach solution is ≤2 times the sample concentration limit, fortify the leach solution so that the concentration added is approximately equal to 2 times the sample concentration limit.
- Prepare 2 test solutions (*a* and *b*) from portions of unfortified leach solution by diluting with 4% acetic acid so that the test solutions produce 0.050 A-s to 0.350-0.400 A-s and so that instrument response of test solution *a* is approximately half that of test solution *b*; *i.e.*, test solution *a* produces 0.100 A-s and test solution *b* produces 0.200 A-s. For leach solutions that produce ≤2 times the sample concentration limit, place 2 undiluted portions (DF=1) in 2 different autosampler cups for analysis.

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

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

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

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

Preparation of Remaining Test Solutions

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

11. Calibration

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

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

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

12. Analysis of Check and Test Solutions

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

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

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

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

13. Report

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

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

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

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

14. Calculations

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

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

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

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

where

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

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

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

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

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

where

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

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

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

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

where

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

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

Sample Concentration (C_{SPL}), µg/mL

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

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

where

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

Recovery of Fortified Analyte (Rec), %

Calculate percent recovery from fortified leach solution as follows:

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

where

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

Calculate A and B as:

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

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

where

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

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

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

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

where

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

Sample Concentration Limit (SCL), µg/mL

Calculate from the slope of the calibration curve as:

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

where

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

Sample Mass Limit (SML), μg

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

$$SML = SCL \times V$$

where

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

15. Method Validation

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

16. References

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

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

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

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

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

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

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

[a] From collaborative study reported in Reference 5.

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

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

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

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

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

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

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

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

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

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

[l] R indicates reference lab.

Table 2. Example of Analytical Sequence[a]

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

[a] Analyses 10-12 are of test solutions prepared as in Fortification Recovery Example 1.

[b] DF indicates dilution factor.

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

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

[a] From Reference 5.

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

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

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

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

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

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

[a] From Reference 5.

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

[c] Values in table were calculated excluding outliers.

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

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

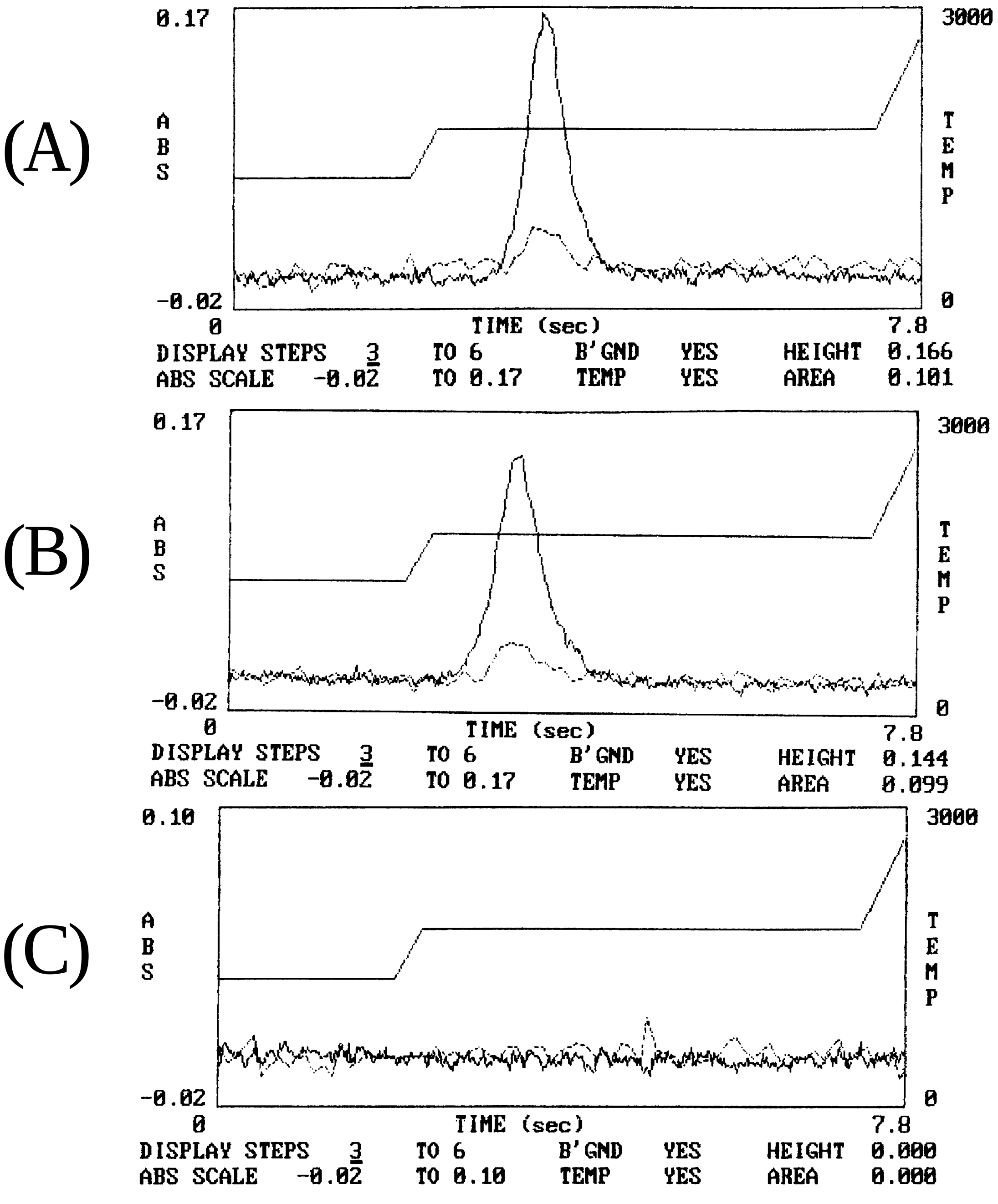
[f] Instrument sensitivity is described by characteristic mass and expressed in this table as a percent of manufacturer specifications. Values <100% indicate sensitivity that is better than manufacturer specifications. Values >100% indicate sensitivity that is not as good as manufacturer specifications.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

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

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

[a] From Reference 5.

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

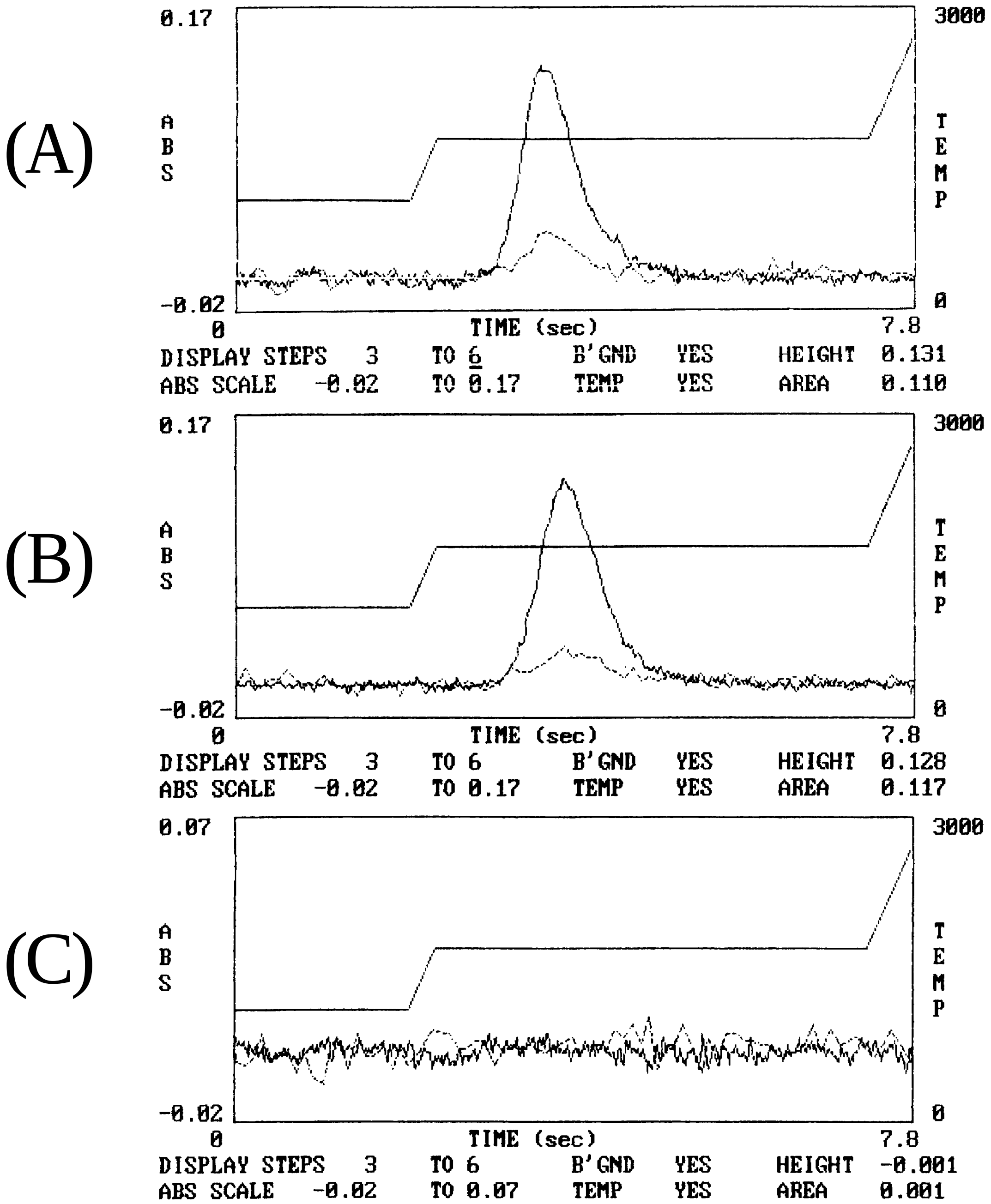


```
DISPLAY STEPS  3   TO 6      B'GND   YES    HEIGHT  0.166
ABS SCALE  -0.02   TO 0.17   TEMP    YES    AREA    0.101
```

```
DISPLAY STEPS  3   TO 6      B'GND   YES    HEIGHT  0.144
ABS SCALE  -0.02   TO 0.17   TEMP    YES    AREA    0.099
```

```
DISPLAY STEPS  3   TO 6      B'GND   YES    HEIGHT  0.000
ABS SCALE  -0.02   TO 0.10   TEMP    YES    AREA    0.000
```

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



Revision History

Revision 1 – Issued April, 2000

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

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

Table 1: Corrected matrix modifier values.

Revision 0 – Issued January, 2000

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 (µg/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 (µg/mL) that can be reliably measured in leach solutions. In this method, the sample concentration limit is the concentration of lead or cadmium that produces 0.050 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 µg/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 µg/mL and SML_{Pb} = (0.020 µg/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}), µg/mL

Use slope and intercept determined from calibration data and instrument response from test solution to calculate concentration in test solution, µg/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)/(µg/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}), µg/mL

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

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

where

$C_{ts\text{-}ls}$ = concentration in test solution prepared from leach solution, µg/mL
DF = dilution factor of test solution
$C_{ts\text{-}mb}$ = concentration in method blank test solution, µg/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 $C_{ts\text{-}mb}$.

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

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

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

where

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

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

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

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

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

where

C_1-C_6 = are sub-sample concentrations (C_{sub}), µg/mL. For sub-sample concentrations <SCL, use C_{sub}=SCL/2, where SCL is the sample concentration limit calculated for lead 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 = µg/mL recovered from fortified leach solution
B = µg/mL added to fortified leach solution

Calculate A and B as:

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

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

where

C = concentration found in fortified leach solution, µg/mL
D = concentration found in unfortified leach solution, µg/mL. When using percent recovery to check for 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, µg/mL

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

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

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

where

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

Sample Concentration Limit (SCL), μg/mL

Calculate from the slope of the calibration curve as:

$$\mathrm{SCL} = 0.050 / \mathrm{m}$$

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:

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

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.

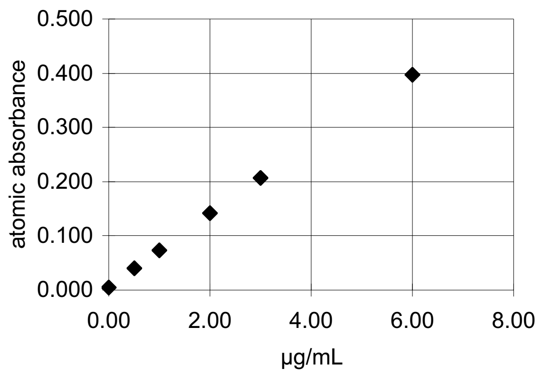
Fig. 1C—percent recovery and relative difference of results calculated from test solutions *a*, *b* and *c* .

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 µg/mL	Atomic Absorbance	Actual Conc. µg/mL	Calc'd Conc. µg/mL	check, % 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 abs/ppm	Intercept 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

Figure 1B.

Flame Atomic Absorption Spectrometry					Date	11/20/96		
Element:	Lead (Pb)				Analyst	S. Hight, K. Cook		
Analysis 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.

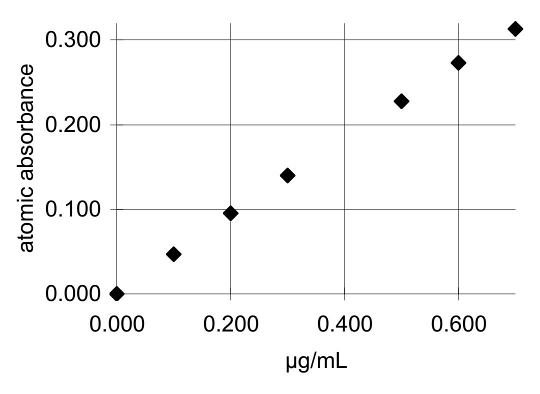
Fig. 2C—percent recovery and relative difference of results calculated from test solutions *a*, *b* and *c* .

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		
Concentration μg/mL	Atomic Absorbance	Actual Conc. μg/mL	Calc'd Conc. μg/mL	Rel. Dif. Conc. check, % 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 abs/ppm	Intercept 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		
Analysis 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							