Elemental Analysis Manual

for Food and Related Products

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U.S. Department of Health & Human Services

FDA U.S. Food and Drug Administration

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4.6 INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRIC DETERMINATION OF CADMIUM AND LEAD EXTRACTED FROM CERAMIC FOODWARE

Version Draft 0.2 (August 2010)
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GLOSSARY

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4.6.1 SCOPE AND APPLICATION

This method describes procedures for using inductively coupled plasma-atomic emission spectrometry (ICP-AES) to quantitatively determine cadmium and lead extracted by acetic acid at room temperature from the food-contact surface of foodware. This method is applicable to food-contact surfaces of silicate-based materials (earthenware, glazed ceramicware, decorated ceramicware, decorated glass, and lead crystal glass). Typical analytical solution limits of detection and quantification are listed in 4.6 Table 1.

4.6 Table 1. Analytical Limits

Element	Symbol	ASDL[a] (mg/L)	ASQL[a] (mg/L)
Cadmium	Cd	0.001	0.006
Lead	Pb	0.005	0.030
[a]Based on replicate measurements of standard solution in axial mode at 214 nm for Cd and 220 nm for Pb.			

The limits listed above are intended as a guide and actual limits are dependent on the sample matrix, instrumentation and selected operating conditions.

This method should be used by analysts experienced in the use of inductively coupled plasma-atomic emission spectrometry, including the interpretation of spectral and matrix interferences, and procedures for their correction; and should be used only by personnel thoroughly trained in the handling and analysis of foodware samples for determination of extracted cadmium and lead.

4.6.2 SUMMARY OF METHOD

Cadmium and lead are extracted from the food-contact surface of test vessels by filling with 4% acetic acid to within 6-7 mm of overflowing and leaching for 24 hours at 22 ± 2 °C (same extraction procedure as in AOAC Official Method 973.32[1], ASTM Standard Test Method C 738-94[2] and EAM Method 4.1). Portions of resulting analytical solutions are used to prepare test solutions for analysis. Cadmium and lead concentrations in test solutions are determined by inductively coupled plasma-atomic emission spectrometry using a standard curve and linear least squares regression. Background correction is used to compensate for variable background emission contribution to analyte signal. Quality control procedures are incorporated for monitoring laboratory contamination and interference effects to ensure data quality.

4.6.3 EQUIPMENT AND SUPPLIES

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

(1) Inductively coupled plasma-atomic emission spectrometer (ICP-AES)—Simultaneous or sequential ICP-AES, preferably axial plasma viewing, capable of measuring cadmium and lead emission line intensities at 2 or more wavelengths for each element. Recommended wavelengths include but are not limited to 214.441, 226.502, and 228.802 nm for cadmium and 217.000, 220.353, 261.418, 280.200, and 283.305 nm for lead. Use

of a background correction technique which compensates for variable background emission is required.

Safety Note: Inductively coupled plasmas emit ultraviolet radiation during operation and should only be viewed with proper eye protection.

4.6.4 REAGENTS AND STANDARDS

Reagents may contain elemental impurities that can affect the quality of analytical results. Reagents should be sought that minimize analyte contamination (ideally, analyte level is below the IDL). Use of trace metals grade reagents is recommended.

Safety Note: Reagents should be regarded as potential health hazards and exposure to these compounds should be limited. Material safety data sheets for these chemicals are to be available to the user.

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(1) Reagent water—Water that meets specifications for ASTM Type I water[3].

(2) Detergent solution for cleaning samples (0.02% v/v)—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.

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(3) Acetic acid—Concentrated glacial acetic acid, trace metals grade.

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

(5) Stock cadmium and lead solutions—Use 1000 or 10,000 mg/L single-element stock solutions in ≤5% 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.

(6) Standard blank—4% v/v acetic acid.

(7) Standard solution(s)— Prepare standard solution(s) volumetrically or gravimetrically by combining appropriate amounts of stock solutions with 4% acetic acid.

(8) Check solution—Use the highest concentration standard solution for the check solution.

(9) Independent check solution (ICS)—Dilute appropriate amount of analyte stock solution obtained from a different source than used to prepare standard solution(s) with 4% acetic acid so that cadmium and lead solution concentration is approximately 1 mg/L.

Note: Daily preparation of standard and independent check solutions is recommended unless longer term stability can be demonstrated.

4.6.5 SAMPLE PREPARATION AND LEACHING

Disposable laboratory gloves should be worn when handling test vessels to prevent contamination. For method blanks (MBK) use a contamination-free laboratory beaker or dish. At least two MBKs must be prepared and analyzed with each sample batch.

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

Note: A laminar flow clean air hood or canopy equipped with high-efficiency particulate filters is recommended for dust-free environment. Contamination can be controlled, however, without using a clean-air canopy if care is taken to prevent contamination from dust.

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(2) Fill MBK 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 4% acetic acid needed to fill each vessel. Immediately cover vessels to minimize evaporation. Use opaque material or place vessels in dark location to prevent photo-oxidation of insoluble cadmium sulfide to soluble cadmium sulfate.

(3) Leach vessels for 24 hours at 22 ± 2 °C.

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

(5) Gently stir leach solution in each test vessel and transfer a sufficient portion by pipet (do not pour) to suitable plastic container for the analytical solution. For best results, analyze within 1 day. Analytical solutions with no precipitate may be held longer if stored with tightly sealed caps. Store in total darkness until analysis. Precipitated matter, if present, may be removed from analytical 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 as a suitable polypropylene syringe.

4.6.6 DETERMINATION PROCEDURE

The determination procedure was developed using a Teledyne Leeman Labs Prodigy DV ICP-AES. 4.6 Table 2 is an example of operating conditions used with this instrument for this application. Each laboratory must determine optimum instrument parameters for radio frequency (RF) power, view height (if using radial mode), argon flow rates and sample uptake (peristaltic pump) rate. Small changes in these critical parameters can greatly affect instrument performance.

4.6 Table 2. Typical ICP-AES Operating Conditions

Conditions for Teledyne Leeman Labs Prodigy DV	
ICPAES Conditions	
Torch[a] view	AXIAL
RF Power (W)	1200
Plasma gas flow rate (L/min)	18
Auxiliary gas flow rate (L/min)	0
Nebulizer[b] (carrier) gas pressure (psi)	30
Peristaltic pump flow rate (mL/min)	1.4
Detector integration time (seconds)	5
Number of integrations per solution	3

[a]Standard torch with integrated 2.5 mm injector
[b]Concentric glass 2 mL/min nebulizer connected to cyclonic double pass spray chamber

Instrument Setup

(1) Setup ICP-AES instrument according to manufacturer's recommendations and with the following conditions:

- Select from available analytical emission lines 2 or more wavelengths for each element. Recommended wavelengths include but are not limited to 214.441, 226.502, and 228.802 nm for cadmium and 217.000, 220.353, 261.418, 280.200, and 283.305 nm for lead.
- Set instrument to correct for variable background emission for all analytical measurements.
- Program instrument for 3 or more replicate reads (exposures) for each solution.
- Program software to report measurement mean and percent relative standard deviation (RSD) for each solution.

(2) Optimize operating conditions.

- Startup instrument according to laboratory standard operating procedures.
- Perform spectrometer wavelength calibration or alignment of analytical lines according to manufacturer recommendations or laboratory standard operating procedures as necessary.

(3) Check instrument performance

- Check instrument sensitivity and short-term measurement precision before standardization and sample analysis. Analyze a standard solution containing approximately 10 mg/L lead for 3 or more replicate readings (exposures) at 220.353 nm, or another solution made for this check such as 1 mg/L manganese at 257.610 nm. The mean and RSD emission counts or other intensity derived response should be within 80-120% of the historical mean and ≤5% RSD, respectively, indicating good instrument performance. Failure of either the sensitivity or precision check usually indicates a sample introduction problem. Correct the problem before proceeding.

Determination of Analyte Concentration Using Standard Curve

(1) Standardize the instrument using the standard blank and standard solution(s).

(2) Check standardization performance.

- Correlation coefficient (r) of linear regression (intensity verses concentration) is ≥0.998 for curves with 2 or more standard solutions.
- Analyze ICS and standard blank immediately following instrument standardization. Acceptance criteria: ICS recovery within 100 ± 5%, standard blank <ASDL.

(3) Analyze analytical and quality control solutions.

- Interpolate analyte concentration in analytical solution from standard curve using least squares linear regression.
- Dilute analytical solutions with diluent if concentration is above the highest standard.
- For each sample, prepare a fortified analytical solution (FAS) by adding known amount of analyte to a portion of analytical solution so that the concentration added by fortification is approximately twice the unfortified level with a minimum fortified solution concentration of 0.5 mg/L cadmium and 1 mg/L lead.
- A typical sequence for an analytical run is listed in 4.6 Table 3.

(4) Check instrument measurement performance

- RSD of analytical solution read (integration) replicates is ≤5% for concentrations ≥ ASQL.
- Relative percent difference (RPD, §3.3.5) of analyte concentration results determined at 2 different wavelengths is ≤10% for concentrations ≥ASQL. A RPD >10% can be due to spectral interference in the analytical solution. If spectral scans (wavelength verses intensity) of the analyte wavelength region indicate spectral overlap or significant background interference, alternate wavelengths must be used.
- FAS recovery is 100 ± 10%. A recovery outside this range can be due to matrix induced effects. Dilute FAS and associated unfortified analytical solutions with standard blank as necessary to comply with criteria.
- Check solution analyzed at a frequency of 10% and at end of the analytical run has a recovery of 100 ± 10%.
- Standard blank analyzed following each check solution analysis is <ASDL (to verify absence of carry-over).
- Measurements are below concentration of highest standard. Dilute analytical solution with diluent as necessary to comply with criteria.

4.6 Table 3. Typical Analytical Sequence

Solution	Purpose	QC Criteria
standard blank standard solution(s)	standardize instrument	r ≥0.998 for curves with 2 or more standard solutions
ICS	verify standardization	95-105% of expected
standard blank	verify absence of carry-over	<ASDL
MBK #1	verify absence of contamination	≤MBK_C
MBK #2		≤MBK_C
sample #1 sub#1 sample #1 sub#2 sample #1 sub#3 sample #1 sub#4 sample #1 sub#5 sample #1 sub#6	determine analyte concentration	If concentration ≥ASQL, ≤5% RSD read (integration) replicates and ≤10% RPD between results at 2 wavelengths
sample #1 sub#6 FAS	spike recovery	90-110% recovery
check solution	verify standardization	90-110% of expected
standard blank	verify absence of carry-over	<ASDL

4.6.7 CALCULATIONS

Calculate analyte concentration in the analytical solution according to the formula

$$\text{Concentration (mg/L)} = (S \times DF) - MBK_L$$

where

S = concentration of analyte in analytical solution (or diluted analytical solution) (mg/L)
MBK_L = laboratory MBK (µg/L)
DF = dilution factor (1 if analytical solution not diluted)

Round calculated concentration to at most 3 significant figures.

4.6.8 METHOD VERIFICATION

The following minimum number of quality control samples are analyzed with each sample batch: 1 fortified analytical solution (FAS), and 2 method blanks (MBKs).

A fortified method blank (FMB) checks the accuracy of the fortification procedure without any matrix effects and is an optional quality control sample. Use same fortification level as the FAS.

FAS Recovery

Control limit for FAS recovery is 100 ± 10%.

Method Blanks (MBK)

Minimum of 2 MBKs analyzed and concentration of both MBKs are ≤MBK_C. If 3 or more MBKs are analyzed then at least two-thirds of MBKs are ≤MBK_C.

FMB Recovery (optional)

Control limit for FMB recovery is 100 ± 10%.

4.6.9 REPORT

Report results only when quality control criteria for a batch have been satisfactorily met. For each element, report the ASQL and quantitative result (if applicable) for the analytical wavelength with the lowest ASQL. Report results that are ≥ASQL as the analyte concentration determined followed by the units of measurement. Report results that are ≥ASDL and <ASQL as the analyte concentration determined followed by the units of measurement and the qualifier that indicates analyte is present at a trace level that is below the limit of reliable quantification (TR). Report results that are <ASDL as 0 followed by the units of measurement and the qualifier that indicates analyte is below the level of reliable detection or is not detected (ND).

Example: ASQL = 0.12 mg/L; ASDL = 0.02 mg/L. Levels found for three different samples were 7.5 mg/L, 0.05 mg/L and 0.01 mg/L.

7.5 µg/kg is ≥ASQL; report 7.5 mg/L

0.05 mg/L is ≥ASDL but also <ASQL; report 0.05 mg/L (TR)

0.01 mg/L is <ASDL; report 0 mg/L (ND)

4.6.10 METHOD VALIDATION

In-house validation. [under development]

Uncertainty. [under development]

A detailed discussion of method uncertainty is presented in §3.3. This method conforms to the information contained in that discussion. Derivation of an estimated uncertainty specific to an analysis is discussed §3.3.2.

Interlaboratory trial. [under development]

REFERENCES

(1) *Official Methods of Analysis of AOAC INTERNATIONAL* (2005) Official Method **973.32**, Lead and Cadmium Extracted from Ceramicware–Atomic Absorption Spectroscopic Method. 18th Ed., AOAC INTERNATIONAL, Gaithersburg, MD, USA, AOAC OMA Online: <http://www.eoma.aoac.org/>.

(2) ASTM International (2006) ASTM C 738-94, "Standard Test Method for Lead and Cadmium Extracted from Glazed Ceramic Surfaces". ASTM: <http://www.astm.org>.

(3) ASTM International (2006) ASTM D 1193-06, "Standard Specification for Reagent Water". ASTM.