DEPARTMENT OF ECOLOGY
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Addendum to Publication 15-03-106
Quality Assurance Project Plan (QAPP)

Mercury in Polyvinyl Chloride and Polyurethane Novelty and Children's Products

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Publication Information

Addendum

This addendum is on the Department of Ecology's website at
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This addendum is an addition to an original Quality Assurance Project Plan. It is not a correction (errata) to the original plan. The addendum uses numbered headers that are identical to the ones used in the original QAPP, except for the noted changed sections in the addendum, all other sections remains as described in the original QAPP, and are not restated in the addendum.

Original Publication

Mercury in Polyvinyl Chloride and Polyurethane Novelty and Children's Products

Publication No. 15-03-106, the Quality Assurance Project Plan is available on the Department of Ecology's website at https://fortress.wa.gov/ecy/publications/SummaryPages/1503106.html.

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Quality Assurance Project Plan Addendum

Mercury in Polyvinyl Chloride and Polyurethane Novelty and Children's Products

March 2016

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Original signatures are not available on the Internet version.
HWTR: Hazardous Waste and Toxics Reduction Program
EAP: Environmental Assessment Program

3.0 Background

In 2015, the Washington State Department of Ecology (Ecology) conducted a study to evaluate the presence of mercury in polyvinyl chloride (PVC) and polyurethane novelty and children's products. This was done in accordance with Washington's Mercury Law (RCW 70.95M) and Children's Safe Products Act (CSPA) (RCW 70.240). Washington's Mercury Law prohibits the sale of mercury-containing novelty products, items intended mainly for the purpose of personal or household enjoyment or adornment. The 2008 CSPA legislation established reporting requirements for children's products that contain toxic chemicals. The final CSPA Reporting Rule requires manufacturers of children's products to notify Ecology of the presence of Chemicals of High Concern to Children, including mercury.

Ecology purchased and analyzed 266 products manufactured of PVC and polyurethane, categorized into three groupings defined by current regulations. All samples were analyzed for mercury by Manchester Environmental Laboratory, using the U.S. Environmental Protection Agency's (EPA's) Method 6020 according to the original Quality Assurance Project Plan (QAPP). This addendum describes requirements for analyzing a subset of the products using a method different from the one in the original QAPP.

Ecology expects there may be more mercury constituents in consumer products that were recently tested using EPA method 6020. For this reason, the addendum describes analysis of a subset of the products using a different method (EPA Method 7473) that does not require sample preparation/extraction steps and is very sensitive. Literature reviewed indicates that a better precision of measurements were observed with Method 7473 – a direct mercury analysis, likely due to the reduction of steps in sample preparation (Melendez et al. 2013; Rogers et al. 2012). The intent of this addendum is not to compare the two methods.

EPA Method 7473 is independent of sample matrix. Solid samples can be run in their native form, direct analysis of sample without digestion, obtaining accurate and reproducible data, and greatly reducing the problem with mercury volatility.

Determinations of mercury in polymeric/plastic samples have been done following EPA Method 7473 (Lau et al, 2006, and Teledyne Leeman Labs).

A final report summarizing the findings will be published in 2016. All data will be entered into a publicly available database on Ecology's website. Data from the project will be provided to Ecology enforcement officials to assess compliance with state laws.

4.0 Project Description

Ecology will conduct a study to measure the presence of mercury in PVC and polyurethane novelty and children's products using Direct Mercury Analyzer (DMA), EPA Method 7473. From the 266 products purchased, 62 product samples will be processed for laboratory analysis (see Table 5). Samples will be analyzed by Analytical Laboratory Services (ALS).

4.1 Project Goals and Objectives

This study will:

- Assess the presence of mercury in PVC and polyurethane novelty, children's novelty, and children's products through quantitative laboratory analysis.
- Provide data to Ecology's Mercury Law Enforcement Officer to assess compliance with Washington's Mercury Law.
- Provide data to Ecology's CSPA Enforcement Officer to verify manufacturer compliance with the CSPA reporting rule.

4.6 Tasks Required

Tasks to be performed for this study include:

- Processing products into samples and submitting samples to ALS.
- Laboratory analysis of mercury.
- Data validation and verification.
- Entering data into the Product Testing Database (PTDB).
- Reviewing quality of data entered into PTDB.
- Submitting the data to Ecology's Compliance Officers.
- Developing the final project report.

5.0 Organization and Schedule

Table 1 lists the people involved in this project. All are employees of the Washington State Department of Ecology. Table 2 presents the proposed schedule for this project.

5.1 Key Individuals and their Responsibilities

Table 1. Organization of project staff and responsibilities

Staff	Title	Responsibilities
Samuel Iwenofu Hazardous Waste and Toxics Reduction Program (HWTR) Phone: (360) 407-6758	Program Chemist & Program QA Officer	Writes the Quality Assurance Project Plan (QAPP) Addendum. Oversees project timeline. Conducts QA review of data, analyzes and interprets data. Performs comparative data analyses/assessments and provides summary of addendum findings for report.
Ian Wesley HWTR Phone: (360) 407-6609	Client	Oversees project timeline and contract laboratory. Provides internal review of QAPP and approves the final QAPP.
Chrissy Wiseman HWTR Phone: (360) 407-7672	Sampling Lead	Leads sample collection, processing, and shipment to laboratory. Assists with data analysis, and enters data into the Product Testing Database.
Carol Kraege HWTR Phone: (360) 407-6724	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft report, and approves the final report.
William Kammin Environmental Assessment Program (EAP) Phone: (360) 407-6964	Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP.
Sara Sekerak EAP Phone: (360) 407-6997	Project Manager	Conducts QA review of data, analyzes and interprets data. Writes draft report and final report.

5.4 Project Schedule

Table 2. Proposed project schedule

Mercury Product Testing – Addendum		
Project Schedule	**Due date**	**Lead**
Sample Selection	March 28-29, 2016	Chrissy Wiseman
Draft QAPP Addendum Review	March 16-23, 2016	Samuel Iwenofu
Draft QAPP review back to author	March 23 2016	Samuel Iwenofu
Final review completed and approved	March 24-25, 2016	Samuel Iwenofu
Samples sent to ALS lab	March 30 2016	Chrissy, Ian, Samuel
ALS Analytical Report	3 weeks from sample delivery	ALS Lab

5.6 Budget and Funding

The proposed cost estimate for laboratory analysis is $4,030. Table 3 shows the estimated costs for this project. Quality control samples are included in the estimated cost.

Table 3. Project budget

Analysis*	Cost/analysis	No. of analyses	Budget
Mercury	$65	62	$4,030
Total			**$4,030**
**Analysis does not include sample treatment such as cyromilling and extraction.*			

6.0 Quality Objectives

Laboratory quality control objectives are included in Table 4, and ALS is expected to meet these criteria. If the objectives are not met, ALS will reanalyze the samples in question in an attempt to conform to the quality control objectives. Tests falling outside of measurement quality control acceptance limits, and any other related data batches, will be reviewed by the project manager for their usability.

Chain-of-custody will be recorded throughout sample processing, screening, shipment, and laboratory analysis.

6.2 Measurement of Quality Objectives

Table 4. Measurement of Quality Objectives for Laboratory Analysis

Analyte	Laboratory Control Samples (recovery)	Matrix Spikes (recovery)	Matrix Spike Duplicates (RPD)	Laboratory Duplicates (RPD)
Mercury	90-110%	80-120%	≤ 20%	≤ 20%

The Method Detection Limit (MDL) is to be 0.2 ppb as established through the analysis of analytes free sand that was spiked with aqueous standard. Percentage recoveries are lab specific. Sample analysis and quality assurance will be performed according to the ALS SOP (Appendix 1):

- Continuing Calibration Verification (CCV) standards are analyzed after every 10 sample analyses. ICV/LCS will be analyzed after every 20 sample analyses.
- The CCV and ICV value must be within ± 10% of the true value or within certified limits for the standard, whichever is larger. The acceptance limits under EPA Method 7473 is ± 20%.

Method Reporting Limit (MRL) is 1 ppb based on a 100 mg sample size. The reporting limit may be adjusted if required for specific project requirements in consultation with the Ecology project manager.

7.0 Sampling Process Design (Experimental Design)

7.1 Study Design

To evaluate the levels of mercury in PVC or polyurethane, approximately 62 product samples will be selected from the purchased consumer products based on the sampling SOP in the original QAPP. The table below lists the consumer product types to be analyzed.

Table 5. Anticipated number and type of samples to be analyzed by the laboratory

Analyte	PVC			Polyurethane(PU)			Total Number of Samples
	Novelty	Novelty Children's Products	Children's Products	Novelty	Novelty Children's Products	Children's Products	
Mercury	6	10	6	15	15	10	62

Sixty-two (62) samples will be analyzed per project budget for total mercury by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry, (EPA Method 7473). The procedure will be performed in accordance with ALS laboratory SOP consistent with EPA Method 7473.

9.0 Measurement Methods

ALS laboratory will conduct the mercury analysis in accordance ALS laboratory SOP following the requirements established in EPA Method 7473.

9.2 Lab Procedures Table

Table 6. Laboratory procedures

Analyte	Samples (number/arrival date)	Matrix	RL (ppb)	Analysis Method	Analysis Instrument
Mercury	62 3/30/16	PVC	1.0	EPA 7473	DMA-AAS
		PU	1.0	EPA 7473	DMA-AAS

9.2.1 Analyte

The target analyte of interest for this study is mercury. No distinction of mercury form (elemental, inorganic, or organic) will be evaluated. Presence of all mercury in any form will be of interest to this study. Analysis method EPA 7473 will quantify total mercury.

9.2.2 Matrix

Matrices collected for the purpose of this study will be products made from PVC and products made from polyurethane. PVC will be in the form of plastics. Polyurethane may be in the form of plastics or foam. At the laboratory, the processing and analysis of these matrices will not be differentiated. A distinction in final reporting will be made for proper data evaluation.

9.5 Lab(s) Accredited for Method(s)

ALS Tucson is already accredited by the State of Arizona and, has been accredited by Ecology for Method 7473 on solid matrices.

10.0 Quality Control (QC) Procedures

10.1 Table of Lab QC Required

Table 7 outlines the quality control tests that ALS will perform. Laboratory control procedures would be as defined in the ALS standard operating procedure. ALS will run method blanks, laboratory control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD) with each batch of 20 samples. Three additional samples will be selected to be run in duplicate: one each from PVC, polyurethane plastic, and polyurethane foam products.

For additional QC, ALS will analyze Ecology purchased similar matrix SRM (DMA certified) when not calibrating with matrix similar standards.

Table 7. Quality control tests

Analyte	Method Blank	Laboratory Duplicate	Laboratory Control Sample	Matrix Spike	Matrix Spike Duplicate
Mercury	1/batch	3/project	1/batch	1/batch	1/batch

11.0 Data Management Procedures

Data management procedures are identical to those in the original *Quality Assurance and Project Plan for Mercury in Polyvinyl Chloride and Polyurethane Novelty and Children's Products* (Ecology, 2014) https://fortress.wa.gov/ecy/publications/SummaryPages/1503106.html. ALS will provide a standard deliverable package with case narratives to the project manager, describing the quality of ALS data. Case narratives should include any problems encountered with the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. Narratives will also address the condition of samples on receipt, sample preparation, methods of analysis, instrument calibration, and results of QC tests.

Case narratives will be in PDF format and electronic data deliverables will be in an Excel spreadsheet format. PDF documents will be sent to the project manager via email and the electronic data deliverable (Excel) will be delivered through a LIMS system.

12.0 Audits and Reports

Audits and reports are identical to those in the original Quality Assurance and Project Plan (Ecology, 2014). A report summarizing findings for this project after an internal review period, will become part of the final report for the overall project.

13.0 Data Verification

ALS will verify that:

1. Methods and protocols specified in this project plan were followed consistent with the method procedure and SOP.
2. All calibrations, QC tests, and intermediate calculations were performed for all samples.
3. Data are consistent, correct, and complete, with no errors or omissions. Evaluation criteria will include the acceptability of procedural blanks, calibration, QC sample results, and appropriateness of data qualifiers assigned.

The project manager will review the QC sample results for precision, bias, and accuracy and will determine whether quality assurance criteria have been met.

14.0 Data Quality (Usability) Assessment

The project manager will assess the quality of the data, based on case narratives and data packages, to determine whether data quality objectives were met for this study. The project manager will determine whether the data should be accepted, accepted with additional qualification, or rejected and re-analysis considered. Data quality and usability will be discussed in the report(s). The project manager in consultation with the HWTR Quality Control Officer will determine if an independent third party data validation and review is necessary.

14.2 Data Analysis and Presentation Methods

Since this project is not a method comparison study, mostly used to assess the relative agreement between two analytical methods that measure the same chemical substance. The final report will be limited only to the statistical summary of the results. Summary statistics, such as minimum, maximum, median, and frequency of detection will be presented in a table.

15.0 References

ALS Standard Operating Procedure, 2014. *Total Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry*. ASTM D6722 and EPA 7473, uncontrolled copy.

EPA. 2014. "Method 7473 (SW-846). *Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry*," Revision 0. 2007. www.epa.gov/sites/production/files/2015-07/documents/epa-7473.pdf

Melendez-Perez, J.J and A.H. Fostier, 2013. *Assessment of Direct Mercury Analyzer to quantify mercury in soils and leaf samples.* Journal of the Brazilian Chemical Society.vol.24 No. 11

Lau, S. and J. Kuczynski, 2006. *STG ROHS Testing Guideline for Determining Lead, Mercury, and Cadmium in Polymer Samples*. No. SG-D-0417. www.+03.ibm.com

Ecology, 2014. *Quality Assurance Project Plan: Mercury in Polyvinyl Chloride and Polyurethane Novelty and Children's Products*. Washington State Department of Ecology, Olympia WA. Publication No. 15-03-106. https://fortress.wa.gov/ecy/publications/SummaryPages/1503106.html

Rogers, W.J.; N. Carriker; J. Gable and P. Lee, 2012. *Factors to Convert Mercury Measurements to Account for Observed Differences in SW- 846 Methods 6020 and 7473 in Standard Reference Materials.* Tennessee valley Authority.

Teledyne Leemanlab. *The Determination of Mercury in Food Grade Plastics by Thermal Decomposition, Amalgamation and Cold Vapor Atomic Absorption*. Application Note #1081. Accessed February 9, 2016. www.leemanlab.com

Appendix 1

ALS Environmental, 2014. Standard operating procedure (SOP) for analysis of total mercury using EPA Method 7473. Available on request.