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Elemental Analysis Manual

for Food and Related Products

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Elemental Analysis Manual

for Food and Related Products

4.6 Inductively Coupled Plasma–Optical Emission Spectrometric Determination of Cadmium and Lead Extracted from Ceramic Foodware

Version 1.0 (January 2020)

Current Validation Status:
Grandfathered Level Three: Multi-Laboratory Validated

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4.6.1 SCOPE AND APPLICATION

This method describes procedures for using inductively coupled plasma-optical emission spectrometry (ICP-OES) 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).

This method should be used by analysts experienced in the use of inductively coupled plasma- optical 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 Methods 973.32 and 999.17[1,2], ASTM Standard Test Method C 738- 94[3], 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-optical 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.

Typical analytical solution limits of detection and quantification are listed in 4.6 Table 1. These are intended as a guide and actual limits are dependent on the sample matrix, instrumentation and selected operating conditions.

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.

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-optical emission spectrometer (ICP-OES) — Simultaneous or sequential ICP-OES, preferably axial plasma viewing, capable of measuring cadmium and lead emission line intensities at two or more wavelengths for each element. Recommended

wavelengths include (but 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 to compensate for variable background emission is required.

(2) Plastic Labware — Use plastic labware (graduated cylinders, beakers, pipette tips, etc.). Labware must be sufficiently clean for trace metals analysis. To clean, rinse plastic labware with 10% nitric acid followed by copious quantities of reagent water. Air-dry in a dust-free environment. Labware can be tested for contamination by testing a 4% acetic acid rinse solution.

(3) Gloves — Use powder free vinyl or nitrile gloves. Do not use powdered or latex gloves because of possible contamination. Gloves intended for clean rooms and that are free from metals contamination are suggested.

(4) PTFE Syringe Filters — use PTFE filters with natural (not colored) polypropylene housings to remove particulate matter from leach solutions, acid-clean filters with a 4% acetic acid rinse immediately before use.

(5) Disposable Polypropylene Syringes — acid-clean syringes with a 4% acetic acid rinse immediately before use.

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.

(1) Reagent water — Water that meets specifications for ASTM Type I water[4].

(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.

(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 1,000 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:***
>
> *Standard and independent check solutions have been shown to be analytically stable for 30 days. Longer term stability may be possible, but should be demonstrated prior to using standards for more than 30 days.*

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.

> ***Note:***
>
> *Contamination can be controlled without using a clean-air hood if care is taken to prevent contamination from dust. However, use of a laminar flow clean-air hood or canopy with high-efficiency particulate filters is recommended.*

(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 a dust-free environment.

(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 (i.e., if a level is more than 7 mm from the edge of vessel), add 4% acetic acid to bring it back up to within 6-7 mm of the edge. 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 one day. Analytical solutions with no precipitate may be held longer if stored with tightly sealed caps. Store in total darkness until analysis. Particulate matter, if present, may be removed from analytical solutions by filtering with PTFE syringe filters attached to polypropylene syringes. Acid-clean filters and syringes with a 4% acetic acid rinse immediately before use.

4.6.6 DETERMINATION PROCEDURE

The determination procedure was developed using a Teledyne Leeman Labs Prodigy DV ICP-OES. 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-OES Operating Conditions

Conditions for Teledyne Leeman Labs Prodigy DV	
ICPOES 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-OES 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 emission lines according to manufacturer recommendations or laboratory standard operating procedures as necessary.

(3) Check instrument performance

- See δ3.6.1.3 for additional details on ICP-OES
- Perform manufacturer recommended or laboratory start-up procedures.

Determination of Analyte Concentration Using Standard Curve

(1) Standardize the instrument using the standard blank and 2 or more standard solution(s).

(2) Check standardization performance.

(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 type, prepare duplicate fortified analytical solutions (FAS) by adding known amount of analyte to a portion of analytical solution. It is recommended that the concentration added by fortification is at the level of interest, or 50-300% of the native elemental concentration, whichever is greater; 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.

4.6 Table 3. Typical Analytical Sequence

standard blank	standardize instrument	r ≥0.998 for curves with 2 or more standard solutions
standard solution(s)		
ICS	verify standardization	90-110% of expected
standard blank	verify absence of carry-over	<ASDL
MBK #1	verify absence of contamination	$\leq \text{MBK}_C$
MBK #2 & #3 (optional)		$\leq \text{MBK}_C$ (2/3 $\leq \text{MBK}_C$)
sample #1 sub#1	determine analyte concentration	If concentration ≥ASQL, ≤10% RSD read (integration) replicates and ≤10% RPD between results at 2 wavelengths
sample #1 sub#2		
sample #1 sub#3		
sample #1 sub#4		
sample #1 sub#5		
sample #1 sub#6		
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

CALCULATIONS

Calculate analyte concentration in the analytical solution. Round calculated concentration to at most 3 significant figures.

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

where:

S = analyte conc. analyte in analytical solution (or diluted analytical solution; mg/L)
MBK_L = laboratory MBK (mg/L)
DF = dilution factor (1 if analytical solution not diluted; unitless)

4.6.8. METHOD QUALITY CONTROL

For each sample batch the following quality control measures must be met. A typical sequence for an analytical run is listed in 4.6 Table 3 along with a summary of quality control criteria.

Standardization and Instrument 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 ± 10%, standard blank <ASDL.
- 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).
- RSD of analytical solution read (integration) replicates is ≤10% for concentrations ≥ASQL.

Method Performance

- Relative percent difference (RPD, §3.4.5) 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.
- Duplicate fortified analytical solutions (FAS) are required with each sample batch. Acceptance criteria: 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.
- Minimum of 2 method blanks (MBKs) are required with each sample batch. Acceptance criteria: concentration of both MBKs are ≤MBK_C (MBK Critical Value). If 3 or more MBKs are analyzed then at least two-thirds of MBKs are ≤MBK_C. (EAM 3.6). If a failure occurs due to contamination, the source of the contamination should be investigated and remedied.

- Optional 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. Acceptance criteria: 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 ≥ASQL as the analyte concentration followed by the units of measurement. Report results ≥ASDL and <ASQL as the analyte concentration followed by the units of measurement and the qualifier that indicates analyte is present at a trace level that is below the limit of quantification (TR). Report results <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 mg/L 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

EAM 4.6 was not validated through a dedicated method validation study. However, it has been used for over 20 years, is universally accepted by FDA's analytical experts, and has generated voluminous amount of data that support validation status.

For validation purposes, selected data have been gathered and summarized in a report (see Appendix A). Standardized methods, scientific literature, an internal laboratory study, individual laboratory verifications, and 10 years of National Check Sample results were reviewed. Based on this review, EAM 4.6 has been grandfathered as equivalent to a multi-laboratory validated method at Validation Level 3[5].

4.6.11 REFERENCES

(1) *Official Methods of Analysis of AOAC INTERNATIONAL* Official Method **973.32**, Lead and Cadmium Extracted from Ceramicware–Atomic Absorption Spectroscopic Method. 18th Ed., AOAC INTERNATIONAL, Gaithersburg, MD, USA, AOAC OMA. Available from AOAC International (accessed December, 2019)

(2) *Official Methods of Analysis of AOAC INTERNATIONAL* AOAC Official Method **999.17**, Lead and Cadmium Extracted from Ceramic Foodware Graphite Furnace Atomic Absorption Spectrometric (GFAAS) Method 2004. AOAC INTERNATIONAL, Gaithersburg, MD, USA, AOAC OMA. Available from AOAC International (Accessed December, 2019)

(3) ASTM International (2006) ASTM C 738-94, "Standard Test Method for Lead and Cadmium Extracted from Glazed Ceramic Surfaces". Available from ASTM (Accessed December, 2019)

(4) ASTM International (2006) ASTM D 1193-06, "Standard Specification for Reagent Water". Available from ASTM (Accessed December, 2019)

(5) Guidelines for the Validation of Chemical Methods for the FDA Foods Program, 3rd Edition (2019) Available from FDA (Accessed December, 2019)

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4.6 Appendix A
Method Validation Report for EAM 4.6 Inductively Coupled Plasma - Optical Emission Spectrometric Determination of Cadmium and Lead Extracted from Ceramic Foodware

January 2019

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Method Validation Report

Elemental Analysis Manual: Section 4.6 Inductively Coupled Plasma – Optical Emission Spectrometric Determination of Cadmium and Lead Extracted from Ceramic Foodware

Date: January 2019
Authors: Douglas T. Heitkemper and John Cheng

SUMMARY

The FDA Elemental Analysis Manual (EAM) method 4.6 (Version Draft 0.2, August 2010) titled, "Inductively Coupled Plasma – Atomic Emission Spectrometric Determination of Cadmium and Lead Extracted from Ceramic Foodware"[1] has been utilized in ORA laboratories for a number of years. In this method, lead and cadmium are extracted from foodware including earthenware, glazed ceramicware, decorated ceramicware, decorated glass, and lead crystal glass by leaching with 4% acetic acid for 24 hours prior to determination using inductively coupled plasma optical emission spectroscopy (ICP-OES). This report summarizes selected data for EAM 4.6 to show there is considerable evidence to support the recommendation that EAM 4.6 be grandfathered to Validation Level 3 (multi-laboratory validated). It will be included in the method's updated and finalized form. No new validation data are provided.

INTRODUCTION

In EAM 4.6, lead and cadmium are extracted from foodware by leaching with 4% acetic acid for 24 hours prior to determination using ICP-OES. Except for the ICP-OES determinative step, this method is considered to be essentially the same analysis as is performed in EAM 4.1, which uses flame atomic absorption spectrometry (FAAS) and EAM 4.2, which uses graphite furnace atomic absorption spectrometry (GFAAS)[2-7] and is identical to that used in AOAC Official Method 999.17[6].

The generally-held 'expert opinion' in the analytical laboratory community is that ICP-OES performs as well, or better, than FAAS and GFAAS in applications such in EAM 4.6. However, EAM 4.6 has not been validated and since FAAS/GFAAS is no longer used in FDA laboratories, FDA will not be conducting an EAM 4.6 multi-laboratory method validation study. Nonetheless, validation is possible.

The data supporting AOAC 999.17 includes a collaborative study in which blind duplicate portions of three ceramicware leach solutions were analyzed by seven participating laboratories[7]. Lead concentrations in the three leachates ranged from 0.02-3.7 mg/L and cadmium concentrations ranged from 0.0024-0.54 mg/L. Accuracy reported was 97-98% for Pb and 93-101% for Cd and was calculated as 100 x collaborator average/reference laboratory average. Reproducibility relative standard deviation (RSD_R) ranged from 4.5-12% for Pb and 7.0-11% for Cd.

With the above as a backdrop and the fact that EAM 4.6 was used at FDA for a number of years, there is considerable evidence to support method validation status. This report shows that the use of ICP-OES in the determinative step yields results that are comparable to AOAC 999.17, which utilizes GFAAS. An internal ICP-OES study, individual laboratory verifications, and ten years of National Check Sample results are reviewed to support the validation status of EAM 4.6.

SUPPORTING EVIDENCE FOR MULTI-LABORATORY VALIDATION DESIGNATION

Selected analytical data are summarized in the three sections below.

(1) FDA Southeast Regional Laboratory internal study - Determination of Lead and Cadmium Extracted from Ceramic Foodware by ICP Optical Emission Spectroscopy using Axial Plasma View

In 2001, FDA's Southeast Regional Laboratory compared axial view ICP-OES (Perkin Elmer Optima 3300DV) and GFAAS for the determination of lead and cadmium in ceramic foodware leachate. Seventeen samples of ceramic foodware were leached according to EAM method 4.2[3] and analyzed using both ICP-OES and GFAAS. Six pieces were leached for each sample to give a total of 102 analyses. From FACTS records, all samples were classified as decorated ceramicware. One of these samples was a quality assurance sample and three of the other samples had been found to be violative for Pb and none for Cd.

The average LOQ was 0.014 mg/L for Pb (n=9) and 0.0014 mg/L for Cd (n=9) based on 10σ method blank replicate analyses. The highest LOQs were 0.017 mg/L Pb and 0.0043 mg/L Cd. Since the procedure given in EAM 3.2 was not used to determine ASQL, the highest LOQs were used to re-examine the comparison data. Table 1 summarizes the findings and Table 2 gives detailed results. For Pb and Cd concentrations ≥ highest reported LOQ, the relative percent difference (RPD) between ICP-OES and GFAAS determinations (AVG ± SD) was 2.6% ± 2.4% and 4.0% ± 4.4% for Pb and Cd, respectively. Furthermore, if only ICP determinations in which the Pb concentration is ≥0.05 mg/L and the Cd concentration is ≥0.01 mg/L are considered, all of the determinations were within ±10% of the GFAAS values obtained. This confirms the ability of ICP to perform well at concentrations well below the lowest action levels for ceramic foodware (0.5 mg/L Pb and 0.25 mg/L Cd)[8,9]. Also, in every case where the ICP determination was <LOQ, the GFAAS results were similarly low. Since the GFAAS LOQ is not available, a more rigorous comparison for these determinations is not possible. An analysis of all non-zero results using single factor analysis of variance shows no apparent difference ($p>0.9$) in mean values between ICP-OES and GFAAS results for both Pb and Cd.

Fortified analytical solution (FAS) spike recoveries for Pb and Cd ranged from 99-104% (n =12) and 97-105% (n=12), respectively. Lead spike levels were 1.00 - 1.25 mg/L (n=11) and 20 mg/L (n=1). Cadmium spike levels were 0.1 - 0.125 mg/L (n=12). In EAM 4.6, the minimum FAS concentrations are 1 mg/L and 0.5 mg/L for Pb and Cd, respectively. Thus, the Cd FAS concentrations used in this study were roughly 4-5 times lower than required in EAM 4.6. These FAS results along with the comparisons between ICP-OES and GFAAS determinations, provide evidence that ICP-OES compares well with GFAAS determinations for Pb and Cd in ceramic foodware leachate at levels of regulatory concern.

There were some limitations to this study. As noted above, only three of the sixteen samples studied had been previously found to be violative for Pb and none were violative for Cd. However, for lead the concentration range studied was relatively large from just above the average LOQ (0.014 mg/L) to 242 mg/L. The range studied for Cd was only <LOD to 0.153 mg/L. The variety of the samples analyzed also appeared to be somewhat limited since all samples were classified as glazed ceramic with decoration.

A comparison of precision obtained between ICP-OES and GFAAS determinations was also not provided. Good precision for replicate subs of the same sample is not expected due to the non-homogenous nature of the products being analyzed. However, a comparison between the precisions obtained using ICP-OES and GFAAS on the same solutions provided evidence of the acceptability of ICP-OES precision. For Pb, concentrations were above the ICP-OES LOQ for all six subs in all 17 samples. The ICP-OES and GFAAS average RPD in RSDs were compared for each sample (n=6 subs) and found to be 2.8% with a range of 0.01% - 8.2%. For Cd, six (out of seventeen samples) had concentrations above the ICP-OES LOQ for all 6 subs. The average RPD in RSDs was 7.2% with a range of 1.9% - 13%. These data indicate that ICP-OES precision is comparable to GFAAS precision.

Table 1. Summary of Comparison of ICP-OES and GFAAS Determinations for 17 Samples of Glazed Ceramic Foodware (6 Subs Each)

Element	Pb	Cd
Number of ICP Determinations	102 (17 X 6 subs = 102)	102 (17 X 6 subs = 102)
Number of ICP Determinations ≥ Highest Reported LOQ	102 (LOQ = 0.017 mg/L)	44 (LOQ = 0.0043 mg/L)
% Difference, AVG[1]	2.6%	4.0%
% Difference, SD[1]	2.4%	4.4%
% Difference, Range[1]	0-13%	0-21%
% of ICP Determinations w/in ±10% of GFAAS Value[1]	100% (102/102 determinations)	91% (40/44 determinations)
Number of ICP Determinations ≥0.05 mg/L Pb or 0.01 mg/L Cd	91	31
% Difference, AVG[2]	2.4%	2.9%
% Difference, SD[2]	2.2%	1.9%
% Difference, Range[2]	0-11.5%	0-7.3%
% of ICP Determinations w/in ±10% of GFAAS Value[2]	99%	100%

[1] Results for when “Number of Determinations ≥ Highest Reported LOQ”
[2] Results for when “Number of Determinations ≥0.05 mg/L Pb or 0.01 mg/L Cd”

Table 2 (part a). Details from a 2001 FDA Southeast Regional Laboratory study - Use of ICP-OES to Determine Lead and Cadmium Extracted from Ceramic Foodware

		Pb				Cd		
Sample ID	Analysis unit	ICP-OES mg/L	GFAAS mg/L	difference %		ICP-OES mg/L	GFAAS mg/L	difference %
QA00F02	Method blank	0.0006	0.000			0.0000	0.0000	
	LOQ	0.0164				0.0043		
	piece #1	0.468	0.457	2.4		0.0260	0.0250	3.9
	piece #2	0.291	0.289	0.7		0.0053	0.0052	1.9
	piece #3	0.274	0.276	-0.7		0.0139	0.0132	5.2
	piece #4	0.239	0.24	-0.4		***0.0023***	0.0023	0.0
	piece #5	0.0343	0.0331	3.6		***0.0010***	0.0010	2.0
	piece #6	0.0381	0.0375	1.6		***0.0011***	0.0010	7.5
	Average	0.224	0.222	1.2		0.0083	0.0080	3.4
F99975	Method blank	0.0006	0			0.0000	0.0000	
	LOQ	0.0164				0.0012		
	piece #1	241.7	240.4	0.5		0.0060	0.0071	-16.8
	piece #2	165.8	165.4	0.2		0.0057	0.0064	-11.6
	piece #3	27.0	26.6	1.5		***0.00079***	0.00076	3.9
	piece #4	139.7	137.5	1.6		0.0047	0.0058	-21.0
	piece #5	12.1	12.2	-0.8		***0.00051***	0.00039	26.7
	piece #6	148.4	146.2	1.5		0.0049	0.0058	-16.8
	Average	122.5	121.4	0.8		0.0038	0.0044	-5.9
F91817	Method blank	0.0063	0.0002			0.0001	0.00001	
	LOQ	0.0116				0.0043		
	piece #1	0.309	0.304	1.6		***0.0003***	0.00003	n/a
	piece #2	0.27	0.273	-1.1		***0.0004***	0.00000	n/a
	piece #3	0.242	0.238	1.7		***0.0000***	0.00000	n/a
	piece #4	0.234	0.231	1.3		***0.0004***	0.00000	n/a
	piece #5	0.307	0.306	0.3		***0.0002***	0.00002	n/a
	piece #6	0.315	0.303	3.9		***0.0002***	0.00000	n/a
	Average	0.280	0.276	1.3		0.0003		
	spike (#6)	1.00				0.100		
	found	1.016				0.1028		
	Recovery (%)	101.6				102.8		
F91821	Method blank	0.0015	0.0003			0.0001	0.00001	
	LOQ	0.0091				0.0006		
	piece #1	0.262	0.26	0.8		0.0098	0.0097	1.0
	piece #2	0.382	0.389	-1.8		0.0119	0.0120	-0.8
	piece #3	0.186	0.188	-1.1		0.0066	0.0066	0.0
	piece #4	0.156	0.152	2.6		0.0062	0.0062	0.0
	piece #5	0.187	0.185	1.1		0.0079	0.0077	2.6
	piece #6	0.386	0.386	0.0		0.0114	0.0114	0.0
	Average	0.260	0.260	0.3		0.0090	0.0089	0.5
F102984	piece #1	1.42	1.4	1.4		0.0981	0.0954	2.8
	piece #2	2.21	2.13	3.7		0.133	0.130	2.3
	piece #3	1.53	1.49	2.6		0.113	0.109	3.6
	piece #4	1.55	1.52	2.0		0.123	0.119	3.3
	piece #5	2.02	1.94	4.0		0.153	0.155	-1.3
	piece #6	0.979	0.987	-0.8		0.0918	0.0918	0.0
	Average	1.62	1.58	2.2		0.119	0.117	1.8

Table 2 (part b). Details from a 2001 FDA Southeast Regional Laboratory study - Use of ICP-OES to Determine Lead and Cadmium Extracted from Ceramic Foodware

		Pb			Cd		
Sample ID	Analysis unit	ICP-OES mg/L	GFAAS mg/L	difference %	ICP-OES mg/L	GFAAS mg/L	difference %
F101035	Method blank	0.0090	0.0007		0.00069		
	LOQ	0.0121			0.001		
	piece #1	0.207	0.191	8.0	***0.0002***	0.00000	n/a
	piece #2	1.53	1.55	-1.3	***0.0002***	0.00008	n/a
	piece #3	0.717	0.7	2.4	***0.0003***	0.00000	n/a
	piece #4	0.515	0.519	-0.8	***0.0002***	0.00000	n/a
	piece #5	0.219	0.208	5.2	***0.0004***	0.00000	n/a
	piece #6	0.183	0.173	5.6	***0.0003***	0.00007	n/a
	Average	0.562	0.557	3.2			
F104598	Method blank	0.0022	0.0000		0.0001	0.0000	
	LOQ	0.0133			0.0013		
	piece #1	0.936	0.882	5.9	***0.0010***	0.0009	10.5
	piece #2	0.162	0.157	3.1	***0.0003***	0.0002	40.0
	piece #3	0.330	0.317	4.0	***0.0005***	0.0001	133.3
	piece #4	0.237	0.236	0.4	***0.0001***	0.00008	22.2
	piece #5	0.564	0.548	2.9	***0.0007***	0.0006	15.4
	piece #6	0.875	0.887	-1.4	***0.0010***	0.001	0.0
	Average	0.517	0.505	2.5			
	spike (#1)	1.25			0.125		
	found	1.29			0.131		
	Recovery (%)	103.2			104.8		
F107468	Method blank	0.000	0.000		0.0000	0.0000	
	piece #1	0.0832	0.0814	2.2	***0.0000***	0.00002	n/a
	piece #2	0.103	0.1009	2.1	***0.0000***	0.00004	n/a
	piece #3	0.0553	0.0535	3.3	***0.0000***	0.00003	n/a
	piece #4	0.0881	0.0908	-3.0	***0.0000***	0.00001	n/a
	piece #5	0.0480	0.0478	0.4	***0.0000***	0.00002	n/a
	piece #6	0.0395	0.0407	-3.0	***0.0001***	0.00002	n/a
	Average	0.0695	0.0692	0.3			
	spike (#1)	1.00			0.100		
	found	1.04			0.097		
	Recovery (%)	104.0			97.0		
F108443	Method blank	0.000	0.0001		0.000000000	0.00001	
	LOQ	0.0169			0.0011		
	piece #1	0.631	0.630	0.2	0.0177	0.0174	1.7
	piece #2	0.665	0.676	-1.6	0.0232	0.0223	4.0
	piece #3	0.923	0.925	-0.2	0.0304	0.0291	4.4
	piece #4	0.516	0.54	-4.5	0.0137	0.0137	0.0
	piece #5	0.603	0.613	-1.6	0.0164	0.0169	-3.0
	piece #6	0.614	0.613	0.2	0.0156	0.0157	-0.6
	Average	0.659	0.666	-1.3	0.0195	0.0192	1.1
	spike (#1)	1.00			0.100		
	found	1.02			0.101		
	Recovery (%)	102.0			101.0		

Table 2 (part c). Details from a 2001 FDA Southeast Regional Laboratory internal study - Use of ICP-OES to Determine Lead and Cadmium Extracted from Ceramic Foodware

		Pb				Cd		
		ICP-OES	GFAAS	difference		ICP-OES	GFAAS	difference
Sample ID	Analysis unit	mg/L	mg/L	%		mg/L	mg/L	%
F113812	Method blank	0.0002				0.0000		
	LOQ	0.0172				0.0009		
	piece #1	0.0601	0.0613	-2.0		0.0030	0.00308	-2.6
	piece #2	0.0788	0.0817	-3.6		0.0038	0.00385	-1.3
	piece #3	0.0593	0.0649	-9.0		0.0022	0.00231	-4.9
	piece #4	0.0617	0.0665	-7.5		0.0023	0.00248	-7.5
	piece #5	0.0493	0.0553	-11.5		0.0017	0.0020	-16.2
	piece #6	0.0933	0.0985	-5.4		0.0047	0.0049	-4.2
	Average	0.0671	0.071	-6.5		0.00295	0.00310	-6.1
	spike (#1)	1.25				0.125		
	found	1.245				0.125		
	recovery	99.6				100.0		
F113815	piece #1	0.0224	0.0226	-0.9		***0.0008***	0.00083	-3.7
	piece #2	0.0206	0.0217	-5.2		***0.0008***	0.00073	9.2
	piece #3	0.0356	0.0364	-2.2		0.0013	0.00141	-8.1
	piece #4	0.0480	0.0507	-5.5		0.0020	0.00201	-0.5
	piece #5	0.0454	0.0480	-5.6		0.0018	0.00189	-4.9
	piece #6	0.0288	0.0328	-13.0		0.0011	0.00112	-1.8
	Average	0.0335	0.0354	-5.4		0.0013	0.00133	-1.6
	spike (#1)	1.25				0.1		
	found	1.249				0.125		
	recovery	99.92				100.0		
F114417	piece #1	0.113	0.120	-6.0		***0.0000***	0.00006	n/a
	piece #2	0.0755	0.0789	-4.4		***0.0000***	0.00006	n/a
	piece #3	0.0889	0.0935	-5.0		***0.0000***	0.00006	n/a
	piece #4	0.0883	0.0927	-4.9		***0.0000***	0.00003	n/a
	piece #5	0.104	0.111	-6.5		***0.0000***	0.00007	n/a
	piece #6	0.104	0.108	-3.8		***0.0000***	0.00007	n/a
	Average	0.096	0.101	-5.1		0.0000		
	spike (#1)	1.25				0.125		
	found	1.237				0.125		
	Recovery (%)	99.0				100.0		
F108455	Method blank	0.000	0.0001			0.0000	0.00001	
	LOQ	0.0088				0.0012		
	piece #1	0.851	0.857	-0.7		0.0972	0.0951	2.2
	piece #2	0.630	0.609	3.4		0.0966	0.102	-5.4
	piece #3	0.553	0.531	4.1		0.105	0.110	-4.7
	piece #4	0.644	0.664	-3.1		0.0941	0.0996	-5.7
	piece #5	0.611	0.614	-0.5		0.0871	0.0886	-1.7
	piece #6	0.778	0.787	-1.2		0.127	0.124	2.4
	Average	0.678	0.677	0.3		0.101	0.103	-2.2
	spike (#1)	1.00				0.100		
	found	0.997				0.102		
	Recovery (%)	99.7				102.0		

Table 2 (part d). Details from a 2001 FDA Southeast Regional Laboratory internal study - Use of ICP-OES to Determine Lead and Cadmium Extracted from Ceramic Foodware

		Pb				Cd		
Sample ID	Analysis unit	ICP-OES mg/L	GFAAS mg/L	difference %		ICP-OES mg/L	GFAAS mg/L	difference %
F118515b	Method blank	0.0018	0.00005			0.0000	0.00001	
	LOQ	0.0186				0.0014		
	piece #1	0.154	0.153	0.7		0.0152	0.0149	2.0
	piece #2	0.0965	0.098	-1.5		0.0132	0.0132	0.0
	piece #3	0.123	0.126	-2.4		0.0096	0.0097	-1.0
	piece #4	0.128	0.129	-0.8		0.0110	0.0114	-3.6
	piece #5	0.058	0.058	0.0		0.0056	0.0060	-6.9
	piece #6	0.097	0.097	0.0		0.0094	0.0097	-3.1
	Average	0.109	0.110	-0.7		0.0107	0.0108	-2.1
	spike (#1)	1.25				0.125		
	found	1.25				0.1266		
	recovery	100.0				101.3		
F119515y	piece #1	5.60	5.39	3.8		0.0133	0.0129	3.1
	piece #2	6.02	5.75	4.6		0.0129	0.0125	3.1
	piece #3	4.19	4.17	0.5		0.0131	0.0124	5.5
	piece #4	4.46	4.49	-0.7		0.0105	0.0102	2.9
	piece #5	10.7	10.78	-0.7		0.0285	0.0265	7.3
	piece #6	6.35	6.37	-0.3		0.0147	0.0144	2.1
	Average	6.22	6.158	1.2		0.0155	0.0148	4.0
	spike (#1)	1.25				0.125		
	found	1.25				0.1285		
	recovery	100.0				102.8		
F118515g	piece #1	0.203	0.2	1.5		***0.0000***	0.00019	n/a
	piece #2	0.354	0.35	1.1		***0.0000***	0.0001	n/a
	piece #3	0.355	0.355	0.0		***0.0000***	0.0002	n/a
	piece #4	0.274	0.271	1.1		***0.0000***	0.00005	n/a
	piece #5	0.252	0.243	3.6		***0.0000***	0.0001	n/a
	piece #6	0.331	0.323	2.4		***0.0000***	0.00003	n/a
	Average	0.295	0.290	1.6				
	spike (#1)	1.25				0.125		
	found	1.25				0.126		
	Recovery (%)	100.0				100.8		
F118515o	piece #1	17.6	17.3	1.7		0.0013	0.0014	-7.4
	piece #2	2.54	2.56	-0.8		***0.0001***	0.00029	-97.4
	piece #3	14.7	14.8	-0.7		***0.0010***	0.0011	-9.5
	piece #4	22.00	22.1	-0.5		0.0018	0.00194	-7.5
	piece #5	15.8	15.7	0.6		***0.0010***	0.00123	-20.6
	piece #6	7.43	7.82	-5.1		***0.0003***	0.00059	-65.2
	Average	13.35	13.38	-0.8		0.0009	0.0011	-34.6
	spike (#1)	20.0				0.125		
	found	20.5				0.129		
	Recovery (%)	102.5				103.2		

(2) Individual Laboratory Verifications

a) **Method Verifications by San Francisco District Laboratory (2009, 2013, 2015)**

The San Francisco District Laboratory performed verifications of EAM 4.6 in 2009 and 2013 on a Varian Vista Pro ICP-OES. In 2015, an additional verification was completed using a Thermo iCAP 6500 Duo ICP-OES system. Demonstrations of accuracy, precision, method detection level and interference check were completed.

- Instrument-based Figures of Merit (2009, 2013, 2015)

Table 3 shows the Analytical Solution Detection Limit (ASDL) and Analytical Solution Quantitation Limit (ASQL), as outlined in the EAM, for each verification study.

Table 3. ASDL and ASQL for Cd and Pb (mg/L)

Analyte	Wavelength (nm)	2009 ASDL (mg/L)	2013 ASDL (mg/L)	2015 ASDL (mg/L)	2009 ASQL (mg/L)	2013 ASQL (mg/L)	2015 ASQL (mg/L)
Cd	214.439	0.0021	0.0035	0.0081	0.016	0.027	0.063
Cd	226.502	0.0024	0.0034	0.0081	0.018	0.026	0.063
Cd	228.802	0.0029	0.0035	0.0080	0.022	0.027	0.062
Pb	217.000	0.017	0.020	0.010	0.13	0.15	0.080
Pb	220.353	0.0095	0.0061	0.0074	0.074	0.047	0.058
Pb	283.305	0.012	0.018	0.011	0.093	0.14	0.086

- Linear Dynamic Range (2009, 2015)

In 2009, the linear dynamic range was determined by analyzing 4% acetic acid spiked at 2X and 3X the highest calibration standard. A calibration curve was prepared using 0.1, 1, and 10 mg/L Pb and Cd standards. Both Pb and Cd were linear at the 20 mg/L level. For Pb, the recoveries at 30 mg/L were also linear; however, Cd showed non-linear behavior at 30 mg/L where recoveries were < 95%. (See Table 4)

In 2015, a similar study was completed. A calibration curve was prepared using 0.1, 1, and 10 mg/L Pb and Cd standards and a 30 mg/L standard was analyzed. The recoveries were 90-93% for Pb and 82-89% for Cd (for both, over the three wavelengths used). These results indicate non-linear behavior at 30 mg/L for both Pb and Cd.

Table 4. Predictable Dynamic Range (2009)

Analyte	Wavelength (nm)	20 mg/L Spike		30 mg/L Spike	
		Result (mg/L)	Recovery (%)	Result (mg/L)	Recovery (%)
Cd	214.439	19.08	95.4	26.47	88.2
Cd	226.502	19.79	99.0	27.58	91.9
Cd	228.802	19.70	98.5	27.85	92.8
Pb	217.000	19.86	99.3	29.45	98.2
Pb	220.353	20.24	101	30.20	101
Pb	283.305	19.90	99.5	29.57	98.6

- Laboratory Reference Values (2009)

Instrument detection limits (IDLs) and method blank levels (MBKs) were determined for the Varian Vista Pro ICP-OES (see Table 5).

Table 5. IDL and MBK for Varian Vista Pro ICP-OES (EID 426)

Analyte	Wavelength (nm)	IDL_R (mg/L)	MBK_R (mg/L)	MBK_C (mg/L)
Cd	214.439	0.000057	-0.000051	0.000092
Cd	226.502	0.00056	0.000009	0.00057
Cd	228.802	0.0016	0.000044	0.00017
Pb	217.000	0.025	0.0026	0.012
Pb	220.353	0.010	-0.0011	0.0020
Pb	283.305	0.025	0.0094	0.024

- System Suitability Requirements (2009)

Instrument sensitivity and short-term precision were demonstrated by analyzing a solution of 1 mg/L Pb and 0.5 mg/L Cd for five replicate readings. The RSD for all three wavelengths of both Pb and Cd was < 1.5%, which is less than 5% requirement specified in EAM 4.6. The mean was within ±20% of the historical mean.

- Standardization Verification (2009, 2013, 2015)

IDL_R verification was demonstrated by analyzing a reagent blank (4% acetic acid) for five replicate readings (see Table 6). The mean should be less than or equal to three times the IDL_R.

Table 6. IDL_R Verification (2009)

	Cd	Cd	Cd	Pb	Pb	Pb
Wavelength (nm)	214.439	226.502	228.802	217.000	220.353	283.305
IDL_R (mg/L)	0.000057	0.00056	0.0016	0.025	0.010	0.025
3 x IDL_R (mg/L)	0.00017	0.0017	0.0048	0.075	0.030	0.075
IDL (mg/L)	-0.00006	-0.00003	-0.00021	-0.0019	-0.0036	0.0018

In all three verifications (2009, 2013, 2015), calibration curves were prepared using 0.1, 1, and 10 mg/L Pb and Cd standards. The correlation coefficients were all ≥ 0.9995 for both Pb and Cd at all three wavelengths.

In the 2009 verification, initial standardization verification was demonstrated successfully by the analysis of a 1 mg/L Pb and 0.5 mg/L Cd solution immediately after standardization. The results ranged from 99-100% of the expected values for all three wavelengths of Pb and Cd. Continuing calibration verification (CCV) was confirmed by analysis of a 1 mg/L Pb and 0.5 mg/L Cd solution every ten solutions and at the end of the analytical sequence. The results for three CCV runs ranged from 95-100% of the expected values, which were within the ±10% limits. In 2013 and 2015, ICV and CCV checks met the requirements of the method with the exception of one CCV check on the Pb-283.3 nm line in which the CCV recovery was 89.3%.

- Analysis Checks (2009, 2013, 2015)

  Precision

  In the 2009 sample batch, four samples were analyzed, each including six subs. Three samples contained no or only trace amounts of Pb, and all four contained no or only trace amounts of Cd. One sample was found to contain Pb above the ASQL; however, only one sampling of leachate for each sub was analyzed. Good precision among subs of the same sample is not expected due to the non-homogenous nature of the products. In this case, the average Pb concentration for six subs was 8.6 mg/L and the RSD among subs was 50%.

  In 2013, National Check Sample QA13F03 was analyzed, consisting of 3 subs of ceramicware leachate and a blank. Subs 1-3 contained 0.58, 0.29, and 1.1 mg/L Cd and 3.1, 1.2 and 0.58 mg/L Pb, respectively. Each sub was analyzed in duplicate and the RPD for each sub was ≤2% for both Cd and Pb.

  In 2015, National Check Sample QA15F03 was analyzed, consisting of 3 subs of ceramicware leachate and a blank. Subs 1-3 contained 0.60, 0.31, and 1.1 mg/L Cd and 3.1, 1.2 and 0.58 mg/L Pb, respectively. Each sub was analyzed in duplicate and the RPD for each sub was ≤2% for both Cd and Pb.

  Accuracy

  In 2009, one FAS was prepared and analyzed for the one sub of the sample found to contain Pb above the ASQL. The Cd spike recovery at 0.5 mg/L was 105%; and the Pb spike recovery at 4 mg/L was 105%.

  In 2013, National Check Sample QA13F03 was analyzed, consisting of 3 subs of ceramicware leachate and a blank. One FAS recovery was performed on each of the 3 subs and the blank. The recoveries were 96-104% for both Pb and Cd. Spike levels were 0.5 mg/L Cd and 1 mg/L Pb in the blank solution and 0.5, 0.5, and 1 mg/L Cd and 0.5, 1, and 3 mg/L Pb in the sample subs 1-3, respectively.

  In 2015, National Check Sample QA15F03 was analyzed, consisting of 3 subs of ceramicware leachate and a blank. Duplicate FAS recoveries (on one sub) were 97-109% for both Pb and Cd. Spike levels were 0.6 mg/L for Cd and 2.9 mg/L for Pb.

  The method requires that for measurement results >ASQL, the concentration found at the first wavelength must agree within ± 10% RPD at the second wavelength. However, the laboratory measured using three wavelengths and provided RSD for the results from those three wavelengths rather than RPD of each pair. In 2009, 2013 and 2015, three wavelengths were monitored for Pb and Cd. For all subs containing analyte above the ASQL, the RSD of results obtained at all three wavelengths was ≤ 2%.

  The MBK results were acceptable (for all years, 2009, 2013 and 2015).

  Interferences

  Wavelength scans showed no spectral interferences (for all years, 2009, 2013 and 2015).

b. **Method Verification by Northeast Regional Laboratory (2017)**

The Northeast Regional Laboratory performed a method verification of EAM 4.6 in 2017 using a Thermo iCAP 6500 Duo ICP-OES instrument. This verification was performed in a single batch where ASDL and ASQL, calibration, and the verification of one spiked sample prepared in duplicate were included. All EAM 4.6 acceptance criteria were met. ICVs and CCVs were 95-105% and 90-110% of expected results, respectively. Calibration correlation factors were ≥0.998. Method blanks, including the standard blank, were all ≤ASDL. Precision was RPD <10% for duplicates. However, the sample analyzed in duplicate did not contain leachable Pb or Cd; therefore, the sample leachate was spiked to ~1 mg/L Pb and Cd. Results were 90-110% of expected concentrations and FAS recoveries were 90-110%. Table 7 shows the ASDL and ASQL results obtained.

Table 7. ASDL and ASQL for Cd and Pb (mg/L)

Analyte	Wavelength (nm)	ASDL (mg/L)	ASQL (mg/L)
Cd	228.802	0.0013	0.010
Pb	220.353	0.0036	0.028

c. **Summary of Individual Laboratory Verification Data Set Results**

There are some limitations to these verification data sets with regards to method validation. These verification studies are based on only a single analytical run or two. Recoveries of FASs provide an indication of accuracy; however, they are not ideal. Also, in most of the data sets above, only one spike level is utilized. Perhaps most importantly, there were no comparisons to the standard methods using FAAS or GFAAS. In addition, no reference materials are available to test accuracy. Regarding precision, these studies all rely on duplicate analyses of the same leaching solution. The leaching process/whole method reproducibility is not being evaluated based on a lack of identical samples which leach the same way. However, it is again important to realize that the extraction used in EAM 4.6 has been part of accepted standard methods for more than 40 years. The primary focus of these verifications is to demonstrate that ICP-OES as an appropriate determinative step in this application. These verification studies do support this demonstration.

(3) National Check Sample Results – Ceramicware Leachate 2007-2016

Ten years' worth of Ceramicware Leachate proficiency test results (2006-2017), performed within the National Check Sample Program were reviewed. Each year, every lab analyzed three blind ceramic leachate solutions and a blank, which were provided by a commercial PT provider. The results, summarized in Tables 8-17, were compared both among the labs and to the established acceptance limits provided with the tests.

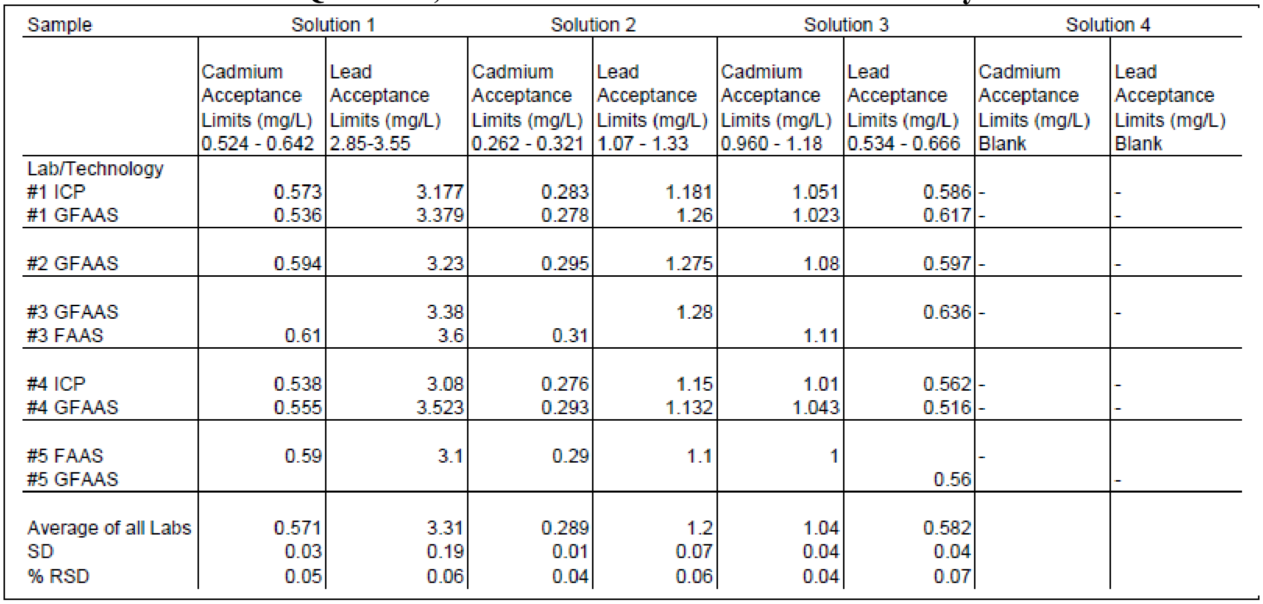
These tests provided useful validation data for the determinative step of the method. Although ICP-OES was used in only one lab in 2007, its usage increased over time such that by the 2012-2016 period, it was used exclusively in all labs. For five of the years, 2007-2011, multiple techniques were used and, in some cases, single laboratories performed the tests using more than one technology (including FAAS, GFAAS, and ICP-MS). Generally, the results compared well between ICP-OES and these other techniques - both within and among laboratories.

Overall, the results were very good with the majority (for both Cd and Pb) being within the PT provider's acceptance limits.

Only two outliers occurred. One was for Cd in one solution in 2014. It was disregarded because half of the labs (2/4) reported results outside of 2σ but within 3σ and the mean for all four participating labs was outside of the 2σ range. This was so unusual that a problem with the solutions was suggested. The other outlier was one Pb result, which was outside of the acceptance limits. Although the data associated with the Cd outlier suggested a problem with the solution, the Pb outlier was not considered unusually problematic because an outlier or two would be statistically expected for such a large number of results.

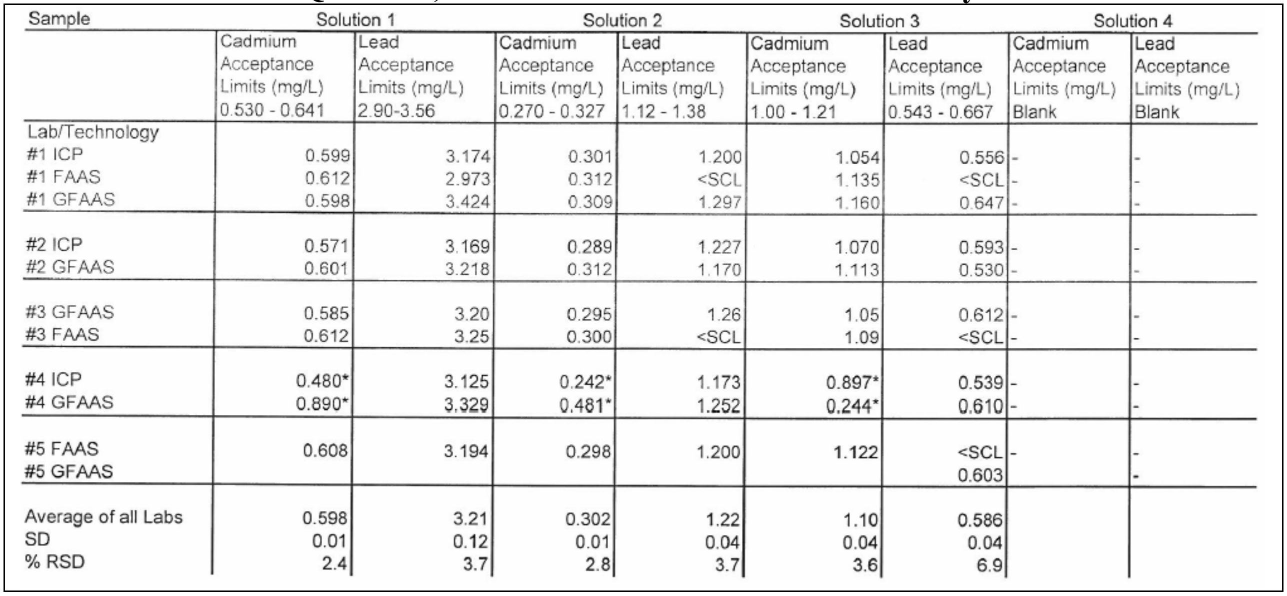
The precision reported for each test solution over the period 2012-2016 was generally very good and ranged from 0.5 – 3.7% RSD overall including both Cd and Pb results. Each of these years 3-4 laboratories participated in the test and generally provide 2 replicate results for each element in each test solution. For Cd and Pb, the average RSDs (average ± 1σ) were 2.2% ± 1.0% and 1.6% ± 0.6%, respectively (n=15, from 3 test solutions per year for 5 years).

Table 8. 2007 NCSP QA07F03, Metals – Ceramicware Leachate Assay Results



Sample	Solution 1		Solution 2		Solution 3		Solution 4	
	Cadmium Acceptance Limits (mg/L) 0.524 - 0.642	Lead Acceptance Limits (mg/L) 2.85-3.55	Cadmium Acceptance Limits (mg/L) 0.262 - 0.321	Lead Acceptance Limits (mg/L) 1.07 - 1.33	Cadmium Acceptance Limits (mg/L) 0.960 - 1.18	Lead Acceptance Limits (mg/L) 0.534 - 0.666	Cadmium Acceptance Limits (mg/L) Blank	Lead Acceptance Limits (mg/L) Blank
Lab/Technology								
#1 ICP	0.573	3.177	0.283	1.181	1.051	0.586	-	-
#1 GFAAS	0.536	3.379	0.278	1.26	1.023	0.617	-	-
#2 GFAAS	0.594	3.23	0.295	1.275	1.08	0.597	-	-
#3 GFAAS		3.38		1.28		0.636	-	-
#3 FAAS	0.61	3.6	0.31		1.11			
#4 ICP	0.538	3.08	0.276	1.15	1.01	0.562	-	-
#4 GFAAS	0.555	3.523	0.293	1.132	1.043	0.516	-	-
#5 FAAS	0.59	3.1	0.29	1.1	1		-	
#5 GFAAS						0.56		-
Average of all Labs	0.571	3.31	0.289	1.2	1.04	0.582		
SD	0.03	0.19	0.01	0.07	0.04	0.04		
% RSD	0.05	0.06	0.04	0.06	0.04	0.07		

Table 9. 2008 NCSP QA08F03, Metals – Ceramicware Leachate Assay Results



Sample	Solution 1		Solution 2		Solution 3		Solution 4	
	Cadmium Acceptance Limits (mg/L) 0.530 - 0.641	Lead Acceptance Limits (mg/L) 2.90-3.56	Cadmium Acceptance Limits (mg/L) 0.270 - 0.327	Lead Acceptance Limits (mg/L) 1.12 - 1.38	Cadmium Acceptance Limits (mg/L) 1.00 - 1.21	Lead Acceptance Limits (mg/L) 0.543 - 0.667	Cadmium Acceptance Limits (mg/L) Blank	Lead Acceptance Limits (mg/L) Blank
Lab/Technology								
#1 ICP	0.599	3.174	0.301	1.200	1.054	0.556	-	-
#1 FAAS	0.612	2.973	0.312	<SCL	1.135	<SCL	-	-
#1 GFAAS	0.598	3.424	0.309	1.297	1.160	0.647	-	-
#2 ICP	0.571	3.169	0.289	1.227	1.070	0.593	-	-
#2 GFAAS	0.601	3.218	0.312	1.170	1.113	0.530	-	-
#3 GFAAS	0.585	3.20	0.295	1.26	1.05	0.612	-	-
#3 FAAS	0.612	3.25	0.300	<SCL	1.09	<SCL	-	-
#4 ICP	0.480*	3.125	0.242*	1.173	0.897*	0.539	-	-
#4 GFAAS	0.890*	3.329	0.481*	1.252	0.244*	0.610	-	-
#5 FAAS	0.608	3.194	0.298	1.200	1.122	<SCL	-	-
#5 GFAAS						0.603		-
Average of all Labs	0.598	3.21	0.302	1.22	1.10	0.586		
SD	0.01	0.12	0.01	0.04	0.04	0.04		
% RSD	2.4	3.7	2.8	3.7	3.6	6.9		

SCL – Sample Concentration Limit

*Outside 3σ – not used in statistical evaluation

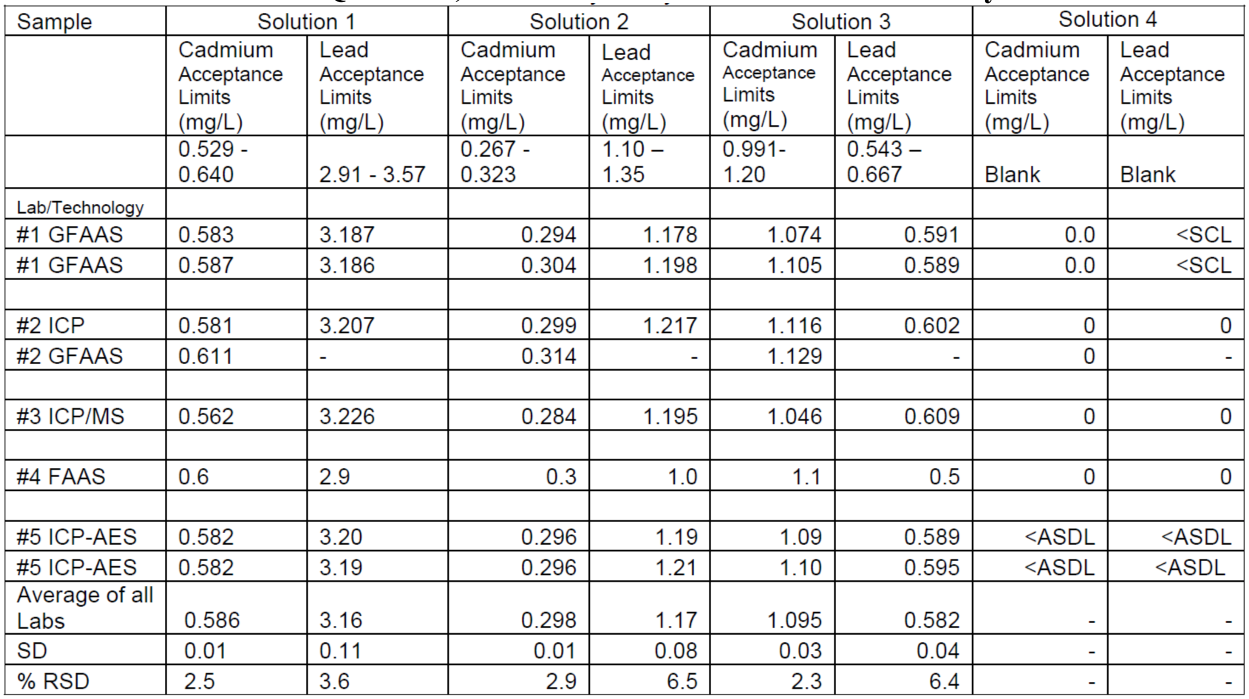
Table 10. 2009 NCSP QA09F03, Metals – Ceramicware Leachate Assay Results

Sample	Solution 1		Solution 2		Solution 3		Solution 4	
	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)
	Blank	Blank	0.527 - 0.638	2.89 - 3.55	0.262 - 0.317	1.09 – 1.33	0.965 - 1.17	0.534 - 0.655
Lab/Technology								
#1 FAAS	-	-	0.621	3.088	0.307	1.067	1.124	0.308*
#1 GFAAS	-	-	0.613	3.201	0.294	1.310	1.167	0.624
#2 ICP	-	-	0.608	3.243	0.307	1.239	1.109	0.602
#2 GFAAS	-	-	0.602	3.360	0.301	1.240	1.106	0.600
#3 ICP	-	-	0.568	3.208	0.281	1.198	1.036	0.589
#4 FAAS	-	-	0.6	3.0	0.3	1.1	1.1	0.6
#5 **	-	-	-	-	-	-	-	-
Average of all Labs			0.602	3.19	0.298	1.19	1.11	0.603
SD			0.02	0.12	0.01	0.04	0.04	0.01
% RSD			3.1	3.9	3.3	7.7	3.7	2.1

*Outside Acceptance Limits – not used in statistical evaluation

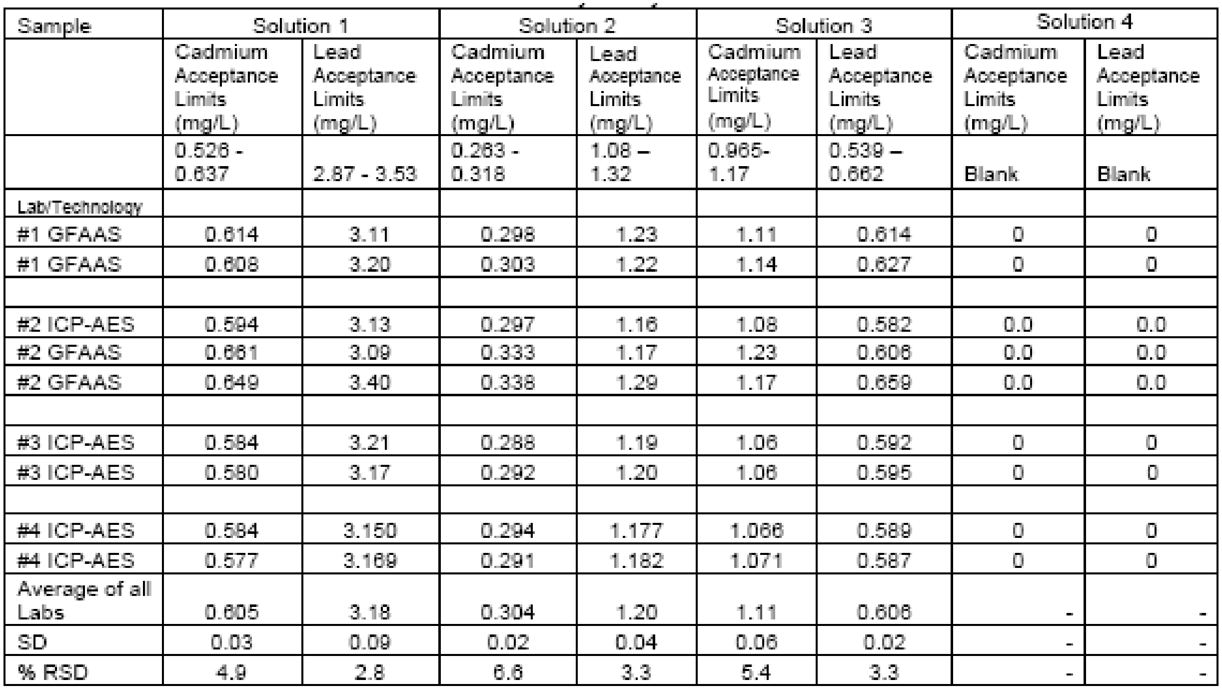
**Shipment not received

Table 11. 2010 NCSP QA10F03, Metals – Ceramicware Leachate Assay Results



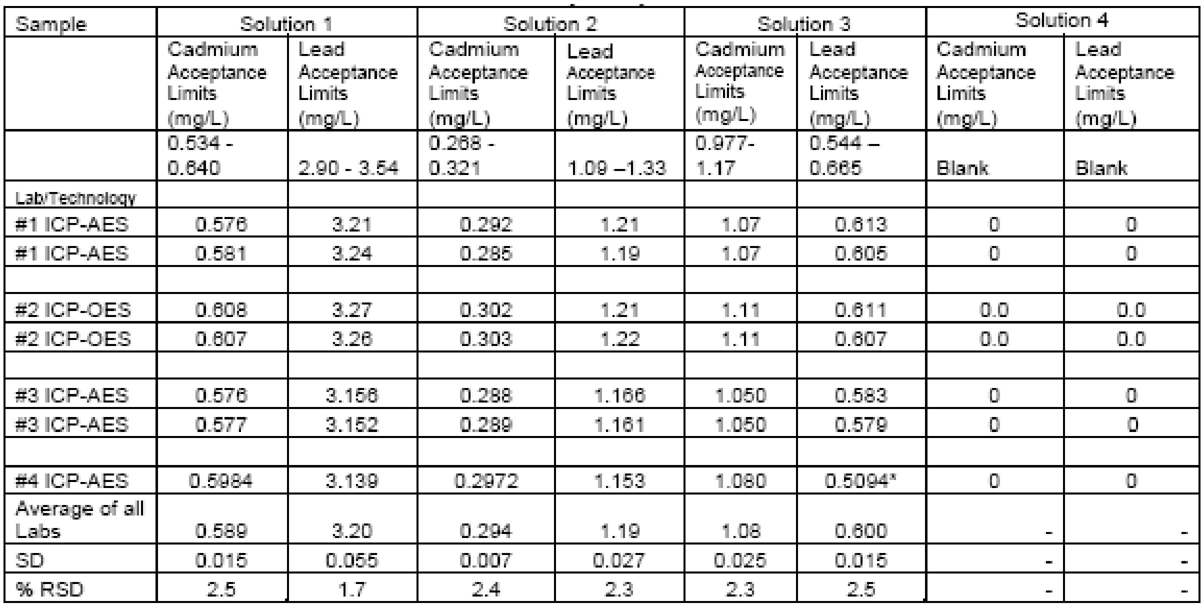
Sample	Solution 1		Solution 2		Solution 3		Solution 4	
	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)
	0.529 - 0.640	2.91 - 3.57	0.267 - 0.323	1.10 – 1.35	0.991- 1.20	0.543 – 0.667	Blank	Blank
Lab/Technology								
#1 GFAAS	0.583	3.187	0.294	1.178	1.074	0.591	0.0	<SCL
#1 GFAAS	0.587	3.186	0.304	1.198	1.105	0.589	0.0	<SCL
#2 ICP	0.581	3.207	0.299	1.217	1.116	0.602	0	0
#2 GFAAS	0.611	-	0.314	-	1.129	-	0	-
#3 ICP/MS	0.562	3.226	0.284	1.195	1.046	0.609	0	0
#4 FAAS	0.6	2.9	0.3	1.0	1.1	0.5	0	0
#5 ICP-AES	0.582	3.20	0.296	1.19	1.09	0.589	<ASDL	<ASDL
#5 ICP-AES	0.582	3.19	0.296	1.21	1.10	0.595	<ASDL	<ASDL
Average of all Labs	0.586	3.16	0.298	1.17	1.095	0.582	-	-
SD	0.01	0.11	0.01	0.08	0.03	0.04	-	-
% RSD	2.5	3.6	2.9	6.5	2.3	6.4	-	-

Table 12. 2011 NCSP QA11F03, Metals – Ceramicware Leachate Assay Results



Sample	Solution 1		Solution 2		Solution 3		Solution 4	
	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)
	0.526 - 0.637	2.87 - 3.53	0.263 - 0.318	1.08 – 1.32	0.965- 1.17	0.539 – 0.662	Blank	Blank
Lab/Technology								
#1 GFAAS	0.614	3.11	0.298	1.23	1.11	0.614	0	0
#1 GFAAS	0.608	3.20	0.303	1.22	1.14	0.627	0	0
#2 ICP-AES	0.594	3.13	0.297	1.16	1.08	0.582	0.0	0.0
#2 GFAAS	0.661	3.09	0.333	1.17	1.23	0.606	0.0	0.0
#2 GFAAS	0.649	3.40	0.338	1.29	1.17	0.659	0.0	0.0
#3 ICP-AES	0.584	3.21	0.288	1.19	1.06	0.592	0	0
#3 ICP-AES	0.580	3.17	0.292	1.20	1.06	0.595	0	0
#4 ICP-AES	0.584	3.150	0.294	1.177	1.066	0.589	0	0
#4 ICP-AES	0.577	3.169	0.291	1.182	1.071	0.587	0	0
Average of all Labs	0.605	3.18	0.304	1.20	1.11	0.606	-	-
SD	0.03	0.09	0.02	0.04	0.06	0.02	-	-
% RSD	4.9	2.8	6.6	3.3	5.4	3.3	-	-

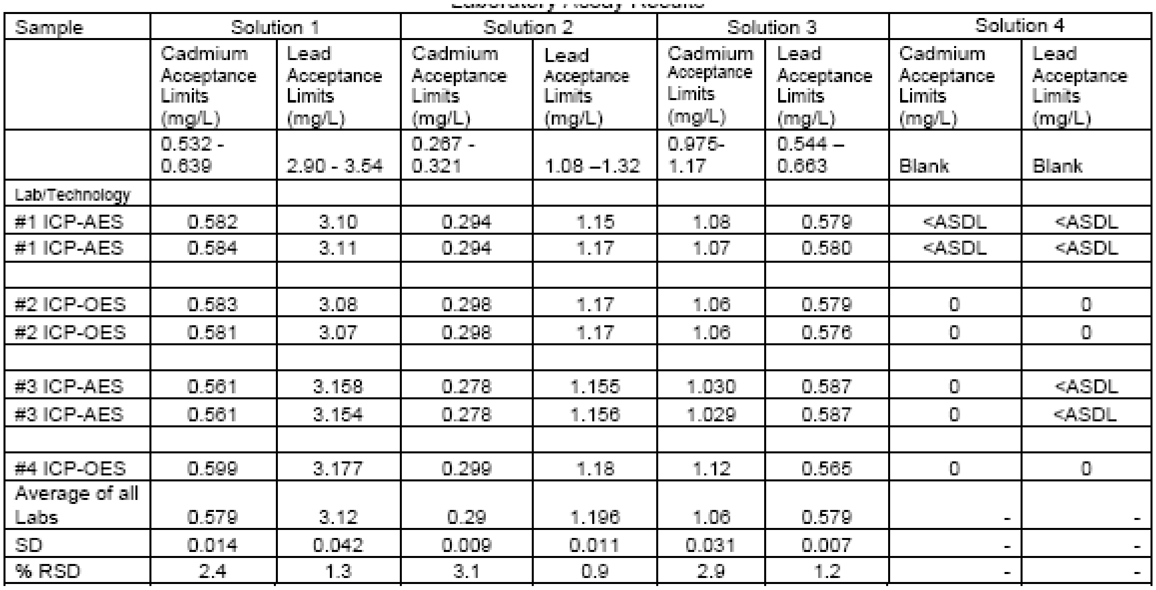
Table 13. 2012 NCSP QA12F03, Metals – Ceramicware Leachate Assay Results



Sample	Solution 1		Solution 2		Solution 3		Solution 4	
	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)
	0.534 - 0.640	2.90 - 3.54	0.268 - 0.321	1.09 –1.33	0.977- 1.17	0.544 – 0.665	Blank	Blank
Lab/Technology								
#1 ICP-AES	0.576	3.21	0.292	1.21	1.07	0.613	0	0
#1 ICP-AES	0.581	3.24	0.285	1.19	1.07	0.605	0	0
#2 ICP-OES	0.608	3.27	0.302	1.21	1.11	0.611	0.0	0.0
#2 ICP-OES	0.607	3.26	0.303	1.22	1.11	0.607	0.0	0.0
#3 ICP-AES	0.576	3.156	0.288	1.166	1.050	0.583	0	0
#3 ICP-AES	0.577	3.152	0.289	1.161	1.050	0.579	0	0
#4 ICP-AES	0.5984	3.139	0.2972	1.153	1.080	0.5094*	0	0
Average of all Labs	0.589	3.20	0.294	1.19	1.08	0.600	-	-
SD	0.015	0.055	0.007	0.027	0.025	0.015	-	-
% RSD	2.5	1.7	2.4	2.3	2.3	2.5	-	-

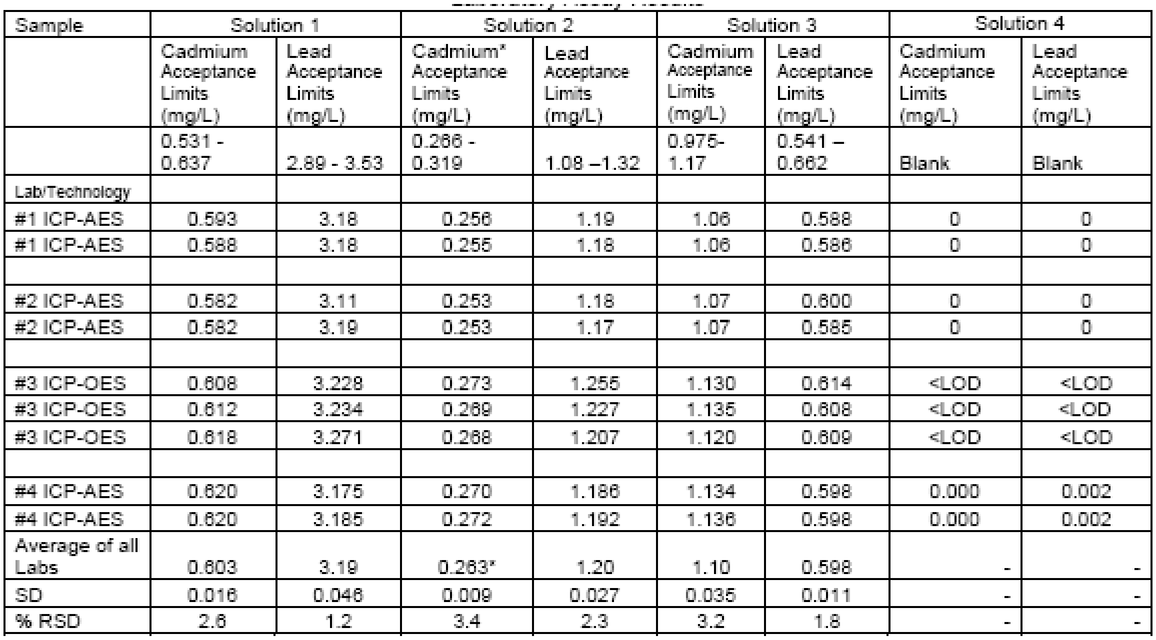
* Out of Acceptance Limits- Not used for statistics

Table 14. 2013 NCSP QA13F03, Metals – Ceramicware Leachate Assay Results



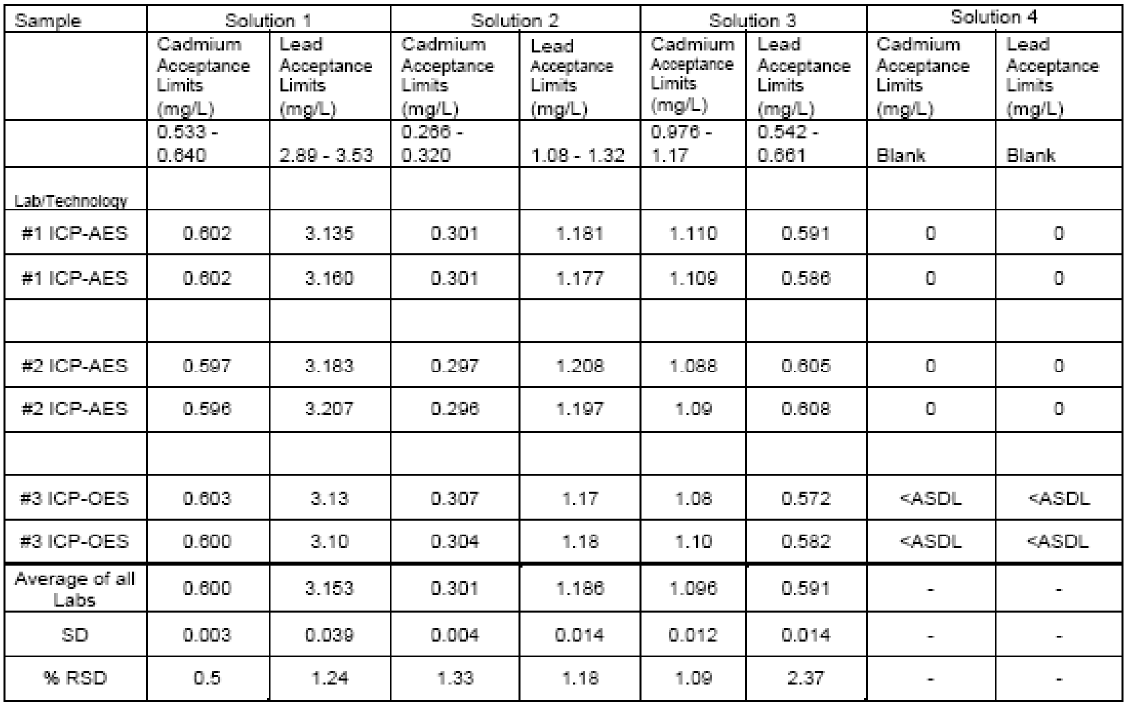
Sample	Solution 1		Solution 2		Solution 3		Solution 4	
	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)
	0.532 - 0.639	2.90 - 3.54	0.267 - 0.321	1.08 –1.32	0.975- 1.17	0.544 – 0.663	Blank	Blank
Lab/Technology								
#1 ICP-AES	0.582	3.10	0.294	1.15	1.08	0.579	<ASDL	<ASDL
#1 ICP-AES	0.584	3.11	0.294	1.17	1.07	0.580	<ASDL	<ASDL
#2 ICP-OES	0.583	3.08	0.298	1.17	1.06	0.579	0	0
#2 ICP-OES	0.581	3.07	0.298	1.17	1.06	0.576	0	0
#3 ICP-AES	0.561	3.158	0.278	1.155	1.030	0.587	0	<ASDL
#3 ICP-AES	0.561	3.154	0.278	1.156	1.029	0.587	0	<ASDL
#4 ICP-OES	0.599	3.177	0.299	1.18	1.12	0.565	0	0
Average of all Labs	0.579	3.12	0.29	1.196	1.06	0.579	-	-
SD	0.014	0.042	0.009	0.011	0.031	0.007	-	-
% RSD	2.4	1.3	3.1	0.9	2.9	1.2	-	-

Table 15. 2014 NCSP QA14F03, Metals – Ceramicware Leachate Assay Results



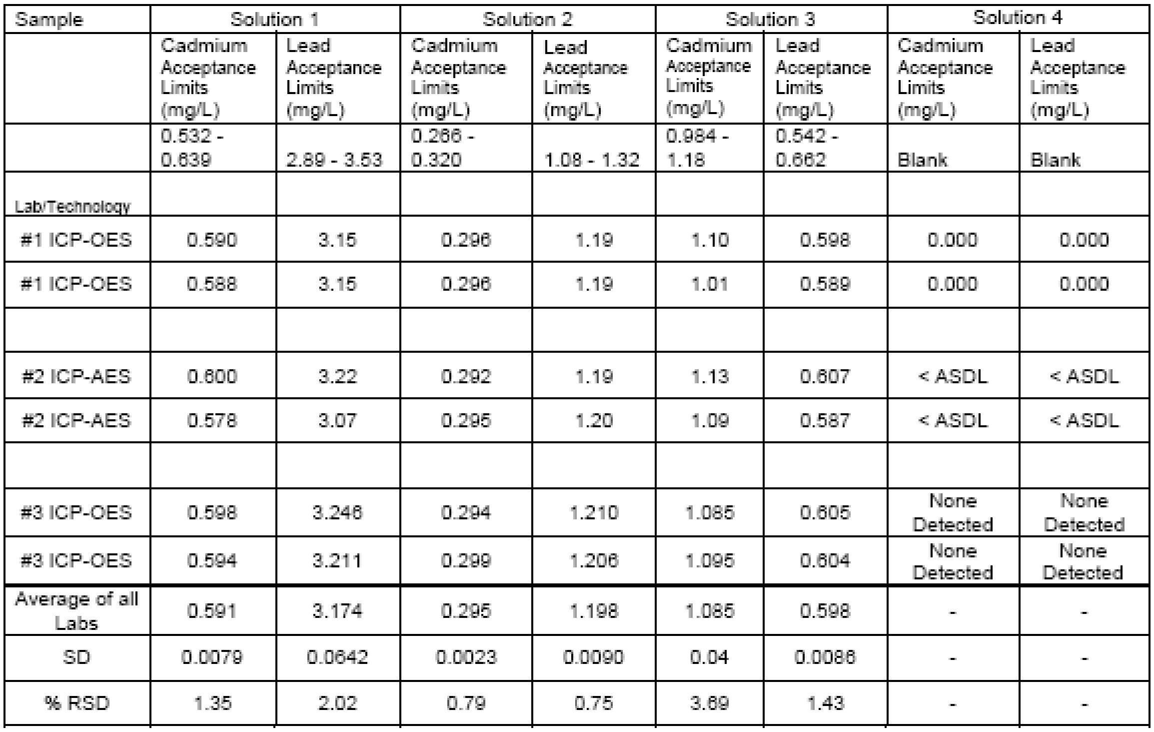
Sample	Solution 1		Solution 2		Solution 3		Solution 4	
	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium* Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)
	0.531 - 0.637	2.89 - 3.53	0.266 - 0.319	1.08 –1.32	0.975- 1.17	0.541 – 0.662	Blank	Blank
Lab/Technology								
#1 ICP-AES	0.593	3.18	0.256	1.19	1.06	0.588	0	0
#1 ICP-AES	0.588	3.18	0.255	1.18	1.06	0.586	0	0
#2 ICP-AES	0.582	3.11	0.253	1.18	1.07	0.600	0	0
#2 ICP-AES	0.582	3.19	0.253	1.17	1.07	0.585	0	0
#3 ICP-OES	0.608	3.228	0.273	1.255	1.130	0.614	<LOD	<LOD
#3 ICP-OES	0.612	3.234	0.269	1.227	1.135	0.608	<LOD	<LOD
#3 ICP-OES	0.618	3.271	0.268	1.207	1.120	0.609	<LOD	<LOD
#4 ICP-AES	0.620	3.175	0.270	1.186	1.134	0.598	0.000	0.002
#4 ICP-AES	0.620	3.185	0.272	1.192	1.136	0.598	0.000	0.002
Average of all Labs	0.603	3.19	0.263*	1.20	1.10	0.598	-	-
SD	0.016	0.046	0.009	0.027	0.035	0.011	-	-
% RSD	2.6	1.2	3.4	2.3	3.2	1.8	-	-

Table 16. 2015 NCSP QA15F03, Metals – Ceramicware Leachate Assay Results



Sample	Solution 1		Solution 2		Solution 3		Solution 4	
	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)
	0.533 - 0.640	2.89 - 3.53	0.266 - 0.320	1.08 - 1.32	0.976 - 1.17	0.542 - 0.661	Blank	Blank
Lab/Technology								
#1 ICP-AES	0.602	3.135	0.301	1.181	1.110	0.591	0	0
#1 ICP-AES	0.602	3.160	0.301	1.177	1.109	0.586	0	0
#2 ICP-AES	0.597	3.183	0.297	1.208	1.088	0.605	0	0
#2 ICP-AES	0.596	3.207	0.296	1.197	1.09	0.608	0	0
#3 ICP-OES	0.603	3.13	0.307	1.17	1.08	0.572	<ASDL	<ASDL
#3 ICP-OES	0.600	3.10	0.304	1.18	1.10	0.582	<ASDL	<ASDL
Average of all Labs	0.600	3.153	0.301	1.186	1.096	0.591	-	-
SD	0.003	0.039	0.004	0.014	0.012	0.014	-	-
% RSD	0.5	1.24	1.33	1.18	1.09	2.37	-	-

Table 17. 2016 NCSP QA16F03, Metals – Ceramicware Leachate Assay Results



Sample	Solution 1		Solution 2		Solution 3		Solution 4	
	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)	Cadmium Acceptance Limits (mg/L)	Lead Acceptance Limits (mg/L)
	0.532 - 0.639	2.89 - 3.53	0.266 - 0.320	1.08 - 1.32	0.984 - 1.18	0.542 - 0.662	Blank	Blank
Lab/Technology								
#1 ICP-OES	0.590	3.15	0.296	1.19	1.10	0.598	0.000	0.000
#1 ICP-OES	0.588	3.15	0.296	1.19	1.01	0.589	0.000	0.000
#2 ICP-AES	0.600	3.22	0.292	1.19	1.13	0.607	< ASDL	< ASDL
#2 ICP-AES	0.578	3.07	0.295	1.20	1.09	0.587	< ASDL	< ASDL
#3 ICP-OES	0.598	3.246	0.294	1.210	1.085	0.605	None Detected	None Detected
#3 ICP-OES	0.594	3.211	0.299	1.206	1.095	0.604	None Detected	None Detected
Average of all Labs	0.591	3.174	0.295	1.198	1.085	0.598	-	-
SD	0.0079	0.0642	0.0023	0.0090	0.04	0.0086	-	-
% RSD	1.35	2.02	0.79	0.75	3.69	1.43	-	-

CONCLUSION

When taken in total, the data sets and testing results provided here agree with the analytical community's expert opinion that ICP-OES is as good, or better, than FAAS and GFAAS in this application. They also provide enough evidence to support the recommendation that EAM 4.6 be grandfathered to Validation Level 3 (multi-laboratory validated) status and that EAM 4.6 be updated to include a validation summary prior to approval.

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(1) Cheng, J., EAM Method 4.6, "Inductively Coupled Plasma-Atomic Emission Spectrometric Determination of Cadmium and Lead Extracted from Ceramic Foodware," FDA Elemental Analysis Manual, Version Draft 0.2 (August 2010), available from https://www.fda.gov/food/laboratory-methods-food/elemental-analysis-manual-eam-food-and-related-products (accessed December, 2019).

(2) Hight, S.C., Capar, S.G., EAM Method 4.1, "Flame Atomic Absorption Spectrometric Determination of Lead and Cadmium Extracted from Ceramic Foodware," FDA Elemental Analysis Manual, Version 1.1 (September 2010) , available from https://www.fda.gov/food/laboratory-methods-food/elemental-analysis-manual-eam-food-and-related-products (accessed December, 2019).

(3) Hight, S.C., Capar, S.G., EAM Method 4.2, "Graphite Furnace Atomic Absorption Spectrometric Determination of Lead and Cadmium Extracted from Ceramic Foodware," FDA Elemental Analysis Manual, Version 1.2 (September 2010) , available from https://www.fda.gov/food/laboratory-methods-food/elemental-analysis-manual-eam-food-and-related-products (accessed December, 2019).

(4) AOAC Official Method 973.32, "Lead and Cadmium Extracted from Ceramicware Atomic Absorption Spectroscopic Method," AOAC-ASTM Method, 1977, available from http://www.aoacofficialmethod.org/index.php?main_page=product_info&cPath=1&products_id=90 (accessed December, 2019).

(5) AOAC Official Method 973.82, "Lead and Cadmium Extracted from Ceramicware Alternative Atomic Absorption Spectroscopic Method," AOAC-ASTM Method, 1977, available from http://www.aoacofficialmethod.org/index.php?main_page=product_info&cPath=1&products_id=2558 (accessed December, 2019).

(6) AOAC Official Method 999.17, "Lead and Cadmium Extracted from Ceramic Foodware Graphite Furnace Atomic Absorption Spectrometric (GFAAS) Method," 2004, available from https://img.21food.cn/img/biaozhun/20100108/177/11285287.pdf (accessed December, 2019).

(7) Hight, S.C., "Graphite Furnace Atomic Absorption Spectrometric Determination of Lead and Cadmium Extracted from Ceramic Foodware: Collaborative Study," *J. AOAC Int*., 83, 2000, 1174-1188.

(8) CPG Sec. 545.450 Pottery (Ceramics); Import and Domestic- Lead Contamination, available from https://www.fda.gov/media/71764/download (accessed December, 2019).

(9) CPG Sec. 545.400 Potter (Ceramics); Import and Domestic – Cadmium Contamination, available from https://www.fda.gov/media/71762/download (accessed December, 2019).