GLASS MATRIX TEST METHODS EVALUATION FOR TOXICS IN PACKAGING

Final Report

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By
Toxics in Packaging Clearinghouse

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- University of Iowa, State Hygienic Laboratory, Coralville, Iowa

Test results presented in this report are not attributed to specific laboratories. It was not the intent of this project to judge laboratory performance. Rather, this research identified appropriate test methods for determining total metals concentration in glass substrates.

TPCH is administered by the Northeast Recycling Council, Inc., based in Brattleboro, Vermont. All TPCH activities are overseen by representatives from member states:

- Ron Ohta, California Department of Toxic Substances Control
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EXECUTIVE SUMMARY

The California Department of Toxics Substances Control (DTSC) contracted with the Northeast Recycling Council Inc. (NERC), the administrator of the Toxics in Packaging Clearinghouse (TPCH), to perform an evaluation of test methods for determining the total concentration of toxic metals in glass matrix packaging components. Nineteen U.S. states, including California, have toxics in packaging laws that prohibit the intentional use and restrict the total concentration of four metals – lead (Pb), cadmium (Cd), mercury (Hg) and hexavalent chromium – in packaging. The goals of this study were to compare and evaluate sample preparation and test methods used to determine total metals concentration for Pb and Cd in glass matrices. The Toxics in Packaging Clearinghouse will use this information to prepare guidance for compliance with state toxics in packaging statutes.

For this project, TPCH sent twelve glass samples to ten analytical laboratories to determine the total concentration of Pb and Cd, two of the four metals restricted by state toxics in packaging laws.[1,2] Nine of the twelve samples were glass bottles, and the remaining three samples were Certified Reference Materials (CRM)/Standard Reference Materials (SRM). TPCH screened the glass bottles using x-ray fluorescence (XRF) analysis, and selected samples with a range of Pb concentrations for analysis.[3]

The results indicated that U.S Environmental Protection Agency SW-846 Method 3052[4] and comparable sample preparation methods using hydrofluoric acid (HF) effectively liberated Pb and Cd from the glass matrix for the determination of total metals concentration. Methods using HF without the application of an external heat source such as microwave, oven bomb or hot plate did not perform as well. EPA Method 3050B, which is a sample preparation method intended to measure “total recoverable metals” was inadequate in the liberation of Pb and Cd from glass matrix samples. Method 3050B consistently detected 99 - 100 percent less Pb or Cd than was present in the glass matrix sample.

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[1] State toxics in packaging laws restrict four metals: Pb, Cd, mercury, and hexavalent chromium.

[2] Given the cost of laboratory analysis, laboratories were asked to analyze only for Pb and Cd, substances that are more likely to be used in glass packaging.

[3] Cd concentration was not used to select samples since this metal was not detected above 100 ppm in retail samples screened for this project.

[4] EPA SW-846 Method 3052, Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices.

Method 3052 requires the use of HF for siliceous matrices (such as glass). Laboratories may be reluctant to use Method 3052 because HF, if used inappropriately or if accidents occur, can have serious health impacts and must be managed carefully. HF can also destroy an instrument's expensive optical components. However, laboratories capable of performing Method 3052 are commercially available in the U.S. as well as globally. Of the ten participating laboratories, eight laboratories performed EPA Method 3052 or a comparable method using HF. These eight are commercial laboratories offering consumer product testing, environmental analyses, and specialty testing services targeting glass, inorganic substances, and metals. About half of the test laboratories offer testing services throughout their global operations, while one laboratory was based in the European Union.

XRF spectroscopy offers an alternative to EPA Method 3052 and the use of HF for non-destructive analysis of metals in glass matrices.[5] In this study, XRF results were most often, but not always, comparable to EPA Method 3052 in determining the concentration of Pb and Cd. XRF analysis detected the presence of Pb and Cd in all samples known to contain these substances and did not produce false positives when a margin of error was taken into account.

Based on the results of this study, TPCH recommends the use of:

- EPA Method 3052 or comparable methods using HF for the analysis of glass matrices when traditional laboratory "wet" chemistry analysis is required. The analysis method should include the application of an external heat source to assist in acid digestion.
- XRF analysis for screening glass matrix samples for compliance with state toxics in packaging laws. Analytical testing may be used to confirm metal concentrations and the compliance status of glass matrices.

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[5] XRF analysis has limitations for the detection of hexavalent chromium, which is restricted by state laws, although not the focus of the current project. The limitations of XRF analysis for chromium are discussed in previous TPCH reports available at: http://www.toxicsinpackaging.org/projects_publications.html.

1.0 INTRODUCTION

The California DTSC contracted with NERC, the administrator of the TPCH, to conduct a study to evaluate sample preparation and analysis methods for glass matrix packaging components and to develop guidance for stakeholders on the applicability of these methods to determine compliance with toxics in packaging statutes.

The goals of this study were to:

- Evaluate and compare sample preparation and analysis methods for determining total metals concentration of Pb and Cd in glass matrices, including but not limited to EPA Method 3052 and comparable methods.
- Identify and evaluate sample preparation and analytical test methods, both destructive and non-destructive, that use alternatives to highly toxic HF, which is used in Method 3052, for the dissolution of siliceous materials.
- Determine the availability of laboratories in the U.S. that can perform analytical testing of glass samples using EPA Method 3052 or comparable method that uses HF.
- Provide guidance to stakeholders on appropriate sample preparation and analytical methods for determining total metals in glass matrices.

DTSC is the state agency tasked with administration and enforcement of the California Toxics in Packaging Prevention Act. As part of its program, DTSC develops technical assistance and outreach information to educate stakeholders (manufacturers, distributors, suppliers, and purchasers of packaging and packaging components, such as retailers, as well as testing laboratories). This includes development of best practices for compliance testing.

The results of the study will be used as the basis to prepare guidance for glass matrices testing for compliance with state toxics in packaging statutes.

2.0 BACKGROUND & CONTEXT FOR THE PROJECT

The objective for determining metals concentration in packaging components is not to determine waste characteristics but to determine compliance with packaging legislation. Packaging statutes prohibit the intentional use of four metals – Pb, Cd, Hg, and hexavalent chromium – and limit the incidental presence of these metals to a combined sum of 100 ppm for total concentration. The objective, therefore, is not to determine total “recoverable” or “acid digestible” metals, but to determine total metals concentrations. This requires complete decomposition of the matrix to release the individual constituents for subsequent detection and measurement.

Laboratories historically provided sample analyses using traditional EPA solid waste testing methods[6] such as Method 3050 or Method 3051 for sample preparation/digestion prior to metals determination. These methods were developed for hazardous waste characterization and designation, and were designed to dissolve most elements that could become "environmentally available". Hence, total metals using these methods have been referred to as "total recoverable" or "acid digestible" metals. These methods, in their scope and applications section, state that in order to obtain complete digestion, Method 3052 is recommended.

Method 3052 requires the use of highly dangerous HF for siliceous matrices. Laboratories may be reluctant to use Method 3052 because HF has serious health impacts if used inappropriately or accidentally released, and must be used with care. HF can also destroy an instrument's expensive optical components. In addition, laboratories that are unfamiliar with the objective of compliance testing for packaging components, select methods that do not completely decompose the sample matrix, failing to completely liberate the metals, and subsequently provide erroneously low total metals results.

Materials other than glass have also been difficult for laboratories to accurately characterize in the past. TPCH has performed several packaging screening projects using XRF devices followed by confirmatory laboratory analyses. Most of the samples for these projects were plastic or flexible polyvinyl chloride (PVC) packaging components. TPCH noted discrepancies between manufacturers' supplied certificates of compliance/laboratory analysis reports and TPCH's XRF screening results. DTSC's Environmental Chemistry Laboratory (ECL) performed comparative analyses on a small set of flexible PVC samples. ECL performed rigorous digestion methods, including the use of microwave-assisted digestion to ensure complete decomposition of the plastic matrix. Samples were digested using Methods 3050, 3051 or 3052. DTSC ECL compiled the results and found that the strongest correlation between XRF and laboratory results occurred with increasing rigorous digestion leading to the complete decomposition of the PVC matrix.[7]

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[6] Test Methods for Evaluating Solid Waste, Physical/Chemical Methods commonly known as SW-846 are available at: http://www.epa.gov/epawaste/hazard/testmethods/sw846/index.htm.

[7] A summary of these results is available in *An Assessment of Toxics in Packaging: 2009 Update*.

DTSC contracted with TPCH to perform an evaluation of laboratories' analytical performance on flexible PVC packaging components. Plastic samples with known metal concentrations were sent to several laboratories to evaluate consistency between laboratories. Completed in June 2011, the results of this study were summarized in a final report, *Laboratory Round Robin Test Project: Assessing Performance in Measuring Toxics in Packaging*.

These studies showed 1) the importance of complete matrix digestion to achieve accurate results, and 2) a general misunderstanding among laboratories of the objectives of packaging compliance testing.

As with other packaging materials, such as plastic, glass offers a unique matrix and challenge to many laboratories. DTSC and TPCH have received inquiries regarding proper test protocols for evaluating compliance with toxics in packaging statutes for package components of various types. To determine compliance of glass packaging components, stakeholders need to know: 1) what methods are viable options, 2) if methods using HF are necessary for the analysis of glass matrices, and 3) if commercial laboratories offer these analytical services.

3.0 PROJECT METHODOLOGY

For this project, TPCH sent twelve packaging samples to ten analytical laboratories for determination of the total concentration of two metals, Pb and Cd, restricted by state toxics in packaging laws. Nine of the twelve samples were retail glass bottles, and the remaining three samples were glass control samples. Laboratories were asked to analyze samples for total metals concentration. Laboratories analyzed samples using several methodologies, including EPA Method 3052, EPA Method 3050B, in-house methods, and XRF analysis. Laboratory results were compared to expected values, or certified values for Certified Reference Materials (CRM)/Standard Reference Materials (SRM), to evaluate the effectiveness of the laboratory test methods in determining total concentration of the regulated metals in glass matrices.

3.1 SELECTION AND PREPARATION OF PACKAGING SAMPLES

The Washington State Department of Ecology (Washington Ecology) prescreened retail bottle samples using an XRF to identify glass bottles with a range of Pb concentrations. The control samples were glass matrix Certified Reference Materials (CRMs) and Standard Reference Materials (SRMs) containing Pb and Cd at different concentrations, purchased from the German

Institute for Materials Research and Testing (BAM)[8] and the U. S. National Institute of Standards and Technology (NIST)[9]. Selecting samples, including CRM/SRMs, with a range of Pb concentrations helped discern whether the performance of test methods was dependent on metals concentration.[10]

The samples sent to laboratories for analysis are shown in Table 1. For the retail glass samples, the metal concentrations shown in the Table are XRF values generated by Washington Ecology using a Niton XL3t 700 portable XRF analyzer. The metals concentrations for the control samples are the certified values provided in the Certificate of Analysis that accompanied the reference material. The Pb concentration in five samples was less than 100 ppm, which is the threshold in state toxics in packaging laws for the incidental presence of the sum of the restricted metals. Six samples had Pb concentrations between 200 and 500 ppm, while the Pb concentration in one sample was 900 ppm. Cd concentrations in all samples were under 100 ppm.

TABLE 1: GLASS PACKAGING SAMPLES

Sample	Sample Description	Metals Concentration[1]	
		Pb (ppm)	Cd (ppm)
1	Retail glass bottle – clear	<LOD	<LOD
2	Retail glass bottle – green	300	8
3	Retail glass bottle – green	100	8
4	CRM BAM-S005A[2]	202	62
5	Retail glass bottle – green	200	24
6	Retail glass bottle – green	900	10
7	Retail glass bottle – green	21	<LOD
8	Retail glass bottle – green	375	6
9	Retail glass bottle – green	475	6
10	Retail glass bottle – green	40	9
11	SRM- NIST 611[3]	426	NA
12	SRM- NIST 615[3]	2.32 +/- 0.04	NA

LOD – Below level of detection; for Pb < 15 ppm; for Cd < 25 ppm; NA – Not applicable

[1] Metals concentrations for retail glass bottles determined by XRF screening using a Niton XL3t 700. Metals concentrations for CRMs/SRMs are certified values reported in certificate of analyses provided with the sample.

[2] Certified values reported are for Pb (III) oxide and Cd oxide.

[3] Certified values reported for Pb only.

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[8] Available from Federal Institute for Materials Research and Testing (BAM), Berlin, Germany, www.bam.de/crm

[9] Available from NIST, U,S. Department of Commerce, Gaithersburg, Maryland, United States, www.nist.gov/srm

[10] Retail samples containing >100 ppm of Cd were not identified.

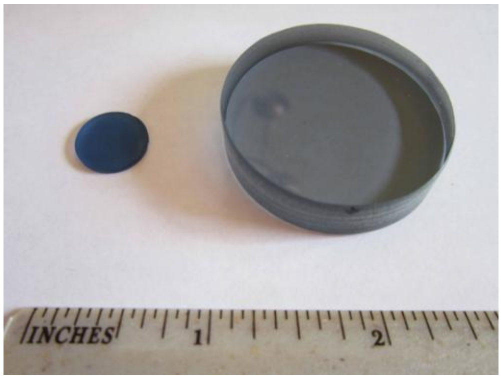
Glass packaging samples were prepared for shipment to laboratories as follows:

1) Remove labels by soaking in water with mild dish detergent.
2) Rinse bottles, inside and out, with tap water. Allow to air dry.
3) Place each bottle in a closed, large plastic bag. Drop bag on hard surface to break bottle into shards.
4) Measure 30 grams of sample and place in 2 oz. natural polypropylene container with lid. Label container with sample number. Create 12 individual samples from each bottle.
5) For CRM/SRMs, place one disc supplied by BAM/NIST in 2 oz. natural polypropylene container.
6) Send 1 container of each bottle sample and CRM/SRM to participating laboratories. Retain one sample at TPCH for reference.

Figure 1 below shows a sample in a 2 oz. container, ready for closure and shipment. Each laboratory received one container with 30 grams of each sample, with the exception of the CRM/SRMs. Laboratories received one disc of each CRM/SRM, as shipped from BAM and NIST. Figure 2 is a photo of the BAM CRM and one of the two NIST SRMs. Each BAM CRM weighed between 26 g to 30 g, while the NIST SRM discs weighed about 0.5 g each.

FIGURE 1: PREPARED SAMPLE

FIGURE 2: BAM CRM (RIGHT) & NIST SRM (LEFT)



EPA SW-846 Sample Preparation

The scope and application of **Method 3052** states that it is applicable to the microwave assisted acid digestion of organic and other complex matrices and that it is not appropriate for regulatory applications that require the use of leachate preparations (such as Method 3050). It further states that Method 3052 is appropriate for those applications requiring a total decomposition in response to a regulation that requires total sample decomposition. A combination of acids, including hydrofluoric acid, is indicated for the acid digestion of siliceous materials. Mixtures of hydrochloric (HCl) and Nitric (HNO_3) acids may be used, if appropriate for non-siliceous materials.

Method 3050B adds nitric acid and hydrogen peroxide to a representative sample which is heated on a hot plate. This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve most elements that could become "environmentally available." By design, elements bound in silicate structures are not normally dissolved by this procedure since they are not usually mobile in the environment. The method may also fail to completely liberate metals bound in polymeric matrices. The method states: "If absolute total digestion is required use Method 3052."

Method 3051A is a microwave assisted acid digestion method designed to mimic Method 3050B. Since this method is not intended to accomplish total decomposition of the sample, the extracted analyte concentrations may not reflect the total concentration in the sample.

3.2 SELECTION OF AND INSTRUCTIONS TO LABORATORIES

Participation in this study was open to laboratories that stated they were capable of analyzing glass matrices for total metals content. Laboratory credentials and certifications were reviewed. However, "capability" to perform total metals analysis for glass matrices was self-declared by interested laboratories and credentials to perform specific analyses for glass samples were not reviewed. Self representation of capabilities would mimic the market for services, where potential clients may not evaluate a laboratory's credentials to determine if they are qualified to performing a specific test method on a specific substrate, in this case, glass.

TPCH used several approaches to solicit laboratory participation. Notices of the project and request for laboratory participation were sent to the Society of Glass and Ceramic Decorated Products (SGCDpro) for distribution to its membership and posting in its newsletter. TPCH also directly contacted laboratories that participated in the first test methods evaluation project. In addition, a notice was posted on a social media site geared to environmental testing laboratory personnel.

Ten laboratories participated in the study, including consumer product testing, environmental, and glass specialty laboratories. Nine of these laboratories were based in the U.S., while one was European-based. Several participating laboratories also had extensive overseas operations. Table 2 generically describes each laboratory. This report does not identify laboratories by name since the purpose of this report is to assess sample preparation and analytical methods, and not to single out laboratories based on their performance, whether “good” or “bad.”

Prior to sending samples to the laboratories, TPCH held a conference call with participating laboratories to reinforce the project objectives and to answer questions. Laboratories were asked to prepare samples using EPA Method 3052 or equivalent methods that would achieve the stated objective of total metals dissolution. Several laboratories capable of performing different sample preparation or analyses methods split samples and analyzed samples using different methods: for example, using EPA Method 3052 and XRF analyses; or EPA Method 3052 and an internal Standard Operating Procedure. These split samples allowed a direct comparison of sample preparation and analytical methods. In addition to the determination of metals concentration, laboratories were required to submit QA/QC data for evaluation.

Table 2 summarizes the methods used by the participating laboratories to process samples for this study, including:

- **Size reduction** of glass shards for subsequent dissolution into solution for “wet” chemistry analysis such as Inductively Coupled Plasma (ICP) analysis. The study did not specify a preferred size reduction method, but requested that laboratories provide this information to assist in the evaluation of results and determine if such methods contribute to the quality of results.

- **Sample preparation method** for the dissolution of the sample and liberation of metals into solution. EPA Method 3052 and CPSC Method CPSC-CH-E1002-08, or comparable methods, using HF.[11] Complete matrix dissolution was the objective of the study. Using HF is one preferred method; however, the study considered and evaluated alternative methods. In addition to the dissolution of samples, a destructive method to prepare samples for wet chemistry techniques, the study also evaluated non-destructive methods, specifically XRF.

- **Analytical methods** included wet chemistry techniques and XRF analysis, a non-destructive analytical technique for determination of elemental composition of materials. Analytical determination of metals concentration by wet chemistry commonly

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[11] “Comparable” methods were procedurally similar to EPA SW 3052, but labeled with a laboratory-specific number or reference to an internal standard operating procedure.

uses ICP analysis. This study did not state a preference for wet chemistry technique or method, since TPCH's past experience indicated that sample preparation and dissolution were the most important factors. All laboratories participating in this study, however, used ICP analysis. Laboratories 1, 2, 3, and 5 identified the capability to perform glass matrix analyses using at least two different methods. Table 2 shows that three of these laboratories (1, 2 and 5) analyzed samples using destructive, traditional methods and non-destructive XRF analysis. Laboratory 3, a glass specialty laboratory, provided results using EPA Method 3052 and a proprietary in-house method.

TABLE 2: LABORATORIES PARTICIPATING IN STUDY & TEST METHODS

Laboratory	Description of Laboratory	Size Reduction Method	Sample Preparation Method for "Wet" Chemistry	Analytical Method	
				Wet Chemistry	XRF if applicable
1	National/ international consumer product testing	Crush with vice	EPA SW-846 Method 3052	ICP-MS	HD-XRF Using Method ASTM F2853-10[1]
2	National/ international consumer product testing	Mortar & pestle	EPA SW-846 Method 3052[2]	ICP-OES IEC 62321:2008	Energy Dispersive XRF Spectroscopy (EDXRF)
3	European specialty glass	Disc mill	EPA SW-846 Method 3052 & In-house method using HF[3]	ICP-OES internal method	NA
4	U.S. inorganic analytical	Mortar & pestle	EPA SW 3052	ICP-AES EPA Method 6010B	NA
5	National/ international consumer product testing	Mortar & pestle	EPA SW-846 Method 3052[4]	ICP-OES internal method	XOS Prime HD-XRF
6	Regional environmental	Cryogenic mill	EPA SW-846 Method 3052	ICP- AES Method 6010C	NA
7	U.S. specialty glass	Adgate ball mill	In-house method using acid dissolution, including HF and hot-plate heating[5]	ICP; internal method	NA
8	U.S. specialty metals	Hammer	In-house method using acid dissolution, including HF, and oven bomb[6]	ICP-MS; modified EPA draft Method 1638	NA
9	Regional environmental	Mortar & pestle	EPA SW 3050B	ICP-AES EPA Method 6010C	NA
10	Regional environmental	Hammer	EPA SW 3050B	ICP-MS EPA Method 6020	NA

NA = Not applicable

[1] Standard Test Method for Determination of Lead in Paint Layers and Similar Coatings or in Substrates and Homogeneous Materials by Energy Dispersive X-Ray Fluorescence Spectrometry using Multiple Monochromatic Excitation Beams

[2] Lab described methodology comparable to EPA Method 3052 with reference to slightly modified IEC 62321:2008

[3] Dissolution through acid digestion using nitric acid and HF; no microwave

[4] Lab described methodology comparable to EPA Method 3052 with reference to internal SOP

[5] Dissolution through acid digestion using perchloric acid and HF, assisted with hot-plate heating

[6] Dissolution in closed-vessel oven bomb with nitric acid, hydrochloric acid, and HF

3.3 EVALUATION OF TEST RESULTS FROM LABORATORIES

For each sample, the concentrations of Pb and Cd reported by the laboratories were compared to three baseline reference points:

1) Relative Percent Difference (RPD) from the mean of all laboratory results for EPA SW 3052 for that sample. The mean included five or six laboratory results. Before calculating the mean, outlier data points were removed from the data set for that sample. An outlier was defined as a test result that varied by more than 40 percent from the closest data point.

2) RPD from mean of three laboratory XRF measurements for that sample. Before calculating the mean, an outlier test result in one sample was removed from the data set.

3) For CRMs and SRMs, the laboratory results were compared to values in the Certificates of Analysis.

A test result was considered “unacceptable” for the retail glass bottles if there was greater than 25 percent variation from all baseline reference points. If a lab result had greater than 25 percent variation for only one of the two reference points (or three reference points for CRM/SRMs), it was considered acceptable.[12]

A senior chemist from Washington Ecology conducted a QA/QC review of all laboratory submittals. The review considered the following issues:

- Sample preparation, including size reduction method, notification of any problems with insoluble material and additional steps taken to evaluate insoluble material

- Analytical method used and laboratory notebook details provided

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[12] In this study, analysis was performed on retail packaging samples, and therefore, a reference sample was not available to evaluate laboratory performance, except for CRMs. TPCH decided to select multiple reference points, rather than a single reference point, to compare laboratory results, and to reduce the potential for bias if one reference point was not accurate.

- QA/QC results including:
  - Method detection limit or method reporting limits, where applicable
  - Matrix spike results and evaluation if within acceptable range
  - Explanation of any matrix spike deviations
  - Sample duplicate results, if included, evaluation if within acceptable range and whether any deviations were explained.

- Chain of Custody documentation

Individual laboratories were requested to provide either additional information or an explanation of any problems identified.

Although no laboratory provided all expected information, they all provided sufficient information to determine whether or not they met minimum QA/QC requirements. This includes instances where, even if the laboratory provided results outside the expected concentrations, their QA/QC analysis was consistent with the results provided.

4.0 RESULTS

Twelve samples were analyzed by the ten laboratories. A summary of the results along with size reduction and sample preparation method are provided in Table 3. All laboratories used ICP spectroscopy. Reported total concentrations that differed from **all** baseline reference points by more than 25 percent were considered "unacceptable." The values reported by all laboratories for all samples are provided in Appendix A.

The laboratories using EPA Method 3050B (Laboratories 9 and 10) reported unacceptable results for all samples with greater than 50 ppm of Pb or Cd. In fact, the two laboratories analyzing glass samples using EPA 3050B did not detect either Pb or Cd in any of the samples. These methods apparently failed to liberate the metals from the glass matrix, so none were detected and reported.

Laboratory 3, a European glass specialty laboratory, analyzed three split samples, utilizing EPA Method 3052 and an in-house method using HF but with no external heat source. For Laboratory 3, EPA Method 3052 yielded acceptable results for all eight samples (total 10 measurements) with greater than 50 ppm Pb, while the in-house method did not produce comparable results to EPA Method 3052. For the 3 split samples, the in-house method detected 30 – 45 percent less Pb in the sample than baseline reference points.

The method of size reduction may influence the outcome. Laboratories used a wide-range of size reduction methods, from crushing with a hammer or vice to processing with a mortar and pestle or different mills, including cryogenic, agate ball, and disc mills. Six of eight samples reported by Laboratory 6, using a cryogenic milling size reduction method, were "unacceptable." Unlike Laboratories 9 and 10 that utilized EPA Method 3050B and did not detect Pb and Cd in samples above the method detection limit, Laboratory 6 consistently yielded metal concentrations above the baseline reference values. These results may be attributable to the laboratory's techniques in the application of Method 3052, or possibly the use of cryogenic milling of the samples, which produces a very fine substrate. Further study of size reduction techniques is needed to determine if size reduction technique impacts the determination of metals concentration.

The last column in Table 3 indicates the performance of laboratories and their chosen sample preparation methods for samples with less than 50 ppm of Pb or Cd. Packaging components with a combined total metals concentration of less than 100 ppm would be in compliance with state toxics in packaging laws, provided the restricted metals were not intentionally added. No laboratories reported "false positives" for these samples, that is, detected Cd or Pb in samples that would be considered in compliance with state toxics in packaging laws.

TABLE 3: SUMMARY OF LABORATORY RESULTS AND SAMPLE PREPARATION METHODS

Laboratory	Description of Laboratory	Size Reduction Method	Sample Preparation Method for "Wet" Chemistry	Results	
				Number of Inaccurate Results for Samples with >50 ppm of Pb or Cd (Total 10 measurements)[1]	Number of Inaccurate Results for Samples with <50 ppm of Pb or Cd
1	National/ international consumer product testing	Crush with vice	EPA SW-846 Method 3052	2	0
2	National/ international consumer product testing	Mortar & pestle	EPA SW-846 Method 3052[2]	0	0
3	European specialty glass	Disc mill	EPA SW-846 Method 3052	0	0
			In-house method using HF[3]	3 (of 3)	0
4	U.S. inorganic analytical	Mortar & pestle	EPA SW 3052	0	0
5	National/ international consumer product testing	Mortar & pestle	EPA SW-846 Method 3052[4]	2	0
6	Regional environmental	Cryogenic mill	EPA SW-846 Method 3052	6	0
7	U.S. specialty glass	Adgate ball mill	In-house method using acid dissolution, including HF and hot plate heating[5]	0	0
8	U.S. specialty metals	Hammer	In-house method using acid dissolution, including HF, and oven bomb[6]	0	0
9	Regional environmental	Mortar & pestle	EPA SW 3050B	10	0
10	Regional environmental	Hammer	EPA SW 3050B	10	0

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[1] These included 8 samples with Pb >50 ppm & 2 with Cd >50 ppm. Two of the samples had both Pb and Cd >50 ppm.

[2] Lab described methodology comparable to EPA Method 3052 with reference IEC 62321:2008

[3] Dissolution through acid digestion using nitric acid and HF; no microwave

[4] Lab described methodology comparable to EPA Method 3052 with reference internal SOP

[5] Dissolution through acid digestion using perchloric acid and HF, assisted with hot-plate heating

[6] Dissolution in closed-vessel oven bomb with nitric acid, hydrochloric acid, and HF

Table 4 provides an example of the reported Pb concentration for all the laboratories. These results for the BAM CRM (with 202 ppm lead) were consistent between laboratories using EPA Method 3052 or comparable methods, with the exception of Laboratory 6 that detected 37 percent more Pb than the certified value.[13] The two laboratories analyzing glass samples using EPA 3050B did not detect Pb in the BAM CRM sample, or any of the ten samples. Results that differed from all baseline values by >25 percent are highlighted in red.

TABLE 4: RESULTS FOR Pb FOR BAM CERTIFIED REFERENCE MATERIAL

		Pb (ppm)	RPD from Mean 3052	RPD from Mean XRF	RPD from certified values
		Reported/Mean	187	204	202
EPA 3052	**Lab 1**	195	4.3%	-4.4%	-3.5%
	Lab 2	182	-2.7%	-11%	-9.9%
	Lab 3	161	-14%	-21%	-20%
	Lab 4	165.6	-11.4%	-19%	-18%
	Lab 5	144	-23%	-29%	-29%
	Lab 6	276	48%	35%	37%
In-House Method	**Lab 7**	200	7%	-2%	-1.0%
	Lab 3[1]	NA	NA	NA	NA
	Lab 8	165	-11.8%	-19%	-18%
EPA 3050B	**Lab 9**	<4[2]	-98%	-98%	-98%
	Lab 10	<1.0[2]	-99%	-99%	-99%

NA=Not applicable

[1] Lab 3 only analyzed select samples using their in-house method

[2] RPD calculated based on upper limit of reported value; for example, if <4 was reported, the RPD is calculated using a reported value of 4.

Table 5 summarizes the Cd results for the BAM CRM. One laboratory (Laboratory 5) failed to detect Cd in the sample. Both laboratories using EPA 3050B performed poorly with results over 90 percent less than the certified value.

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[13] "Comparable" methods were procedurally similar to EPA SW 3052, but with a laboratory-specific number or reference to an internal standard operating procedure.

TABLE 5: RESULTS FOR CD FOR BAM CERTIFIED REFERENCE MATERIAL

		Cd (ppm)	RPD from Mean 3052	RPD from Mean XRF	RPD from certified values
		Reported/Mean	55	83	62
EPA 3052	**Lab 1**	57	3.6%	-31%	-8.1%
	Lab 2	59	7.3%	-29%	-4.8%
	Lab 3	49.3	-10%	-41%	-20%
	Lab 4	48.8	-11%	-41%	-21%
	Lab 5	ND	*	*	*
	Lab 6	61	11%	-27%	-1.6%
In-House Method	**Lab 7**	60	9.1%	-28%	-3.2%
	Lab 3[1]	NA	NA	NA	NA
	Lab 8	46.5	-15%	-44%	-25%
EPA 3050B	**Lab 9**	<4[2]	-93%	-95%	-94%
	Lab 10	<1.0[2]	-98%	-99%	-98%

NA=Not applicable; * Not calculable since Cd not detected in sample.

[1] Lab 3 only analyzed select samples using their in-house method

[2] RPD calculated based on upper limit of reported value; for example, if <4 was reported, the RPD is calculated using a reported value of 4.

Table 6 provides the test results for four samples with Pb concentrations less than 50 ppm. No laboratories reported false positive results.

TABLE 6: EXAMPLE OF RESULTS FOR SAMPLES WITH PB CONCENTRATIONS <50 PPM

		Total Pb Concentration (ppm)			
Sample		**1 COR**	**7 ACO**	**10 PEP**	**12 NIS**
Certified Reference Value		**NA**	**NA**	**NA**	**2.32**
Mean	**XRF [1]**	**<20**	**9**	**28**	**<10**
	3052[2]	**<12**	**<13**	**22**	**<13**
EPA 3052	**Lab 1**	ND	ND	26	ND
	Lab 2	<6	<3	18	<6
	Lab 3	1.8	10.9	22.8	6.1
	Lab 4	11.4	12.4	23	12.7
	Lab 5	ND	ND	22	ND
	Lab 6	<100	<100	<100	<100
In-House Method	**Lab 7[3]**	<4	11	28	30
	Lab 3[4]	NA	NA	NA	NA
	Lab 8	2.22	8.87	26.0	2.48
EPA 3050B	**Lab 9**	<4	<4	<4	<9
	Lab 10	<1	<1	<1	<1

NA= not applicable; ND = not detected

[1] Mean based on XRF results from 3 laboratories

[2] Mean based on results from 5 laboratories; laboratory 6 results removed from mean calculations due to high reported MDL value

[3] Results reported as percentage and converted to ppm

[4] Laboratory 3 only analyzed select samples using their in-house method

Table 7 summarizes the XRF analysis performed by three laboratories for Pb for all samples. The XRF results are compared to two baseline reference values—the CRM certified value and the EPA Method 3052 mean—for all samples with >50 ppm Pb. The XRF results for Laboratory 5 fall within 10% of the two baseline reference values for all samples. Laboratories 1 and 2 reported XRF results 25-50 percent different than the reference values for three of 12 samples, as highlighted in red below. The XRF results for all laboratories and all samples showed no false positives. These results indicate that XRF analysis often produces comparable results to EPA Method 3052,, and did not yield false positives for Pb.

Table 7: XRF Analysis Results for All Samples with > 50 ppm Pb & RPD from CRM value and EPA 3052 Mean

	CRM Certified Value	EPA Method 3052 Mean	Lab 1 XRF Results			Lab 2 XRF Results			Lab 5 XRF Results		
Sample	ppm	ppm	ppm	RPD from CRM	RPD from 3052	ppm	RPD from CRM	RPD from 3052	Ppm	RPD from CRM	RPD from 3052
1 COR	NA	5	ND			ND			41		
2 PEL	NA	225	237		5.3%	276		23%	242		7.6%
3 CUP	NA	66	84		27%	97		47%	70		6.1%
4 BAM	202	187	197	-2.5%	5.3%	223	10%	19%	192	-5.0%	2.7%
5 MAN	NA	151	138		8.6%	165		9.3%	137		-9.3%
6 CON	NA	632	660		4.4%	769		22%	570		-9.8%
7 ACO	NA	7	12			8			8.2		
8 TOR	NA	279	291		4.3%	322		15%	291		4.3%
9 FRO	NA	343	229		-33%	454		32%	332		-3.2%
10 PEP	NA	22	24			37			23		
11 NT	426	377	483	13%	28%	226	-47%	-40%	389	-8.7%	3.2%
12 NIS	NA	6	ND			ND			1.9		

NA= Not applicable; ND = Not detected; * Not calculated since Pb not detected in sample

Table 8 summarizes the XRF results for three laboratories for the two samples with Cd concentrations greater than 50 ppm. For the remaining 10 samples Cd concentrations were reported as “Not Detected” or <20 ppm. One of the three laboratories reported a Cd concentration of 104 ppm with a margin of error of +/- 11 ppm. Given the margin of error, this is not considered a false positive result since the concentration could be as low as 93 ppm.

Table 8: XRF Analysis Results for All Samples with > 50 ppm Cd & RPD from CRM value and EPA 3052 Mean

	CRM Certified Value	EPA Method 3052 Mean	Lab 1 XRF Results			Lab 2 XRF Results			Lab 5 XRF Results		
Sample	ppm	ppm	ppm	RPD from CRM	RPD from 3052	ppm	RPD from CRM	RPD from 3052	ppm	RPD from CRM	RPD from 3052
4 BAM	62	55	61	-1.6%	11%	ND	*	*	104[2]	68%	89%
11 NT[1]	NA	246	240	NA	-2.4%	ND	*	*	387	NA	57%

NA= Not applicable; ND = Not detected; * Not calculated since Cd not detected in sample

[1] Cd was not certified value for this sample.

[2] Reported range of uncertainty +/- 11 ppm

5.0 Conclusions

EPA Method 3052 and comparable sample preparation methods using HF effectively liberated Pb and Cd from the glass matrix for the determination of total metals concentration. Sample preparation methods using HF without the application of an external heat source such as microwave, oven bomb or hot plate did not perform as well. EPA Method 3050B, which is designed to measure "total recoverable metals" was inadequate in the liberation of Pb and Cd from glass matrix samples. Method 3050B consistently failed to detect Pb or Cd in glass matrices.

Method 3052 requires the use of HF for siliceous matrices. Laboratories capable of performing Method 3052 are commercially available in the U.S. and globally. Of the ten participating laboratories, eight laboratories performed EPA Method 3052 or a comparable method. These eight are commercial laboratories offering consumer product testing, environmental analyses, and specialty testing services targeting glass, inorganic substances, and metals. About half of the test laboratories offer testing services throughout their global operations, while one laboratory was based in the European Union.

XRF spectroscopy offers an alternative to EPA Method 3052 and the use of HF for the non-destructive analysis of metals in glass matrices. In this study, XRF results were often, but not always, comparable to EPA Method 3052 in determining the concentration of Pb and Cd. XRF analysis is appropriate for screening glass matrix samples for compliance with state toxics in packaging laws. In this study, XRF analysis detected the presence of Pb and Cd in all samples known to contain these substances and did not produce false positives when the margin of error was taken into account.

While this study focused on the detection of two metals, Pb and Cd, it is important to note one limitation of XRF analysis when used for screening. XRF instruments only detect total chromium, not hexavalent chromium, which is another metal restricted by state toxics in packaging laws. This limitation does not preclude the use of XRF analysis as an alternative to laboratory "wet" chemistry. Instead, if chromium is detected using XRF, further analysis for chromium may be warranted to determine if the chromium is hexavalent chromium.

6.0 RECOMMENDATIONS

The results of this study provide the basis for the following recommendations. These recommendations provide guidance to:

- Regulated entities when requesting analytical services or for in-house compliance screening programs
- Analytical laboratories performing testing for regulated entities
- States with toxics in packaging requirements for conducting compliance screening programs and reviewing submissions of data from regulated entities intended to demonstrate compliance with state laws

TPCH recommends the use of:

- EPA Method 3052 or comparable method using HF for the analysis of glass matrices when traditional laboratory "wet" chemistry analysis is required. The analysis method should include the application of an external heat source to assist in acid digestion.
- XRF analysis for compliance screening. When restricted metals are detected above 100 ppm further action is warranted. For example:
    - If Pb concentration is greater than 100 pm, the sample may be considered non-compliant with state toxics in packaging laws and action should be taken to prevent the glass packaging from entering the supply stream and/or removing non-

compliant glass from the supply stream.[14] Analytical testing using EPA Method 3052 may be undertaken to confirm Pb concentrations and to verify the compliance status of the glass.

  - If Pb concentration is close to 100 ppm (e.g., within +/- 25 ppm), analytical testing using EPA Method 3052 should be undertaken to confirm Pb concentrations.
  - If chromium is detected above 100 ppm, analytical testing may be needed to confirm the valence state of chromium, and specifically to determine if hexavalent chromium is present in the sample. Alternatively, knowledge of the raw material inputs into the process, and specifically the source and valence state of the chromium introduced into the manufacturing process, may substitute for further laboratory analysis.

- Laboratories with a demonstrated capability to perform EPA Method 3052 and total sample dissolution. It is important to select laboratories that employ effective QA/QC procedures, and to clearly communicate with the laboratory that the intended outcome is to measure the total concentration of the restricted metals in the sample, which can only be achieved with total sample dissolution.

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[14] The Model Toxics in Packaging Legislation currently provides an exemption for the use of recycled content (exemption 5c) with a threshold limit of 200 ppm. States are not bound by the Model but are strongly encouraged to adopt revised provisions to stay in sync. However, only one TPCH member state (New Hampshire) has adopted these revisions.Other member states have allowed their exemptions for recycled content to lapseor maintain an exemption for recycled content with a threshold limit of 100 ppm. State toxics in packaging laws prevail over the Model Legislation.

APPENDIX A: LABORATORY RESULTS

The tables below summarize laboratory results for Pb and Cd. Unacceptable laboratory results, as summarized in Table 3 in Section 4.0, are highlighted in red in the tables below. Any laboratory result with greater than 25 percent difference (Relative Percent Difference - RPD) from the baseline reference points was considered an "unacceptable" result. If a lab result was greater than 25 percent for only one of two or two of three reference point, it was considered acceptable.

Samples with Pb or Cd concentrations > 50 ppm are presented first, followed by samples with concentrations < 50 ppm.

TABLE A1: Pb RESULTS SAMPLE 2

		Reported Pb (ppm)	RPD from Mean 3052	RPD from Mean XRF
		Reported/Mean	225	252
EPA 3052	**Lab 1**	219	-2.7%	-13%
	Lab 2	235	4.4%	-6.7%
	Lab 3	205	-8.9%	-19%
	Lab 4	201.6	-10%	-20%
	Lab 5	164	-27%	-35%
	Lab 6	328	46%	30%
In-House Method	**Lab 7**	250	11%	-0.8%
	Lab 3[1]	NA	NA	NA
	Lab 8	198	-12%	-21%
EPA 3050B	**Lab 9**	<4[2]	-98%	-98%
	Lab 10	<1.0[2]	-100%	-100%

NA= Not applicable; ND= Not detected; * Not calculated since target metal not detected in sample

[1] Lab 3 only analyzed select samples using their in-house method

[2] RPD calculated based on upper limit of reported value; for example, if <4 was reported, the RPD is calculated using a reported value of 4.

TABLE A2: Pb RESULTS SAMPLE 3

		Reported Pb (ppm)	RPD from Mean 3052	RPD from Mean XRF
		Reported/Mean	66	84
EPA 3052	**Lab 1**	74	12%	-12%
	Lab 2	68	3.0%	-19%
	Lab 3	63.2	-4.2%	-25%
	Lab 4	81.3	23%	-3.2%
	Lab 5	57	-14%	-32%
	Lab 6	<100[1]	-51%	-19%
In-House Method	**Lab 7**	83	26%	-1.2%
	Lab 3	46.5	-30%	-45%
	Lab 8	75.8	15%	-9.8%
EPA 3050B	**Lab 9**	<4[1]	-94%	-95%
	Lab 10	<1.0[1]	-98%	-99%

NA= Not applicable; ND= Not detected; * Not calculated since target metal not detected in sample

[1] RPD calculated based on upper limit of reported value; for example, if <4 was reported, the RPD is calculated using a reported value of 4.

TABLE A3: Pb RESULTS SAMPLE 4 (BAM CRM)

		Reported Pb (ppm)	RPD from Mean 3052	RPD from Mean XRF	RPD from certified values
		Reported/Mean	187	204	202
EPA 3052	**Lab 1**	195	4.3%	-4.4%	-3.5%
	Lab 2	182	-2.7%	-11%	-9.9%
	Lab 3	161	-14%	-21%	-20%
	Lab 4	165.6	-11%	-19%	-18%
	Lab 5	144	-23%	-29%	-29%
	Lab 6	276	48%	35%	37%
In-House Method	**Lab 7**	200	7%	-2%	-1.0%
	Lab 3[1]	NA	NA	NA	NA
	Lab 8	165	-11%	-19%	-18%
EPA 3050B	**Lab 9**	<4[2]	-99%	-99%	-99%
	Lab 10	<1.0[2]	-100%	-100%	-100%

NA= Not applicable; ND= Not detected; * Not calculated since target metal not detected in sample

[1] Lab 3 only analyzed select samples using their in-house method

[2] RPD calculated based on upper limit of reported value; for example, if <4 was reported, the RPD is calculated using a reported value of 4.

TABLE A4: Cd FOR SAMPLE 4 (BAM CRM)

		Reported Cd (ppm)	RPD from Mean 3052	RPD from Mean XRF	RPD from certified values
		Reported/ Mean	55	83	62
EPA 3052	**Lab 1**	57	3.6%	-31%	-8.1%
	Lab 2	59	7.3%	-29%	-4.8%
	Lab 3	49.3	-10%	-41%	-20%
	Lab 4	48.8	-11%	-41%	-21%
	Lab 5	ND	*	*	*
	Lab 6	61	11%	-27%	-1.6%
In-House Method	**Lab 7**	60	9.1%	-28%	-3.2%
	Lab 3[1]	NA	NA	NA	NA
	Lab 8	46.5	-15%	-44%	-25%
EPA 3050B	**Lab 9**	<4[2]	-93%	-95%	-94%
	Lab 10	<1.0[2]	-98%	-99%	-98%

NA=Not applicable

[1] Lab 3 only analyzed select samples using their in-house method

[2] RPD calculated based on upper limit of reported value; for example, if <4 was reported, the RPD is calculated using a reported value of 4.

TABLE A5: Pb RESULTS SAMPLE 5

		Reported Pb (ppm)	RPD from Mean 3052	RPD from Mean XRF
		Mean	151	147
EPA 3052	**Lab 1**	148	-2.0%	0.7%
	Lab 2	138	-8.6%	-6.1%
	Lab 3	138	-8.6%	-6.1%
	Lab 4	127.0	-16%	-14%
	Lab 5	119	-21%	-19%
	Lab 6	235	56%	60%
In-House Method	**Lab 7**	150	-0.7%	2.0%
	Lab 3[1]	NA	NA	NA
	Lab 8	147	-2.6%	0.0%
EPA 3050B	**Lab 9**	<4[2]	-97%	-97%
	Lab 10	<1.0[2]	-99%	-99%

NA= Not applicable; ND= Not detected; * Not calculated since target metal not detected in sample

[1] Lab 3 only analyzed select samples using their in-house method

[2] RPD calculated based on upper limit of reported value; for example, if <4 was reported, the RPD is calculated using a reported value of 4.

TABLE A6: Pb RESULTS SAMPLE 6

		Reported Pb (ppm)	RPD from Mean 3052	RPD from Mean XRF
		Reported/ Mean	632	666
EPA 3052	**Lab 1**	629	-0.5%	-5.6%
	Lab 2	657	4.0%	-1.4%
	Lab 3	628	-0.6%	-5.7%
	Lab 4	594.1	-6.0%	-11%
	Lab 5	500	-21%	-25%
	Lab 6	781	24%	17%
In-House Method	**Lab 7**	690	9%	3.6%
	Lab 3	385	-39%	-42%
	Lab 8	579	-8.4%	-13%
EPA 3050B	**Lab 9**	<4[1]	-100%	-100%
	Lab 10	<1.0[1]	-100%	-100%

NA= Not applicable; ND= Not detected; * Not calculated since target metal not detected in sample

[1] RPD calculated based on upper limit of reported value; for example, if <4 was reported, the RPD is calculated using a reported value of 4.

Table A7: Pb Results Sample 8

		Reported Pb (ppm)	RPD from Mean 3052	RPD from Mean XRF
		Reported/ Mean	279	301
EPA 3052	**Lab 1**	270	-3.2%	-10%
	Lab 2	291	4.3%	-3.3%
	Lab 3	269	-3.6%	-11%
	Lab 4	241.2	-14%	-20%
	Lab 5	222	-20%	-26%
	Lab 6	380	36%	26%
In-House Method	**Lab 7**	300	8%	-0.3%
	Lab 3	169	-39%	-44%
	Lab 8	296	6.1%	-1.7%
EPA 3050B	**Lab 9**	<4[1]	-99%	-99%
	Lab 10	<1.0[1]	-100%	-100%

NA= Not applicable; ND= Not detected; * Not calculated since target metal not detected in sample

[1] RPD calculated based on upper limit of reported value; for example, if <4 was reported, the RPD is calculated using a reported value of 4.

TABLE A8: Pb RESULTS SAMPLE 9

		Reported Pb (ppm)	RPD from Mean 3052	RPD from Mean XRF
		Reported/ Mean	343	338
EPA 3052	**Lab 1**	326	-5.0%	-3.6%
	Lab 2	358	4.4%	5.9%
	Lab 3	332	-3.2%	-1.8%
	Lab 4	289.6	-16%	-14%
	Lab 5	305	-11%	-10%
	Lab 6	450	31%	33%
In-House Method	**Lab 7**	380	11%	12%
	Lab 3[1]	NA	NA	NA
	Lab 8	284	-17%	-16%
EPA 3050B	**Lab 9**	<4[2]	-99%	-99%
	Lab 10	<1.0[2]	-100%	-100%

NA= Not applicable; ND= Not detected; * Not calculated since target metal not detected in sample

[1] Lab 3 only analyzed select samples using their in-house method

[2] RPD calculated based on upper limit of reported value; for example, if <4 was reported, the RPD is calculated using a reported value of 4.

Table A9: Pb Results Sample 11 (NIST SRM)

		Reported Pb (ppm)	RPD from Mean 3052	RPD from Mean XRF	RPD from Certified Values
		Reported/ Mean or certified value	377	366	426
EPA 3052	**Lab 1**	105	-72%	-71%	-75%
	Lab 2	376	0%	2.7%	-12%
	Lab 3	354	-6%	-3%	-17%
	Lab 4	308.4	-18%	-16%	-28%
	Lab 5	373	-1%	1.9%	-12%
	Lab 6	476	26%	30%	12%
In-House Method	**Lab 7**	440	17%	20%	3.3%
	Lab 3[1]	NA	NA	NA	NA
	Lab 8	374	-1%	2.2%	-12%
EPA 3050B	**Lab 9**	<7[2]	-98%	-98%	-98%
	Lab 10	<1.0[2]	-100%	-100%	-100%

NA= Not applicable; ND= Not detected; * Not calculated since target metal not detected in sample

[1] Lab 3 only analyzed select samples using their in-house method

[2] RPD calculated based on upper limit of reported value; for example, if <4 was reported, the RPD is calculated using a reported value of 4.

TABLE A10: Cd RESULTS SAMPLE 11 (NIST SRM)[1]

		Reported Cd (ppm)	RPD from Mean 3052	RPD from Mean XRF
		Reported/Mean	**241**	**314**
EPA 3052	**Lab 1**	65	-73%	-79%
	Lab 2	265	10%	-16%
	Lab 3	242	0.4%	-23%
	Lab 4[l]	197.3	-18%	-37%
	Lab 5	245	1.7%	-22%
	Lab 6	280	16%	-11%
In-House Method	**Lab 7**	280	16%	-11%
	Lab 3[2]	NA	NA	NA
	Lab 8	258	7.1%	-18%
EPA 3050B	**Lab 9**	<7[3]	-99%	-99%
	Lab 10	<1[3]	-100%	-100%

[1] Value for Cd not certified

[2] Lab 3 only analyzed select samples using their in-house method

[3] RPD calculated based on upper limit of reported value; for example, if <4 was reported, the RPD is calculated using a reported value of 4.

Table A11: Results for Samples with Pb Concentrations <50 ppm

		Total Pb Concentration (ppm)			
Sample		**1 COR**	**7 ACO**	**10 PEP**	**12 NIS**
Certified Reference Value		**NA**	**NA**	**NA**	**2.32**
Mean	**XRF** [1]	**<20**	**9**	**28**	**<10**
	3052 [2]	**<12**	**<13**	**22**	**<13**
EPA 3052	**Lab 1**	ND	ND	26	ND
	Lab 2	<6	<3	18	<6
	Lab 3	1.8	10.9	22.8	6.1
	Lab 4	11.4	12.4	23	12.7
	Lab 5	ND	ND	22	ND
	Lab 6	<100	<100	<100	<100
In-House Method	**Lab 7** [3]	<4	11	28	30
	Lab 3 [4]	NA	NA	NA	NA
	Lab 8	2.22	8.87	26.0	2.48
EPA 3050B	**Lab 9**	<4	<4	<4	<9
	Lab 10	<1	<1	<1	<1

N/A= not applicable; ND = not detected

[1] Mean based on XRF results from 3 laboratories

[2] Mean based on results from 5 laboratories; laboratory 6 results removed from mean calculations due to high MDL value

[3] Results reported as percentage and converted to ppm

[4] Lab 3 only analyzed select samples using their in-house method

Table A12: Results for Samples with Cd Concentrations <50 ppm

		Total Cd Concentration (ppm)									
Sample		**1 COR**	**2 PEL**	**3 CUP**	**5 MAN**	**6 CON**	**7 ACO**	**8 TOR**	**9 FRO**	**10 PEP**	**12 NIS**
Certified Reference Value		**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**
Mean	**XRF [1]**	**<6**	**<5**	**<6**	**<5**	**<6**	**<5**	**<5**	**<12**	**<5**	**<5**
	3052[2]	**<4**	**<3**	**<4**	**<4**	**<3**	**<3**	**<3**	**<3**	**<3**	**<3**
EPA 3052	**Lab 1**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Lab 2	<3	<2	<2	<2	<2	<2	<2	<2	<2	<3
	Lab 3	<0.1	<0.1	<0.1	0.3	<0.1	<0.1	<0.1	<0.1	<0.1	2.8
	Lab 4	3.0	2.7	3.6	3.1	2.7	2.3	2.7	2.5	2.1	2.5
	Lab 5	ND	ND	ND	46 [5]	ND	ND	ND	ND	ND	ND
	Lab 6	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
In-House Method	**Lab 7[3]**	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
	Lab 3[4]	NA	NA	0.3	NA	<0.1	NA	<0.1	NA	NA	NA
	Lab 8	0.031	0.189	0.587	0.665	0.113	0.046	0.133	0.111	0.056	0.571
EPA 3050B	**Lab 9**	<4	<4	<4	<4	<4	<4	<4	<4	<4	<9
	Lab 10	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

N/A= not applicable; ND = not detected

[1] Mean based on XRF results from 3 laboratories

[2] Mean based on results from 5 laboratories, except for sample 5 MAN, as noted; laboratory 6 results removed from all mean calculations due to high reported MDL value

[3] Results reported as percentage and converted to ppm

[4] Laboratory 3 analyzed several samples using both an in-house method and EPA Method 3052

[5] Not included in mean calculations for Method 3052, since it's an order of magnitude greater than other results.