Contents

6.1 **Introduction**
6.1.1 FDA Center for Food Safety
6.1.2 Lead and Cadmium in Foods and Foodware
6.1.2.1 Lead and Cadmium in Foods
6.1.2.2 Lead and Cadmium in Housewares
6.1.3 Mercury in Food
6.1.4 Other Elements in Food
6.2 **Exercises**
6.2.1 Qualitative Identification of Lead in Ceramicware and Solder Alloys
6.2.2 Qualitative analysis by XRF
6.2.3 Leachable Lead and Cadmium in Ceramicware by GFAAS
6.2.4 Leachable Lead and Cadmium in Ceramicware by ICP-OES
6.2.5 Mercury (total) in Seafood
6.2.6 Multi-Element, Simultaneous/Sequential Analysis in Foods by ICP-MS
6.3 **References**
6.4 **Appendix – Answer Key**
6.5 **Document Change History**

6.1 Introduction

Man and other animals are exposed daily to numerous elements, in varying forms and levels, through food (feed), water, and other FDA-regulated products.

Major essential elements include C, H, O, N, S, Ca, P, K, Na, Cl, and Mg. C, H, O, N, and S make up the bulk of the elemental constituents of plants and animals, and are the major components of the organic substances in tissues.

Fe, Zn, Cu, Co Mn, I, Mo, Cr, Se, F, (B for plants) have identified functions meeting the definition of essential elements in animals including man (References 1, 2). Whether an element is essential has little, but some bearing on an element's toxicity. Essential elements under homeostasis, (i.e. the level of absorption, body stores, and or excretion is under physiological control), tend to have a lower relative toxicity. However, many factors, such as the level of exposure, the form of the element, the sensitivity of the host, the physiological and nutritional status of the host, affect the toxicity of an element.

Nonessential and essential elements can be toxic. Nonessential elements where human toxicity has been reported includes Pb, Cd, Hg, As, Al, Ba, Li, Pt, Te, Ti, Sb, Be, Ga, In, V, Ni, Sr, Sn, Ge, Ag, Au, Bi, Tl, and U. The essential elements, F, Co, Fe, Mo, Cu, Mg, Se, Cr, Mn, and Zn, are of practical toxicological significance. Se is the most toxic essential mineral elements. Presently, Pb, Cd, Hg (as methylmercury), and As (inorganic forms) are of the greatest concern and have the greatest program emphasis.

This training chapter will provide the following information:

- Sources of Contamination,
- Compliance Policy Guide References,
  - lead and cadmium in food and foodware,
  - methylmercury in food, and
- Instruction for the analytical exercises.

6.1.1 FDA Center for Food Safety

As part of its responsibilities for ensuring food safety, the FDA Center for Food Safety and Applied Nutrition (CFSAN) routinely monitors the level and potential dietary uptake of these toxic elements (contaminants) in foods and foodware. FDA Compliance Program Guides detail the sample collection and analysis for the determination of lead and cadmium in foods and foodware, and methyl mercury, arsenic and selenium in food.

The Total Diet Study (TDS), sometimes called the Market Basket Study, is an ongoing FDA program that determines levels of various pesticides, contaminants, and nutrients in foods for the purpose of estimated intakes of these substances in representing diets of selected age-sex groups in the United States Population. Elements analyzed include the following: arsenic, cadmium, calcium, copper, iron, lead, magnesium, manganese, mercury, nickel, phosphorous, potassium, selenium, sodium, and zinc (Reference 22).

6.1.2 Lead and Cadmium in Foods and Foodware

Presently, the compliance programs cover toxic elements in food (CPG 7304.019A), and housewares (CPG 7304.019B). See Reference 3.

Lead in the diet can be attributed to natural sources of lead in the soil, deposition of lead particles onto crops, pollution (lead gasoline usage), food processing and packaging techniques, herbal supplements and folk remedies. The use of lead-based solders in food cans is now prohibited (21CFR 189.240). Although the use of lead based pigments in food wrappers is not prohibited, the United States and European Commission voluntarily stopped this practice. Candy food wrappers from other countries, particularly Mexico, have been found to contain percent levels of lead. Lead is found in folk remedies such as Azarcon, Greta, herbal medicines, and unapproved dyes in eye cosmetics (kajal, surma, kohl) from the Far and Middle Eastern countries (Reference 19).

Cadmium is found in foods naturally and due to pollution. Cadmium is emitted into the atmosphere from smelters and waste incineration plants; the use of municipal sludge can dramatically increase cadmium levels in food. Recently cultivated agricultural areas derived from ancient seabeds are prone to producing elevated levels of cadmium in foods (e.g. spinach, lettuce). See Reference 17.

Pigments used to decorate ceramicware, or glazes coating ceramicware may contain lead or cadmium. Traditional wares (e.g. Chinese classic enamel-on-porcelain wares, Mexican glazed folk terra cotta) have been found to contain excessive amounts of lead (Reference 3). Glazes that are improperly formulated, applied, or fired may permit unacceptable amounts of lead or cadmium to leach into food. The following colors in glaze or decorations are often indicative of ceramicware that may release cadmium: red, orange, yellow.

6.1.2.1 Lead and Cadmium in Foods

See Compliance Program Guidance Manual 7304.019A, Toxic Elements in Foods. Lead and cadmium are identified as the toxic elements of concern in foods; particular emphasis is placed on foods consumed by children who are the most sensitive to adverse side effects.

There are no regulatory limits, i.e. tolerances, for toxic elements in foods; sample results that exceed normal concentrations are brought to the attention of CFSAN, who will conduct an assessment of potential health hazards from the quantity of the toxic element found based upon food consumption of the product.

FDA has established Provisional Daily Total Tolerable Intakes (PDTTI) for lead for several at-risk groups (Reference 7). When the consumption of a contaminated food has exceeded a PDTTI, regulatory action *may be* taken on an *ad hoc* basis. Food Chemical CODEX (FCC) lists many internationally recognized standards for lead in foods and food ingredients. While these are not regulatory tolerances, the FFC are often employed as lowest limits of actions for imported foods.

The prohibition of lead soldered cans and the removal of lead from gasoline have significantly reduced the lead exposure to the average consumer. The Total Diet Surveys indicate the average lead intake from food has decreased more than 95% since the 1970s. Nonetheless, FDA remains concerned about lead in regulated products, especially since more than half of our foods now come from outside the U.S., and a significant number of children in the U.S. remain exposed to excessive amounts of lead.

6.1.2.2 Lead and Cadmium in Housewares

See Compliance Program Guidance Manual 7303.019B.
The Food Additives provision of the FD&C Act does not permit a harmful level of a substance to migrate from the surface onto a food or beverage. Toxic Elements in Houswares (CPGM 7303.019B) focuses on lead and cadmium found in ceramicware and silver plated hollowware used for eating, storing, holding and cooking foods.

The FDA and the State Administration of Entry/Exit Inspection and Quarantine of China (recently renamed the China National Certification and Accreditation Administration or CNCA) implemented an Memorandum of Understanding (MOU) pertaining to the safety of ceramic table ware produced in China and exported to the United States. The MOU specifies a certification system for ceramic tableware production facilities in China. This certification system is expected to provide FDA with reasonable assurance that ceramicware produced in these facilities and exported to the United States will not exceed FDA action levels for leachable lead and cadmium (Reference 20).

The CPGM focuses on the following areas: investigates the rate of compliance for Chinese Ceramicware from non-certified and certified factories, audits the effectiveness of the China certification program in improving the safety of ceramicware exported to the United States, and concentrates on sampling countries with prior violations, particularly small shipments entering from Mexico.

Monitoring of ceramicware is conducted in two steps. Screening tests for ceramicware are conducted in the field to identify items that are likely to contain leachable lead. Based on the results of the screening tests, official samples are collected and sent to the laboratory for further testing. There is no screening test for cadmium in ceramicware, or lead and cadmium in silver-plated hollowware. The investigator is directed to look for signs of improper glazing on the product, and/or collecting samples with those colors that may contain lead or cadmium.

In the absence of codified regulations or tolerances for ceramicware, FDA has established interim action guidelines for lead (CPG Sec 545.450) and cadmium (CPG Sec 545.400). See References 4 and 5. The surveillance of leachable lead and cadmium in ceramicware continues to be a program priority.

Past FDA regulatory efforts, an MOU with China, efforts by the commercial sector, and state regulations (e.g. California Proposition-65), have led to a vast improvement in the performance of daily-use tableware regarding the leachability of lead and cadmium. Most daily-use ceramicware pose relatively few regulatory problems for leachable levels of lead and cadmium. The traditional wares (especially from China) and folk terra cotta wares from Mexico and Central American countries continue to pose an extreme lead exposure risk, especially for children and the fetus. Many other elements are used in ceramicware bodies, their glazes, and decorations. Ba, Sb, Co, Cr, and others may leach from ceramicware. However, the regulatory significance of these elements has not been evaluated.

6.1.3 Mercury in Food

See Compliance Policy Guide, Section 540.600, Fish, Shellfish, Crustaceans and other Aquatic Animals – Methyl Mercury (Reference 9).

Mercury, primarily as methyl mercury, was first identified as a regulatory issue in seafood in the 1970s. Mercury occurs naturally in the environment, and is released from the Earth's crusts and oceans. Mercury is also released from fossil fuels such as coal, and burning industrial wastes. Fish absorb methyl mercury from water as it passes over their gills and through feeding aquatic organisms; methyl mercury binds tightly to proteins in fish tissue (Reference 21).

Studies where people were exposed to high levels occurred in highly contaminated fish in Minnamata, Japan. Over one hundred people died from eating fish (often daily over extended periods) from waters that were severely polluted with mercury from industrial discharge. Mercury poisoning occurred in unborn fetuses and children. An epidemic of mercury poisoning occurred with a wheat seed treated with alkyl mercury fungicide (Reference 21).

Presently, the FDA regulatory guideline for methyl mercury in seafood (CPG Sec 540.600) is one part per million (ppm) methyl-mercury expressed as Hg. FDA's action level of one ppm for methyl mercury in fish was established to limit the consumers methyl mercury exposure to levels ten times lower than the lowest levels associated with adverse effects.

6.1.4 Other Elements in Foods

Arsenic and Selenium occur naturally in foods. Both can be present at toxicologically significant levels in groundwater and in soils.

Arsenic compounds are released to the atmosphere from natural and industrial sources. The major sources of arsenic emissions are the smelting of metals, burning of fossil fuels, and application of pesticides and herbicides. The arsenic compounds may accumulate in agricultural and horticultural soils and plants.

Arsenic in food is most often in alkylated forms. The alkylated forms of arsenic that arise in plants, shrimp (Reference 16), and some other animals have a relative low order of toxicity. Arsenate and arsenite are far more toxic and have proven to be carcinogenic in humans.

Selenium is the most toxic essential mineral element. Selenium often occurs as selenium analogues of sulfur-containing amino acids and metabolites in plants. While there have been numerous selenium intoxications reported for man and other animals, these poisonings have been mainly due to errors in manufacturing dietary supplements and feed selenium supplements. Although human toxicity to selenium has been reported in China and other parts of the world where extreme selenium pollution exists, selenium deficiency appears to be the more significant public health concern.

6.2 Exercises

The exercises in this section are intended to expose the analyst to some of the more frequently used methods for detecting lead and for quantifying lead and cadmium. For more detailed information regarding methods on the determination of these and additional elements, standards, sample preparation, digestions, instrumentation, or data treatment consult the CFSAN web site and the Elemental Analysis Manual (EAM).
View manual at http://www.cfsan.fda.gov/~dms/eam-toc.html

6.2.1 Qualitative Identification of Lead in Ceramicware and Solder Alloys

A. Introduction

Because the scope of the ceramicware program is limited to leachable lead and cadmium, and the use of lead is routine in ceramicware items, FDA investigators often employ qualitative tests to determine whether the item leaches (or contains) lead, and therefore warrants collection. Analysts need to be familiar with these methods and techniques, since they are ultimately responsible for training investigators to use these tests. An equivalent, FDA validated test kit does not exist for cadmium. The presence of Cadmium is usually “signaled” by the presence of rich yellow or red decorations on the food-bearing surface of the item. FDA developed the Quick Color Test (QCT) for Lead (References 10, 11, 12). The QCT test for lead, and similar forms of the test (e.g. the Rapid Abrasion Test (RAT), Reference13), have been commercialized (e.g. LeadCheck Swabs^{TM}, by Hybrivet, Reference 14). The tests determine if an item bears leachable lead or the item bears a leachable or non-leachable lead in the glaze or a decoration (Reference 13). Some of these commercial test kits have also been validated for testing for the presence of lead in the solder of food cans, a prohibited practice (Reference 15). Test method LIB 4041 serves as a definitive test for detecting lead and can be used to support regulatory action in canned products.

B. Prerequisites

None

C. Assignment

1. Read the following documents, articles and methods: Compliance Program Guide 7304.019B Toxic Elements in Foods (Domestic & Import); Gould et al. (1988). *Analytical Letters*, 2145-2154; Capar, S. G. (1998, August). Ceramic foodware lead screening using test kits. Laboratory Information Bulletin, LIB No. 4127, *14,* 1-8; Dolan, S.P. (1994). *Journal of AOAC International,* 719-722; Capar, S. G., Anderson, D.L., Hughes, D. D., Jacobs, R.M. (1996). Identification of lead solder on a metal can seam. Laboratory Information Bulletin, LIB No. 4041, *12*(12).

2. Obtain articles to be tested from trainer (test items: lead containing solder, food grade tin solder; ceramicware bearing lead containing glazes; ceramicware bearing lead based decorations).

3. Prepare reagents and obtain the test kits.

4. Conduct qualitative tests on all the items noting color development.

5. Demonstrate the presence of leachable lead in ceramicware.

6. Demonstrate the presence of lead in ceramicware by the Rapid Abrasion Test.

7. Demonstrate the presence of lead in solder.

D. Questions

1. Which ions interfere with the test for leachable lead in ceramicware and lead in tin-lead solders?

2. What are the principal chemical reactions embodied in these test methods and kits?

3. How would someone utilize each test in selecting items ceramicware for quantitative analysis?

6.2.2 Qualitative analysis by XRF

A. Method (SOPs indicated below are located in e-room)

Elemental Analysis Using the Thermo Quant-X X-Ray Fluorescence Instrument
Bruker Tracer III X-Ray Fluorescence Analyzer
Detection and Confirmation of Toxic Element Using the Innov-X-X-5000 Field Portable X-Ray Fluorescence Analyzer

6.2.3 Leachable Lead and Cadmium from Ceramics by GFAAS

A. Method

Elemental Analysis Manual (EAM) 4.2., Determination of Leachable Lead and Cadmium from Ceramicware by Graphite Furnace AAS,

B. Prerequisites

Volumetric and gravimetric procedures, good pipetting techniques and contamination control practices.

C. Assignment

1. Using EAM method 4.2 and the instrument manufacturer's manual, conduct an analysis of lead and cadmium in ceramicware.

2. Identify those instrument parameters that can affect the determination.

3. Determine the highest sensitivity for lead and cadmium for this FAAS instrument.

4. Compare the sensitivities with those of the manufacturer’s specifications.

5. Determine the characteristic masses for lead and cadmium.

6. Determine the reporting limits for the two elements, as per EAM 4.2.

7. Determine the linear ranges for these two elements.

8. Prepare standards for the determinations.

9. Prepare check standards that have traceability to a certified reference solution.

10. Obtain a six-unit sample of ceramicware and examine it for leachable lead and cadmium using the graphite furnace atomic absorption method EAM 4.2.

D. Questions

1. For the brand and model of instrument utilized, demonstrate the steps employed to obtain maximum sensitivity for the two elements, and to eliminate or minimize interference.

2. What are the possible sources of interference?

3. How does an instrument minimize or reduce these interferences?

4. What steps could be used to correct background interference?

5. What measures of instrumental performance verify instrumental “calibration”?

6. Identify and give the acceptable range for other method quality control measures that are utilized to assure accuracy and precision of analysis?

7. Why are samples stored in the dark during leaching with 4% acetic acid?

6.2.4 Leachable Lead and Cadmium from Ceramicware by ICP-OES

A. Method

Elemental Analysis Manual (EAM) 4.6.
Inductivly Couled Plasma-Atomic Emission Spectrometric Determination of Cadmium and Lead Extraced from Ceramic Foodware

6.2.5 Mercury (total) in Seafood by CVAAS

A. Method

EAM 4.6 (method presently in draft status)
Determination of Mercury (total) in Seafood by Cold Vapor AAS .

6.2.6 Multi-Element, Simultaneous Sequential/Quantitative Analysis of Foods by ICP-MS

A. Method

EAM 4.7 (method presently in draft status)
Multi-Element, Simultaneous Quantitative Analysis of Foods by ICP-MS

6.3 References

1. (1989). *Recommended dietary allowances* (10th ed.). Washington DC: National Academy Press.

2. (2001). *Dietary Reference Intakes for Vitamin A, Vitamin K, Arsenic, Boron, Chromium, Copper, Iodine, Iron, Manganese, Molybdenum, Nickel, Silicon, Vanadium, and Zinc.* Washington DC: National Academy Press.

3. U.S. Food and Drug Administration, Center for Food Safety and Applied Nutrition. (2001, May 25). Compliance program guidance manual, Compliance Program Guide: 7304.019 - Toxic Elements in Food and Foodware, Imported and Domestic (FY 03 - 05). Washington DC: U.S. Government Printing Office.

4. U.S. Food and Drug Administration, Office of Enforcement. (Rev. 1995, December 12). Compliance policy guides, sec. 545.450 Pottery (Ceramics); Imported and Domestic Lead Contamination (CPG 7117.07), pp. 296-298.

5. U.S. Food and Drug Administration, Office of Enforcement. (Rev. 1995, December 12). Compliance policy guides, sec. 545.400 Pottery (Ceramics); Imported and Domestic Cadmium Contamination, pp. 294-296.

6. California Proposition-65, Lead, *California Code of Regulations*, Title 22, sec.12805 (b).

7. Carrington, C. and Bolger. P. M. (1992). *Regulatory toxicology & pharmacology, 16*, 265.

8. Friberg, L., Piscator, M., and Nordberg, G. (Eds.). (1981). *Cadmium in the environment.* Boca Raton, FL: CRC Press.

9. U.S. Food and Drug Administration, Office of Enforcement. (Rev. 1995, March). Compliance policy guides, sec. 540.600 Fish, Shellfish, Crustaceans and Other Aquatic Animals - Fresh, Frozen or Processed - Methyl Mercury (CPG 7108.07), p. 288.

10. Gould, J. H., Capar, S. G., Jacobs, R. M., Plunkett, R. (1988). A quick color test to detect lead release from glazed ceramic and enameled metalware. *Anaytical Letters, 21*, 2145-

2154.

11. Dolan, S. P., Capar, S. G., Jacobs, R. M., Plunkett, R. J., Hawkins, G. S. (1994). Sensitivity of the quick color test for indicating lead release from ceramicware. *Journal of Association of Official Analytical Chemists, 77*, 454-457.

12. Gould, J. H., Capar, S. G. (1990). Comparison of lead check swabs to AOAC method for determination of lead in ceramic glazes. Laboratory Information Bulletin, LIB No. 3445 *6*(2), 1-3.

13. Dolan, S. P. (1994). Rapid abrasion test to indicate lead on the surface of ceramicware. *Journal of Association of Official Analytical Chemists International, 77*, 718-722.

14. Capar, S. G. (1998, August). Ceramic foodware lead screening using test kits. Laboratory Information Bulletin, LIB No. 4127, *14*, 1-8.

15. Capar, S. G., Anderson, D.L., Hughes, D. D., Jacobs, R.M. (1996). Identification of lead solder on a metal can seam. Laboratory Information Bulletin, LIB No. 4041, *12*(12).

16. U.S. Food & Drug Administration, Center for Food Safety and Applied Nutrition. (1993, January). *Guidance Document for Arsenic in Shellfish.*

17. U.S. Food & Drug Administration, Center for Food Safety and Applied Nutrition. (1993, January). *Guidance Document for Cadmium in Shellfish.*

18. U.S. Food & Drug Administration, Center for Food Safety and Applied Nutrition. (1993, January). *Guidance Document for Lead in Shellfish.*

19. U.S. Food & Drug Administration, Center for Food Safety and Applied Nutrition. (2000, February/March). Ask the regulators, emerging international contaminant issues: development of Codex Alimentarius standards to address these issues. *Food Safety Magazine* (reprinted from February – March 2000 issue).

20. *Federal Register.* (1999, July 8). FDA-State administration of entry/exit inspection and quarantine of China (SAIQ) memorandum of understanding, Vol. 64, No. 144, 40875.

21. (1994, September). Mercury in Fish: Cause for Concern? *FDA Consumer Magazine* (Rev. May 1995).

22. U.S. Food & Drug Administration, Center for Food Safety and Applied Nutrition. (2001, April). *History of FDA's Total Diet Study.*

6.4 Appendix – Answer Key

6.2.1 Qualitative Identification of Lead in Ceramicware and Solder Alloys Using Test Kits

1. **Which ions interfere with the test for leachable Pb in ceramicware and Pb in solders?** In principle, other than Pb, Sn and Ba form colored complexes with the rhodizonate salt. The Sn complex is purple. The Ba complex is yellow-orange. Both are persistent and can obscure a positive response to Pb. Sn interference is not a practical issue for ceramicware because Sn is not utilized in ceramic pigments or glazes. However, BaO is used as a base in a number of glazes. Most Ba-based glazes yield a matte finish. If the Ba is leachable, one will get a reaction to Ba. For solders, Sn is a serious but a manageable problem, since most solder alloys have a high percentage of Sn. However, the limit of Pb detection in a Sn-Pb solder ranges from 10-20% Pb. The precautions in the method (e.g. cleaning the surface in order to remove oxides with silicon carbide paper and dabbing the swab rather than rubbing with the swab) minimizes the Sn interference.

2. **What are the principal chemical reactions (no chemical formula are required) embodied in these test methods and kits?** There are three reaction steps that need to be identified: (1) oxidation of the Pb, if the lead is in the metallic state, (2) chelation of the Pb by the food acid (citrate or tartrate) employed by the kit, and (3) the formation of the color complex, Pb-rhodizonate.

3. **How would one utilize each test in selecting ceramicware items for quantitative analysis?** For ceramicware, any positive result on a decoration or glaze on the food-bearing surface would trigger a sample collection. The collection of cups, mugs, or pitchers would be based on a positive test of either the QCT or RAT.

6.2.3 Leachable Lead and Cadmium in Ceramics by Graphite Atomic Absorption Spectrometry

1. **For the brand and model of instrument utilized, demonstrate the steps employed to obtain maximum sensitivity for the two elements, and to eliminate or minimize interferences.** See GFAAS manual.

2. **What are the possible sources of interference?** See GFAAS manual.
3. **How does an instrument minimize or reduce these interferences?** Explain how the particular instrument in the laboratory accomplishes background correction (deuterium lamp, optics, and electronics).

4. **What steps could one use to correct background interference?** Aside from the instrumental techniques, some or all of the following may prove useful: sample dilution, standard additions, suppressors, different wavelength, etc.

5. **What measures of instrumental performance verify instrumental "calibration"?** Characteristic concentration, detection limit, quantitation limit, linearity, and range of linearity.

6. **Identify and give the acceptable range for other method quality control measures that are utilized to assure accuracy and precision of the analysis?** See EAM 4.2

7. **Why are samples stored in the dark during leaching with 4% acetic acid?** Leaching ceramicware in the presence of light causes accelerated cadmium leaching.

6.5 Document Change History

Version 1.2 Revision Approved: 09-01-05 Author: LMEB Approver: LMEB
Version 1.3 Revision Approved: 02-06-12 Author: LMEB Approver: LMEB

Version 1.2 changes:
Table of Contents – Titles changed for 6.1.4, 6.2.2, 6.3.1, deleted 6.3.3, Arsenic (total) and Selenium (total) in Food, 6.3.4 now 6.3.3 and 6.3.4 now 6.3.5
Added Section 6.6.
Revised Section 6.1; method cited in 6.3.2 A.; method changed in Section 6.3.5 A.

Version 1.3 changes;
Table of Contents – Titles changed for 6.2, 6.2.2, 6.2.4., & 6.6; deleted 6.3
6.2 – title changed; "novice" deleted from first sentence
6.2.2 – changed to Qualitative analysis by XRF & added Method
6.2.3 A. & C. – changed to GFAAS,GFAAS method & references
6.2.4 – changed to ICP-OES and changed method reference in A.
6.4 Appendix – changed to 6.2.3 & GFAAS;answers to questions 1., 2., & 6 changed to GFAAS Manual or EAM 4.2