LABORATORY ROUND ROBIN TEST PROJECT:
ASSESSING PERFORMANCE IN MEASURING TOXICS IN PACKAGING

Final Report

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By
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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 a round-robin study to evaluate the performance of testing laboratories in determining compliance with toxics in packaging statutes. At the request of DTSC, the study specifically focused on the potential for inconsistencies in testing results for polyvinyl chloride (PVC) matrices.

For the past five years, TPCH has screened packaging for compliance with state toxics in packaging laws using x-ray fluorescent (XRF) analysis. XRF analysis is a rapid and inexpensive screening tool for measuring the elemental composition of samples, including the four metals restricted by state laws – cadmium, lead, mercury, and hexavalent chromium.[1] Companies claimed compliance and submitted supporting laboratory test reports for many of the packages that failed the TPCH screening tests. When TPCH compared XRF screening results obtained for packaging samples with laboratory analysis, TPCH learned that the results obtained from laboratory analysis did not necessarily correlate with XRF screening results. The underlying cause of the discrepancy between XRF and laboratory analysis appeared to be the selection of appropriate dissolution methods for preparing packaging samples for analysis. Simply put, if the sample is not completely digested, the restricted metals, if present, are not sufficiently liberated from the plastic and cannot be completely measured by the laboratory analytical equipment, since analytical instruments, such as ICP, measure the concentration of substances in the solution. By ensuring complete dissolution of the matrix, analytical results demonstrated a much better correlation with XRF screening results. Ultimately, a lack of correlation between XRF and laboratory analysis, as well as inconsistent laboratory results, led to the decision to conduct this round-robin study.

For this project, TPCH sent eight identical packaging samples to seven analytical laboratories for determination of the total concentration of the four metals (cadmium, lead, mercury, and hexavalent chromium) restricted by state toxics in packaging laws.[2] Of the eight packaging samples, seven were expected to contain cadmium and/or lead, based on XRF screening results. One of the seven samples was a reference sample with a known

[1] XRF measures total chromium, not hexavalent chromium. If chromium is detected using XRF, laboratory analysis would be needed to determine if the chromium is hexavalent chromium.

[2] Given the cost of laboratory analysis, two laboratories were asked to only analyze for cadmium and lead, which were expected in the samples, based on XRF screening.

concentration of cadmium and lead. The remaining sample was a control sample that contained no detectable cadmium or lead. Laboratories were not informed prior to testing that they were participating in a comparative assessment of laboratory performance in measuring toxics in packaging. DTSC requested that the study focus on PVC packaging samples since this matrix poses particular challenges for sample digestion. TPCH also requested that one non-PVC sample routinely subject to TPCH screening using XRF analysis be included in the study. The non-PVC sample was included to provide a preliminary, although extremely limited, assessment of laboratory performance for non-PVC samples.

Sixteen percent of the test results (9 of 56 samples) were considered "unacceptable," defined as varying by more than 25 percent from established baseline reference points. Only one sample out of 56 (<2 percent) resulted in a "false negative," that is, a test result that indicates compliance with state laws when the sample contained restricted metals, and therefore, was not in compliance with state laws. No laboratories, however, reported "false positives," that is, detected cadmium or lead in samples that the XRF results demonstrated were in compliance with state toxics in packaging laws.

Over half the laboratories (4 of 7) reported one or more unacceptable result; one of these laboratories produced unacceptable results for 5 of 7 samples, including all PVC samples that contained cadmium and/or lead. For the non-PVC sample and the control sample (PVC with no detected metals), all laboratories submitted consistent test results (i.e., variance not greater than 25 percent of baseline reference points).

Given past experiences with laboratory test data in comparison to XRF screening results, overall, the quality and consistency in laboratory testing results was better than expected (with the exception of one laboratory). One possible explanation is that laboratory analysis for total concentration of heavy metals has improved over the past couple of years, likely due to the new sample preparation protocols published by the Consumer Product Safety Commission (CPSC) for testing of children's products.[3]

The test results did not vary based on the sample preparation methodology reported by the laboratory. For example, the three laboratories with the best overall performance (i.e., no unacceptable results) reported using one of the following test methods: EPA SW-846 Method

[3] Test Method CPSC-CH-E1002-08, Standard Operating Procedure for Determining Total Lead (Pb) in Non-Metal Children's Products, February 1, 2009.

3050B/3051, CPSC-CH-E1002-08.1, or EPA SW-846 Method 3052. U.S. Environmental Protection Agency (EPA) SW-846 Method 3050B and3051A[4] are designed to measure "total recoverable metals," while CPSC-CH-E1002.08.1 and EPA SW-846 Method 3052[5] is appropriately used to determine the total concentration of metals through complete sample decomposition. In addition, three of the four labs that reported using EPA SW-846 Method 3052 had one or more unacceptable results. The laboratory that performed the worst in this study (with 5 of 7 samples with unacceptable results) reported using EPA SW- 846 Method 3052. Follow up queries with laboratories that produced unacceptable results revealed that the samples were not completely dissolved in solution.

Some valuable lessons were learned from this round-robin testing project, resulting in the following recommendations.

When requesting testing services from laboratories, it is important to communicate testing requirements and data quality objectives, specifically, total concentration of the restricted metals, which is possible only through complete sample decomposition. Achieving these data quality objectives appears more important than the stated test method of the laboratory.

If total sample decomposition is not achieved, this fact must be reported on the test report as it strongly impacts the accuracy of the results. This is very important when dealing with laboratories that typically conduct analyses for "total recoverable" metals (hazardous waste or site characterization) as they might not be as familiar with requests for absolute total concentration of metals in products, packaging, or otherwise unique matrices.

Testing Laboratories should:

- Evaluate their current sample preparation methods for determining the restricted metals content of PVC matrices to ensure that the methods used achieve complete decomposition of the sample. Complete sample decomposition should be considered as the objective of methods such as EPA SW-846 Method 3052 or an equivalent

[4] EPA SW-846 Method 3050B, Acid Digestion of Sediments, Sludges, and Soils; EPA SW-846 Method 3051A, Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils.
[5] EPA SW-846 Method 3052, Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices

methodology. Note that EPA SW-846 Method 3052 does NOT require the use of hydrofluoric acid for decomposition of organically-based matrices like PVC.

- Consider adding a comment field to test reports that document whether the sample was totally decomposed (e.g., percent dissolution of the sample). TPCH has found that the data quality objective of "total sample decomposition" is the most important factor in accurate reporting under toxic in packaging statutes. A simple statement of the test method used does not convey this information, as the application of test methods by laboratories differ, as shown in this study.

- Re-analyze samples if total sample decomposition is not achieved. Some matrices may require experimentation with sample preparation methods until total sample decomposition is achieved.

Regulated entities such as manufacturers. purchasers, and retailers should:

- Communicate the data quality objective of "total sample decomposition" to laboratories and request that laboratories include in their test reports information on sample decomposition. This information will provide regulated entities with some assurance that appropriate test methods were used by the laboratory for determining compliance with state toxic in packaging laws.

- If test reports indicate that any amount of the four metals restricted by state laws are present in the sample, it is prudent to follow-up with laboratories to determine whether the sample was totally decomposed, if this information is not available on the test report. If the sample was not totally decomposed, the analysis, including sample preparation, should be repeated.

1.0 INTRODUCTION

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 a round-robin study to evaluate the performance of testing laboratories in determining compliance with toxics in packaging statutes. At the request of DTSC, the study specifically focused on the potential for inconsistencies in testing results for polyvinyl chloride (PVC) matrices.

DTSC develops technical assistance and outreach to educate stakeholders (manufacturers, distributors, suppliers, and purchasers of packaging and packaging components, such as retailers, as well as testing laboratories). Outreach and assistance includes such topics as best practices for compliance testing pursuant to toxics in packaging statutes. The overall goals of this round-robin testing project are to increase awareness of 1) the challenges and problems of obtaining consistent laboratory results, and 2) the importance of communicating data quality objectives to laboratories.

2.0 BACKGROUND & CONTEXT FOR THE PROJECT

For the past five years, TPCH has screened packaging for compliance with state toxics in packaging laws using x-ray fluorescent (XRF) analysis. XRF analysis is a rapid and inexpensive screening tool for measuring the elemental composition of samples, including the four metals restricted by state laws – cadmium, lead, mercury, and hexavalent chromium.[6] When TPCH compared XRF screening results obtained for packaging samples with laboratory analysis, TPCH learned that the results obtained from laboratory analysis did not necessarily correlate with XRF screening results.

The following sections discuss the results of several past projects and studies conducted by TPCH and its member states that compared results obtained by XRF and laboratory analysis of packaging samples. Ultimately, a lack of correlation between XRF and laboratory analysis, as well as inconsistent laboratory results, led to the decision to conduct this round-robin study.

[6] XRF measures total chromium, not hexavalent chromium. If chromium is detected using XRF, laboratory analysis would be needed to determine if the chromium is hexavalent chromium.

2.1 TPCH 2006 XRF SCREENING RESULTS COMPARED TO LABORATORY ANALYSIS

TPCH and its member states have encountered irregularities with laboratory test results since its first packaging screening project using XRF analysis in 2006[7]. In this initial project, TPCH found a poor correlation between XRF screening results performed by TPCH and laboratory test results submitted by companies to demonstrate compliance with state laws. Companies claimed compliance and submitted supporting laboratory test reports for almost 70% of the packages that failed the TPCH screening tests. Several possible explanations for these inconsistencies were proposed, including the selection and implementation of sample preparation methodologies by testing laboratories. More specifically, TPCH speculated that testing laboratories might be measuring "leachable," "total recoverable," or "environmentally available" metals in the packaging samples, rather than absolute "total concentration" as required by state statutes.

The DTSC Environmental Chemistry Laboratory (ECL) conducted further testing to assist TPCH in identifying the underlying causes of the discrepancy between XRF screening results and laboratory test reports. Three of the TPCH packaging samples were analyzed by XRF and by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The XRF analysis was conducted by ECL using a portable XRF instrument and by one of its XRF equipment vendors, Oxford Instruments, using a bench-top unit. For the ICP-AES analysis, ECL prepared the samples according to EPA SW- 846 Method 3050B using acid digestion over a hot plate; the methodology for ICP-AES analysis of metals was EPA SW-846 Method 6010B.

Table 1 compares the results for the packaging samples. For all three samples, the ICP-AES test results were inconsistent with the XRF screening results obtained by three different organizations, each using a different device (2 Oxford Instrument models and a Niton analyzer). The ICP-AES results were at least an order of magnitude less than the XRF results for all samples. The ICP-AES only detected metal concentrations over 100 ppm when the XRF results indicated concentrations greater than 1,000 ppm. Based on these ICP-AES results, two of the three samples would be in violation of state laws, while one sample (the textile bag) would appear to be in compliance with the 100 ppm limit of state toxics in packaging laws.

[7] See the report, *Assessment of Heavy Metals in Packaging: Screening Results Using a Portable X-Ray Fluorescent Analyzer*, 2007, available at http://www.toxicsinpackaging.org/adobe/TPCH_Final_Report_June_2007.pdf.

TABLE 1: COMPARISON OF CALIFORNIA XRF AND ICP-AES RESULTS (PPM)

		XRF Results			ICP-AES[4] Results
Sample Description	**Restricted Metal**	**TPCH[1]**	**DTSC ECL[2]**	**Oxford Instruments[3]**	**DTSC**
Shopping Bag 1	**Lead**	1,296	718	1,163	138
	Chromium	494	279	161	30.2
Shopping Bag 2	**Lead**	9,334	12,752	9,203	322
	Chromium	2,548	2,188	1,617	71.6
Textile Bag – Flexible PVC	**Cadmium**	430	360	591	20.4
	Lead	404	432	565	19.2

1 Performed using a Niton XLt797; results are an average of two readings of a sample with a minimum thickness of 5mm.

2 DTSC XRF testing was performed using Oxford Instruments, X-MET 3000TX; results were the average of two readings; shopping bag samples were 32 layers thick (2-3 mm); the textile bag was 8 layers thick (1mm).

3 Oxford Instruments tested the samples using a bench-top energy-dispersive x-ray fluorescence spectrometer, Oxford Instruments Model XGT 1000WR-Type II.

4 Samples digested with 1:1 HNO3 (and 30% H2O2, and 1:1 HCl, if applicable) over a hot plate. Digests were cooled, filtered and made to final volume with deionized H2O (EPA SW-846 Method 3050B). Metal analysis of the digests was by ICP-AES (EPA SW-846 Method 6010B).

The Connecticut Department of Environmental Protection obtained similar results when it submitted four different TPCH flexible PVC samples to an accredited contract laboratory for analysis. The instructions given to the laboratory were to analyze for "total metals concentration" in the samples. Table 2 summarizes the results of these laboratory tests compared to the TPCH XRF measurements. The laboratory test results were only 3 to 9 percent of the XRF screening results. The lab report referenced "6010/E200.7" for lead and cadmium analysis. It appears they performed a "total recoverable metals" analysis, instead of a total metals analysis. When later questioned, the lab manager admitted they had "incomplete digestion" and therefore "unknown recovery" of the metals contained in the samples.

EPA SW-846 Sample Preparation

Method 3050B uses nitric acid and hydrogen peroxide added to a representative sample and 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 almost all 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 content in the sample.

The scope and application of **Method 3052** states that it is applicable to the microwave assisted acid digestion of organic matrices and other complex matrices and that the technique 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.

TABLE 2: CT LABORATORY RESULTS COMPARED TO TPCH XRF ANALYSIS

Sample Description (All PVC matrices)	Restricted Metal	TPCH XRF Screening[1]	Contract Laboratory[2]
Toy Bag	Cadmium	500	21.2
	Lead	137	11.8
Small Electrical Appliance Bag	Cadmium	320	17.3
Textile Bag 1	Cadmium	990	31.8
Textile Bag 2	Cadmium	528	31.2

[1] Using Niton XLt 797
[2] Using EPA SW-846 Method 6010/E200.7

Given the laboratory test results obtained by both DTSC and the Connecticut contract laboratory, in hindsight, it was not surprising that many of the companies that received failure notifications from TPCH in 2006 claimed compliance based on independent laboratory test results.

2.2 DTSC 2008 EVALUATION OF SAMPLE PREPARATION METHODOLOGIES

In 2008, DTSC sought answers to the discrepancies between XRF screening and its laboratory "wet chemistry" (i.e., chemical digestion and analysis) test results, specifically for the hard-to-digest PVC matrices. DTSC compared several sample digestion methods specified in EPA SW-846, which are summarized in the left sidebar, followed by analysis using ICP-AES. Method 3050B utilizes acid digestion over a hot plate, while Methods 3051A and 3052 employ a more rigorous approach to sample dissolution using microwave assisted acid digestion.

As shown in Table 3, the concentration of heavy metals in the packaging samples detected by ICP-AES analysis increased as more rigorous sample preparation methods were used to digest the sample and liberate the

TABLE 3: DTSC COMPARISON OF EPA SW-846 SAMPLE PREPARATION METHODS: CONCENTRATION (PPM) OF METALS IN FLEXIBLE PVC PACKAGES

Sample	Elements	XRF Screening	3050B/ICP	3051/ICP Microwave	3052/ICP Microwave Contract Lab A	3052/ICP Microwave Contract Lab B
1	Cadmium	ND	ND	ND	NA	ND
	Lead	1,300	138	779	NA	1,101
	Chromium	420	30	198	NA	264
2	Cadmium	ND	ND	ND	NA	ND
	Lead	650	74	544	NA	561
	Chromium	ND	18	135	NA	142
3	Cadmium	ND	ND	ND	ND	ND
	Lead	257	154	187	332	305
	Chromium	ND	37	55	143	81

ND = not detected; NA = not applicable

metals. EPA SW-846 Method 3052 achieved the most consistent and comparable results to XRF analysis, while Method 3050B resulted in significantly lower concentrations of heavy metals in all samples tested, compared to Method 3052 and XRF analysis.

These results are not surprising since the two sample preparation methods differ in their stated objective. Method 3050B (*Acid Digestion of Sediments, Sludges and Soils*) is designed to measure "total recoverable metals." Section 1.2 of the Scope and Applications specifically states: "This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become 'environmentally available.'" The scope goes on to say: "If absolute total digestion is required use Method 3052." Method 3052 *(Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices)* is appropriately used to determine the total concentration of cadmium and lead in flexible PVC because PVC is organic. Section 1.3 of Scope and Application states "The goal of this method is total sample decomposition and with judicious choice of acid combinations this is achievable for most matrices."

The results obtained by DTSC demonstrated the importance of selecting appropriate dissolution methods for packaging material, and specifically, flexible PVC matrices. Simply put,

if the sample is not completely digested, the cadmium and lead are not sufficiently liberated from the plastic and cannot be completely measured by the laboratory analytical equipment, since analytical instruments, such as ICP, measure the concentration of substances in the solution. By ensuring complete dissolution of the matrix, analytical results demonstrate a much better correlation with XRF screening results.

2.3 TPCH 2010 PILOT ROUND ROBIN

In early 2010, TPCH decided to test its hypothesis that testing laboratories may not be applying appropriate sample preparation methods for the detection of total concentration of restricted metals, as required by state toxics in packaging laws through a pilot round robin testing program. TPCH sent a flexible PVC packaging sample[8] to four testing laboratories with instructions to analyze the sample for compliance with toxics in packaging requirements. Instructions were communicated to the laboratories using standard laboratory protocols; for example, three laboratories had standard test request forms while one lab asked for written instructions to accompany the sample. The packaging sample was screened by TPCH using XRF analysis prior to shipping, and based on these results, was expected to contain cadmium. The results for cadmium are shown in Table 4. The variability in results was astounding, but not unexpected given TPCH's past experience. Of the four laboratories, two detected cadmium concentrations in excess of 100 ppm, while two laboratories (#3 and #4) reported cadmium under 100 ppm. Only Lab 4 concluded that the packaging sample was in compliance with toxics in packaging requirements, while Lab 3 reported "does not comply" since the sum of the 4 restricted heavy metals exceeded 100 ppm.

The results of this pilot project indicated a need for a more extensive study of laboratory performance in measuring the total concentration of restricted heavy metals in packaging. As a result, DTSC contracted with TPCH to conduct this round-robin study.

[8] The sample was cut into five equal-sized pieces; four of the samples were sent to four laboratories for testing using "wet" chemistry and one piece was retained by TPCH.

TABLE 4: PILOT ROUND ROBIN LABORATORY RESULTS

Laboratory	Instructions to Lab	Sample Preparation & Test Methods[1]	Cadmium (ppm)
State of Illinois XRF Analysis[2]	Not applicable	Not applicable	475 +/- 7
Lab 1	Memo requested testing for toxics in packaging and, specifically, total concentration	Laboratory SOP equivalent to EPA SW-3052 & ICP; cryogenic mill used to grind sample	660
Lab 2	Test request form; checked box on form for toxics in packaging	Not specified	385
Lab 3	Test request form; checked box on form for toxics in packaging	ICP	78
Lab 4	Test request form that provided space to list required tests; requested testing for toxics in packaging and, specifically, total concentration using EPA SW 3052 for sample preparation or equivalent	EPA 3050B/3051 Acid Digestion Method/ICP	22

1 As referenced in Service Agreement and/or Laboratory Test Report
2 Using an Innov-X Systems Alpha Series analyzer

3.0 PROJECT METHODOLOGY

For this project, TPCH sent eight identical packaging samples to seven analytical laboratories for determination of the total concentration of the four metals (cadmium, lead, mercury, and hexavalent chromium) restricted by state toxics in packaging laws.[9] Laboratories were not informed prior to testing that they were participating in a comparative assessment of laboratory performance. Instructions were communicated to the laboratories using standard laboratory protocols; for example, contacting designated customer service representative and

[9] Given the cost of laboratory analysis, two laboratories were asked to only analyze for cadmium and lead, which were expected in the samples, based on XRF screening.

submitting required test request forms. After receiving test reports, TPCH staff followed up with laboratories, as needed, to obtain additional information.

3.1 SELECTION OF AND INSTRUCTIONS TO LABORATORIES

TPCH selected laboratories to participate in the "blind" study using two criteria. The laboratories selected met one of the following criteria:

1) Prominent national or international laboratory that routinely performs toxics in packaging testing for manufacturers, suppliers, distributors and retailers subject to toxics in packaging laws. These laboratories were identified through TPCH and member state archives of correspondence with companies and retailers that submitted test reports to demonstrate compliance with state toxics in packaging laws. Four laboratories participating in the study met this criterion;[10]or
2) Laboratories used by TPCH member states to support enforcement efforts. Three of the seven laboratories participating in the study met this criterion. Included in this group were the DTSC ECL and two independent laboratories.

For this study, it was important to seek analytical services in the same manner as a regulated entity. TPCH wanted its samples handled and its reports communicated like any other samples processed by the selected laboratory. Therefore, requests for testing services were communicated to the laboratories using standard laboratory protocols. This typically involved contacting a designated customer service representative, filling out a test request form, and signing a service agreement. Some test request forms or protocols provided an opportunity to specify test requirements or methods, while others were simply comprised of boxes to check (e.g., toxics in packaging.)

Table 5 generically describes each laboratory and the request for testing services made by TPCH. This report does not identify laboratories by name since the purpose of this report is to assess laboratory performance overall in testing for toxics in packaging, and NOT to single out laboratories based on their performance, whether "good" or "bad."

[10] A fifth laboratory declined to test TPCH samples, citing that the company only provides services to manufacturers and retailers.

TABLE 5: LABORATORIES PARTICIPATING IN STUDY

Laboratory	Description of Laboratory	Instructions to Lab
1	State laboratory	• Test request form • Metals scan for toxics in packaging
2	State contract lab – regional	• Test request form • Checked box for RoHS Metals (Hg, Cd, CrVI, Pb) per customer service representative instructions
3	National/international serving regulated entities	• Test request form • Checked box for toxics in packaging
4	National/international serving regulated entities	• Test request form • Checked box for toxics in packaging
5	National/international serving regulated entities	• Test request form • Checked box for toxics in packaging
6	National/international serving regulated entities	Memo requested testing for toxics in packaging, and specifically, total concentration
7	State contract laboratory – national	Memo requesting testing for total concentration using EPA SW-846 Method 3052

3.2 SELECTION AND PREPARATION OF PACKAGING SAMPLES

DTSC requested that the study focus on PVC packaging samples since this matrix poses particular challenges for sample digestion. TPCH also requested that one non-PVC sample routinely subject to TPCH screening using XRF analysis be included in the study. The non-PVC sample would provide a preliminary, although very limited, assessment of laboratory performance for non-PVC samples.

As shown in Table 6, the study included five PVC samples with varying concentrations of cadmium and/or lead as detected through portable XRF screening[11] plus one non-PVC plastic with inks/colorants. The description of the metals concentration in the samples – high, medium, and low – are relative to the concentrations typically detected by TPCH in packaging samples, and are NOT a statement about the impact on the environment and/or human health. Laboratories also received two control samples, a reference sample with known concentrations

[11] XRF screening performed using either an Innov-X Systems Alpha Series or NITON XLt and standard operating procedures provided by the manufacturer.

TABLE 6: PACKAGING SAMPLES

Sample	Sample Description	Metals Concentration[1]	
		Cadmium (ppm)	Lead (ppm)
1	PVC Cadmium – High concentration	687	<LOD
2	PVC Cadmium Medium concentration	404	<LOD
3	PVC Cadmium - Low concentration	207	<LOD
4	PVC Cadmium & Lead	273	245
5	PVC Lead – Medium concentration[2]	648	413
6	Non-PVC plastic with ink/colorant[3]	<LOD[3]	441
7	PVC – no detection of restricted metals	<LOD	<LOD
8	PVC reference sample[4]	250	350

LOD – Below level of detection

[1] Determined by XRF analysis using Innov-X System Alpha Series analyzer.

[2]There were no PVC samples that contained lead only, so a sample with medium lead concentration was selected that also contained cadmium

[3]HDPE shopping bag

[4]The metal concentration was reported on the certificate of analysis.

of cadmium and lead (sample 8) and a PVC sample without any of the four restricted metals as determined by XRF analysis (sample 7).

Each packaging sample was cut into eight equal-sized pieces. One piece was sent to each laboratory for testing using "wet" chemistry and one piece was retained by TPCH.

3.3 EVALUATION OF TEST RESULTS FROM LABORATORIES

For each sample, the concentration of cadmium and lead reported by the laboratories was compared to three baseline reference points:

1) XRF measurement as determined by TPCH. See Table 6 above.
2) Mean of all laboratory results for that sample. Before calculating the mean, any outlier test results 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 both reference points 1 and 3.[12]
3) DTSC laboratory result as determined by EPA SW-846 Method 3052.

[12] Four of the five "outlier" test results were more than 60 percent different than reference points 1 and 3.

The number of unacceptable results was reported for each sample. A laboratory result was considered "unacceptable" if there was greater than 25 percent variation from all three baseline reference points for one or both metals, if applicable. If a lab result had greater than 25 percent variation for only one or two of the reference points, it was considered acceptable.[13]

Some samples contained both cadmium and lead. For these samples, laboratories were evaluated on their performance in determining the concentration of both metals. Laboratory performance was reported by sample (which considered whether the results for both metals were acceptable or unacceptable) and by data points (which considered cadmium and lead results separately). For the sample, if the result for one metal was "unacceptable," then the sample result was considered unacceptable.

4.0 RESULTS

Sample 2: PEL		Pb (ppm)	Variance from Mean 3052	Variance from Mean XRF	Variance from CA DTSC 3052
			220	259	187
EPA 3052	SGS	219	-0.5%	-15.4%	17.1%
	CTL	235	6.8%	-9.3%	25.7%
	Ceram	205	-6.8%	-20.8%	9.6%
	CA DTSC	187	-15.0%	-27.8%	
	First Anal	201.6	-8.4%	-22.2%	7.8%
	ULE-STR	164	-25.5%	-36.7%	-12.3%
	Chemserv	328	49.1%	26.6%	75.4%
In-House Method	Am Glass	250	13.6%	-3.5%	33.7%
	Ceram				
	Brooks	198	-10.0%	-23.6%	5.9%
EPA 3050B/	Schneider	2.0	-99.1%	-99.2%	-98.9%
	IA Hyg	0.5	-99.8%	-99.8%	-99.7%

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

3051	**CA DTSC**	1.0	-99.5%	-99.6%	-99.5%

Eight samples were analyzed by each of the seven laboratories for a total of 56 samples. In these eight unique samples, there were a total of 10 data points, that is, where lead and cadmium were expected to be detected, based on TPCH XRF screening. Three samples, including the reference sample, had both cadmium and lead (as shown in Table 6 above), for a total of 70 data points evaluated in this study. [14]

Table 7 summarizes the performance of laboratories as well as the reported sample preparation methods for each laboratory. All laboratories analyzed the samples using Inductively Coupled Plasma (ICP) spectrometry. Appendix A provides the laboratory results for each of the 8 samples.

[14] Laboratories analyzed all samples for four metals – cadmium, lead, mercury, and hexavalent chromium—with two exceptions. Given the cost of laboratory analysis, TPCH requested analysis for only lead and cadmium from two laboratories. This report evaluates laboratory performance in detecting the metal(s) suspected of being present in the sample only (cadmium and/or lead). None of the laboratories, when applicable, detected the other metals in any of the samples above the detection limit.

TABLE 7: SUMMARY OF LABORATORY TEST RESULTS

Laboratory	Description of Laboratory	Reported Sample Preparation Method	Overall Performance		
			Number of Unacceptable Sample Results (out of 8 total samples analyzed by each lab)	Number of Unacceptable Data Points[1] (out of 10 total data points analyzed by each lab)	Number of False Negatives[2]
1	State laboratory	EPA SW-846 Method 3052	0	0	0
2	State contract laboratory – regional	EPA SW-846 Method 3052	1	1	0
3	National/ international serving regulated entities	CPSC-CH-E1002-08.1[3]	0	0	0
4	National/ international serving regulated entities	Microwave digestion with nitric acid	1	1	0
5	National/ international serving regulated entities	EPA SW-846 Method 3050B/3051	0[4]	0	0
6	National/ international serving regulated entities	Laboratory SOP equivalent to EPA SW-3052; cryogenic mill used to grind sample	2	2	0
7	State contract laboratory - national	EPA SW-846 Method 3052	5	7	1
	TOTAL		9	11	1

[1] Data points were defined as the expected detection of cadmium and/or lead in a sample, based on TPCH XRF screening. Some samples were expected to contain both cadmium and lead. For these samples, laboratories were evaluated on their performance in determining the concentration of the metals separately. Four samples had 1 data point; three samples had 2 data points; and one control sample had 0 data points.

[2] A "false negative" occurs when laboratory results indicate compliance with toxics in packaging requirements, when the restricted metals are present.

[3] CPSC-CH-E1002-08, Standard Operating Procedure for Determining Total Lead (Pb) in Non-Metal Children's Products, February 1, 2009. This method is similar to EPA SW-846 Method 3052, however, complete sample digestion is not explicitly described.

[4] Results for this laboratory includes 7 samples. TPCH suspects that the laboratory analyzed the "packaging" that contained the reference sample and not the reference material. Numerous requests to the laboratory to confirm this assumption were not answered. This sample was NOT in tabulations of "unacceptable" results.

Overall Laboratory Performance

- The reported concentrations of restricted metals in 16.1 percent (9 of 56) of the samples varied more than 25 percent from the three baseline reference points. Similarly, the number of data points for cadmium and/or lead that varied by more than 25 percent from the baseline reference points was 15.7 percent (11 of 70 data points).
- Over half the laboratories (4 of 7) reported one or more unacceptable result. Three of these laboratories had one or two unacceptable results, while the fourth produced unacceptable results for 5 of 7 samples, including all PVC samples that contained cadmium and/or lead.
- The laboratory (#7) with the overall poorest correlation with the reference samples was a laboratory under contract with a TPCH member state for hazardous waste analysis.
- Only one test result (from Laboratory #7) resulted in a "false negative," that is, a reported concentration of restricted metals below the 100 ppm threshold for compliance with the incidental limit for toxics in packaging in state laws.[15]
- No laboratories reported "false positives," that is, detected cadmium or lead in samples that the XRF results demonstrated were in compliance with state toxics in packaging laws.

Test Methods

- The test results did not vary based on the sample preparation methodology reported by the laboratory. For example, the three laboratories with the best overall performance (i.e., no unacceptable results) reported using one of the following test methods: EPA SW-846 Method 3050B/3051, CPSC-CH-E1002-08.1, or EPA SW-846 Method 3052. In addition, three of the four labs that reported using EPA SW-846 Method 3052 had one or more unacceptable results. The laboratory that performed the worst in this study (with 5 of 7 samples with unacceptable results) reported using EPA SW- 846 Method 3052.
- It is important to note that in follow up queries with laboratories that produced unacceptable results, two laboratories, including Laboratory #7, revealed that the samples were not completely dissolved in solution. This information was not communicated to TPCH initially.

[15] Toxics in packaging laws prohibit the intentional use of any amount of the four restricted metals, and limit the incidental presence of the four metals combined to 100 ppm. Laboratories often report "pass" or "fail" based on the 100 ppm limit since this is measurable. A false negative would indicate compliance with state laws when one or more of the restricted metals should be detected in the sample.

Results for Sample Analysis

Appendix A provides the laboratory results for each packaging sample.

- For the non-PVC sample and the control sample (PVC with no detected metals), all laboratories submitted consistent test results (i.e., variance not greater than 25 percent of baseline reference points).
- One laboratory (#7) submitted test results with a variance from the reference samples greater than 25 percent for all PVC samples that contained cadmium and/or lead (samples 1 through 5 and 8). Yet, this laboratory submitted results consistent with other laboratories and the XRF reference data point for the non-PVC sample. Upon inquiry, it was discovered that the samples had not been completely dissolved in solution. The laboratory clearly did not achieve the stated objective of the test method, which is "total sample decomposition," which is critical to the validity of the reported results.

5.0 DISCUSSION & CONCLUSIONS

Laboratory Performance

The quality and consistency in laboratory testing results (with the exception of one laboratory) was unexpected, given past experiences with laboratory test data in comparison to XRF screening results. While 16 percent of the test results varied by >25 percent from the reference points, only one sample out of 56 (<2 percent) resulted in a "false negative" (i.e., a test result that would indicate compliance with state laws.) One possible explanation is that laboratory analysis for total concentration of heavy metals has improved over the past couple of years, likely due to the new sample preparation protocols published by the Consumer Product Safety Commission for testing of children's products.[16] This conclusion is supported by the TPCH Pilot Round Robin test data shown in Table 4. Two of the laboratories (Laboratories #4 and #5) that performed well in this study also participated in the pilot (listed in that study as Laboratories #3 and #4), where they reported false negatives.

[16] Test Method CPSC-CH-E1002-08, Standard Operating Procedure for Determining Total Lead (Pb) in Non-Metal Children's Products, February 1, 2009.

Test Methods & Communications with Laboratories

When requesting testing services from laboratories, it is important to communicate testing requirements and data quality objectives, specifically, the performance criteria of complete matrix decomposition, which is required in order to obtain the true total concentration of the restricted metals. Achieving these data quality objectives appears more important than the stated test method of the laboratory.

If complete sample matrix decomposition is not achieved, this fact must be reported on the test report as it strongly impacts the accuracy of the results. This is very important when dealing with laboratories that typically conduct analyses for ”total recoverable” metals (hazardous waste or site characterization) as they might not be as familiar with requests for absolute total concentration of metals in products, packaging, or otherwise unique matrices.

Conventional communication mechanisms with laboratories may not be ideal for achieving the abovementioned goals. For example, most of the laboratories participating in the study utilize standardized test request forms and “check” boxes. Further, when requesting testing services, TPCH was directed to a designated customer service representative, some of whom were more knowledgeable than others. This concern may be overcome by having detailed conversations with the laboratory, including assurances from the technical staff, before securing the laboratory’s testing services.

PVC Matrices

This study dealt with a limited number of unique samples, including only one non-PVC plastic sample. However, based on the available results, it appears that PVC samples are more challenging to completely decompose in solution, than more traditional “environmental” samples such as soils and sludges. This may explain, for example, why the state contract laboratory that routinely performs hazardous waste analyses provided test results consistent with XRF analysis and other laboratories for the non-PVC plastic material with inks/colorants.

Finally, laboratory certifications and accreditations may not guarantee the ability to perform test methods required to certify to or demonstrate compliance with toxics in packaging requirements.

6.0 RECOMMENDATIONS

Some valuable lessons were learned from this round-robin testing project, resulting in the following recommendations.

Testing Laboratories should:

- Evaluate their current sample preparation methods for determining the restricted metals content of PVC matrices to ensure that the methods used achieve complete decomposition of the sample matrix. EPA SW-846 Method 3052 or an equivalent methodology should be considered as the objective of this method is complete sample matrix decomposition.
- Note that EPA SW-846 Method 3052 does NOT require the use of hydrofluoric acid for decomposition of organically-based matrices like PVC. Over the years, a number of laboratories or their customers have reported to TPCH that the laboratory will not use Method 3052 as it requires the use of hydrofluoric acid. A careful review of the sample preparation procedure for Method 3052 reveals that hydrofluoric acid is not required. Rather, a combination of other acids (e.g., hydrochloric acid, nitric acid, hydrogen peroxide) may accomplish the goal of complete sample matrix decomposition.
- Consider adding a comment field to test reports that document whether the sample matrix was completely decomposed (e.g., percent dissolution of the sample). The data quality objective of "complete sample matrix decomposition" is the most important factor in accurate reporting under toxic in packaging statutes. A simple statement of the test method used does not convey this information, as the application of test methods by laboratories differ, as shown in this study. Providing information on whether the test method used by the laboratory achieved complete sample matrix decomposition (or not) will allow regulated entities and state agencies to better evaluate the data provided in laboratory testing reports. Re-analyze samples if complete sample matrix decomposition is not achieved. Some matrices may require experimentation with sample preparation methods until complete sample matrix decomposition is achieved. Re-analyzing samples is particularly important if any amount of the restricted metals is detected in the initial test, since further or complete decomposition of the sample matrix may result in detection of one or more of the restricted metals in excess of the regulatory limits.

Regulated entities such as manufacturers. purchasers, and retailers should:

- Communicate the data quality objective of "complete sample matrix decomposition" to laboratories and request that laboratories include in their test reports information on sample matrix decomposition. This information will provide regulated entities with some assurance that appropriate test methods were used by the laboratory for determining compliance with state toxic in packaging laws. Providing this information up front in test reports will also save all stakeholders (regulated entities, laboratories, state agencies) the time of having to ask for this information or dig through laboratory records for this information if laboratory test reports are questioned by state agencies.
- If test reports indicate that any amount of the four metals restricted by state laws are present in the sample, it is prudent to ask laboratories whether the sample matrix was completely decomposed, if this information is not available on the test report. If the sample matrix was not totally decomposed, the analysis, including sample preparation, should be repeated.

State agencies with toxics in packaging requirements should:

- Conduct outreach to laboratories and regulated entities about the findings of this study.
- Consider additional round-robin studies for non-PVC matrices to evaluate laboratory performance.

APPENDIX A: LABORATORY RESULTS

The tables below summarize laboratory results for cadmium and/or lead, if expected in the sample, based on XRF analysis. Cadmium and lead results are reported for the PVC control sample (sample 7) that was not expected to contain either metal.

Note: Unacceptable laboratory results, as summarized in Table 7 in Section 4.0, are highlighted in orange in the tables below. Any laboratory results with greater than 25 percent variability from all three baseline reference points was considered an "unacceptable" result. If a lab result was greater than 25 percent for only one or two of the reference points, it was considered acceptable.

Sample 1: PVC Cadmium – High concentration

Laboratory	Cd (ppm)	Variance from CA DTSC	Variance from Mean	Variance from TPCH XRF
TPCH XRF	687			
Lab 1	730		5.8%	6.3%
Lab 2	778	6.6%	12.8%	13.3%
Lab 3	805	10.3%	16.7%	17.5%
Lab 4	678	-7.1%	-1.7%	-1.2%
Lab 5	732	0.3%	6.1%	6.6%
Lab 6	475	-34.9%	-31.1%	-30.8%
Lab 7	271	-62.9%	-60.7%	-60.5%
Mean[1]	**689.9**			

[1] Lab 7 result considered an "outlier" and not included in mean.

Sample 2: PVC Cadmium – Medium concentration

Laboratory	Cd (ppm)	Variance from CA DTSC	Variance from Mean	Variance from TPCH XRF
TPCH XRF	404			
Lab 1	400		2.0%	0%
Lab 2	423	5.8%	7.8%	4.6%
Lab 3	351	-12.3%	-10.5%	-13.2%
Lab 4	375	-6.3%	-4.4%	-7.3%
Lab 5	465	16.3%	16.3%	15.0%
Lab 6	352	-12.0%	-12.0%	-12.9%
Lab 7	60.2	-85.0%	-84.7%	-90.1%
Mean[1]	**392.3**			

[1] Lab 7 result considered an "outlier" and not included in mean.

Sample 3: PVC Cadmium – Low concentration

Laboratory	Cd (ppm)	Variance from CA DTSC	Variance from Mean	Variance from TPCH XRF
TPCH XRF	207			
Lab 1	200		-6.6%	-3.2%
Lab 2	188	-6.0%	-12.2%	-9.0%
Lab 3	240	20.0%	12.0%	16.1%
Lab 4	205	2.5%	-4.3%	-0.8%
Lab 5	231	15.5%	7.8%	11.8%
Lab 6	226	13.0%	5.5%	9.4%
Lab 7	113	-43.5%	-47.2%	-63.5%
Mean[1]	**214.2**			

[1] Lab 7 result considered an "outlier" and not included in mean.

Sample 4: PVC Cadmium & Lead

Laboratory	Cd (ppm)	Variance from CA DTSC	Variance from Mean	Variance from TPCH XRF	Pb (ppm)	Variance from CA DTSC	Variance from Mean	Variance from TPCH XRF
TPCH XRF	273				245			
Lab 1	330		8.1%	21.0%	220		16.0%	-10.2%
Lab 2	332	0.6%	8.7%	21.8%	225	2.3%	18.6%	-8.2%
Lab 3	318	-3.6%	4.1%	16.6%	193	-12.3%	1.8%	-21.2%
Lab 4	235	-28.8%	-23.0%	-13.8%	119	-45.9%	-37.3%	-51.4%
Lab 5	309	-6.4%	1.2%	13.3%	190	-13.6%	0.2%	-22.4%
Lab 6	308	-6.7%	0.9%	13.0%	191	-13.2%	0.7%	-22.0%
Lab 7	93.6	-71.6%	-69.3%	-65.7%	58.6	-73.4%	-69.1%	-75.7%
Mean[1]	**305.3**				**189.7**			

[1] Lab 7 result considered an "outlier" and not included in mean.

Sample 5: PVC Lead – Medium concentration

Laboratory	Cd (ppm)	Variance from CA DTSC	Variance from Mean	Variance from TPCH XRF	Pb (ppm)	Variance from CA DTSC	Variance from Mean	Variance from TPCH XRF
TPCH XRF	648				413			
Lab 1	690		0.8%	6.6%	380		14.3%	-7.9%
Lab 2	688	-0.3%	0.5%	3.1%	320	-15.8%	-3.8%	-20.8%
Lab 3	760	10.1%	11.0%	17.4%	337	-11.3%	1.4%	-18.3%
Lab 4	732	6.1%	6.9%	13.1%	315	-17.1%	-5.3%	-23.6%
Lab 5	769	11.4%	12.3%	18.8%	345	-9.2%	3.8%	-16.4%
Lab 6	468	-32.2%	-31.6%	-27.7%	298	-21.6%	-10.4%	-27.8%
Lab 7	110	-84.1%	-83.9%	-83.0%	61.6	-83.8%	-81.5%	-85.1%
Mean[1]	**684.5**				**332.5**			

[1] Lab 7 result considered an "outlier" and not included in mean.

Sample 6: Non-PVC with Ink/colorant

Laboratory	Pb (ppm)	Variance from CA DTSC	Variance from Mean	Variance from TPCH XRF
TPCH XRF	441			
Lab 1	460		13.1%	4.4%
Lab 2	373	-18.9%	-8.3%	-15.3%
Lab 3	436	-5.2%	7.2%	-1.0%
Lab 4	431	-6.3%	5.9%	-2.2%
Lab 5	399	-13.3%	-1.9%	-9.4%
Lab 6	423	-8.0%	4.0%	-4.0%
Lab 7	418	-9.1%	2.7%	-5.1%
Mean	**406.8**			

Sample 7: PVC – No detection of metals

Laboratory	Cd (ppm)	Pb (ppm)
TPCH XRF	<LOD	<LOD
Lab 1	<2.0	<20
Lab 2	<0.5	<5
Lab 3	<1.2	<4.8
Lab 4	<10	<10
Lab 5	ND	ND
Lab 6	3	ND
Lab 7	ND	ND

<LOD – Below level of detection
ND – Not detected

Sample 8: PVC Reference Sample

Laboratory	Cd (ppm)	Variance from CA DTSC	Variance from Mean	Variance from TPCH XRF	Pb (ppm)	Variance from CA DTSC	Variance from Mean	Variance from TPCH XRF
COA[1]	250				350			
Lab 1	210		5.8%	-16.0%	390		28.1%	11.4%
Lab 2	149	-29.9%	-24.9%	-40.4%	226	-42.1%	-25.8%	-35.4%
Lab 3	231	10.0%	16.4%	-7.6%	347	-11.0%	14.0%	-0.9%
Lab 4	183	-13.1%	-8.0%	-27.0%	278	-28.6%	-8.5%	-20.5%
Lab 5	ND[2]				ND			
Lab 6	199	-5.2%	0.3%	-20.4%	314	-19.5%	3.2%	-10.3%
Lab 7	219	4.3%	10.4%	-24.6%	271	-30.5%	-11.0%	-13.0%
Mean	**198.4**				**304.4**			

[1]Certificate of Analysis (COA) was verified by the supplier by XRF analysis: Cd 265 ppm; Pb 330 ppm.
[2]TPCH suspects that the laboratory analyzed the "packaging" that contained the reference sample and not the reference material. Numerous requests to the laboratory to confirm this assumption were not answered. This sample was NOT in tabulations of "unacceptable" results.

