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State of Washington

Quality Assurance Project Plan

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

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Each study conducted by the Washington State Department of Ecology (Ecology) must have an approved Quality Assurance Project Plan. The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completing the study, Ecology will post the final report of the study to the Internet.

This Quality Assurance Project Plan is available on Ecology's website at https://fortress.wa.gov/ecy/publications/SummaryPages/1503106.html

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Quality Assurance Project Plan

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August 2015

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

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Not applicable.

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2.0 Abstract

The Washington State Department of Ecology (Ecology) will conduct a study to evaluate the presence of mercury in polyvinyl chloride (PVC) and polyurethane novelty and children's products 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 which are 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 will purchase a total of 266 products manufactured of PVC and polyurethane, categorized into three groupings defined by current regulations. Approximately 44 products will contain PVC and 222 products will contain polyurethane. All samples will be analyzed for mercury by Manchester Environmental Laboratory.

A final report summarizing findings will be published in 2015. All data will be entered into a publicly available database on Ecology's website. Data from this project will be provided to Ecology enforcement officials to assess compliance with state laws.

3.0 Background

Mercury, a persistent, bioaccumulative toxic substance, is of concern to the Washington State Department of Ecology (Ecology) because it is known to cause long-term harm to human and environmental health. Ecology is working to virtually eliminate[1] human-caused[2] use and release of mercury in Washington. Through the Mercury Chemical Action Plan, Washington State is taking steps to minimize human exposure to mercury (Peele et al., 2003).

As of January 1, 2006, Washington's Mercury Education and Reduction Act (MERA) was implemented. MERA bans the sale of various items that contain mercury, including novelties, clothing and toys. By definition:

> *Mercury-added novelty" means a mercury-added product intended mainly for personal or household enjoyment or adornment. Mercury-added novelties include, but are not limited to, items intended for use as practical jokes, figurines, adornments, toys, games, cards, ornaments, yard statues and figures, candles, jewelry, holiday decorations, items of apparel, and other similar products. Mercury-added novelty does not include games, toys, or products that require a button-cell or lithium battery, liquid crystal display screens, or a lamp that contains mercury (RCW 70.95 M.010).*

Mercury, when intentionally added to a novelty product, must be reported by the manufacturer to the retailers selling their merchandise. Manufacturers must also notify retailers of the provisions of the law (RCW 70.95 M.050), as well as how to properly dispose of any remaining mercury-added novelty inventory. Other than the exempted mercury-added items specified in the law, retailers cannot "knowingly" sell mercury-added novelties.

Additionally, the 2013 Children's Safe Products Act (CSPA) Reporting Rule requires manufacturers of children's products to report on the presence of certain chemicals in their products (Chapter 173-334 WAC). Chemicals of High Concern to Children (CHCC) include classified toxic chemicals that have been documented to be present in hair, blood, and urine of Washington residents, or have been found in children's products. Currently, sixty-six toxic chemicals, including mercury, have been collectively defined by Washington State Departments of Health and Ecology for inclusion in the CHCC list (Ecology, 2011a).

The reporting rule requires manufacturers of children's products to notify Ecology if their products have a product component that contains mercury in any concentration greater than practical quantitation limit of 0.5 ppm, defined by Ecology (2012), when the chemical was intentionally added to the product. Manufacturers must also notify Ecology when their products have a component that contains mercury at a concentration of 100 ppm or higher and the manufacturer has identified the chemical as a contaminant.

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[1] The Mercury Chemical Action Plan defines "virtual elimination" as a reduction of mercury releases to the air, water and land from human-made sources using life-cycle management practices (e.g., pollution prevention and release controls) so as to approach the levels and fluxes of mercury that would be expected from naturally-occurring processes.

[2] "Human-caused" can also be referred to as "anthropogenic", meaning to be caused or produced by humans and human activities.

Ecology conducts studies of consumer products to support the Mercury Chemical Action Plan objectives and to assure compliance with Washington's laws and rules.

3.1 Study area and surroundings

3.1.1 Identification of study area

Ecology will evaluate the presence of mercury in PVC and polyurethane consumer goods sold in Washington. This statewide assessment of mercury in products will contribute to the global effort to increase the study of mercury, as identified by:

- The United Nations Environment Programme **(**UNEP) Global Mercury Partnership has defined priorities for action to reduce human-caused mercury releases into the environment. The partnership established focus areas in the collective global effort to effectively manage mercury-related activities. Two goals set for reducing worldwide mercury use are: minimizing mercury in consumer products and supporting research and development of mercury-free catalysts used in production of the vinyl chloride monomer, the precursor to PVC.

- The Environmental Council of the States, a conglomeration of representatives of state and territorial environmental protection agencies, and the Quicksilver Caucus (QSC) recommend, as a high priority, studies on manufacturing and on products made of mercury-catalyzed polyurethane (QSC, 2013).

Mercury and its contamination levels in the end products of PVC and polyurethane consumer goods have not been sufficiently studied and are not adequately known.

3.1.2 Parameters of interest

Ecology will assess the presence of mercury, in any form, reported as total mercury (referred to as mercury throughout this project plan) in PVC and polyurethane novelty and children's products.

3.1.3 Logistical problems

Ecology staff may encounter issues in collecting sufficient numbers of PVC and polyurethane novelty and children's products. When choosing products to test, staff may have difficulty correctly distinguishing PVC and polyurethane from other types of plastics and foams.

3.1.4 Results of previous studies

Studies of mercury content in PVC and polyurethane products are limited.

There are no readily available studies that specifically focus on mercury in consumer products made from PVC.

In 2006, the Danish Ministry of the Environment conducted studies to identify chemical substances in a number of consumer products, including one specifically in children's products produced from foam plastic (Borling et al., 2006). This study targeted mercury, as well as other metals, set by the European Union's (EU) The Toy Standard EN 71-3:1994, limiting concentrations of chemicals in products produced for children. Only eight products were tested for mercury, and none contained measured concentrations of concern (>0.05 ppm).

Ecology began independent testing of children's and consumer products in 2012 to assess the manufacturer and retailer compliance with CSPA legislation and other consumer products laws. In these studies, only a few products analyzed for mercury contained portions of either PVC or polyurethane components.

Mathieu and Bookter (2014) tested mercury, in addition to metals and phthalates, in Tier 3 children's products. Ten of the 35 product components tested for mercury were identified as made of plastic; only one product was specially described as vinyl (PVC) and one as foam (indeterminate source). None of the tested products contained mercury above the reporting limit (1.0 ppm).

3.1.5 Regulatory criteria or standards

Ecology's enforcement officers will review the data from this study to determine if manufacturers are complying with Washington's Mercury Law and the CSPA Reporting Rule for mercury in novelty and children's products, as applicable. These regulations are described in Section 3.0.

4.0 Project Description

Ecology will conduct a study to measure the presence of mercury in PVC and polyurethane novelty and children's products. During the spring of 2015, approximately 266 samples will be purchased, screened by XRF, processed for laboratory analysis, and analyzed by Manchester Environmental Laboratory (MEL).

4.1 Project goals

This study is being carried out to:

- Assess the presence of mercury in PVC and polyurethane novelty, children's novelty and children's products through quantitative laboratory analysis. (See section 4.4 for description of these 3 categories, derived from various laws.)
- 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.
- Screen all products for the presence of low-level mercury with an XRF analyzer. This will continue the evaluation of XRF technology as a screening tool with children's products and consumer goods (Furl, 2011 and Furl et al., 2012).
- Evaluate the need for pre-treating PVC and polyurethane consumer products by cryomilling; determine the best preparation methodology for acid-assisted microwaving digestion.

4.2 Project objectives

To meet the project goals, the following activities will be carried out:

- Conduct Internet research to help select novelty and children's products, made from PVC or polyurethane, to analyze for mercury content.
- Collect products through online retailers and "off the shelf" at stores around Puget Sound.
- Confirm, with the XRF, the presence of chlorine (>15%)[3] in products collected and identified as made of PVC.
- Screen all products, with the XRF, for the presence of low-level mercury.

[3] High levels of chlorine will be inferred as an indication of polyvinyl chloride (PVC). Chlorine at lower concentrations may be a result of other chlorine containing plastics, pigments, preservatives or contaminates. An Ecology (2012) study used XRF detectable concentrations above 10,000 ppm (1%) to determine chlorine compounds, such as PVC, in interior automotive applications. Dependent on levels of additives, levels of chlorine content in PVC ranges between 28 and 57%. Mathieu et al. (2014) used > 15% concentrations of chlorine to determine PVC-based products for further assessment of phthalates.

- Perform a cryomill treatment and acid-assisted microwave digestion method study. MEL will conduct.
- Analyze all product samples for mercury.

4.3 Information needed and sources

The following sources will be reviewed before products are collected for this project:

- Survey, Migration and Health Evaluation of Chemical Substances in Toys and Childcare Products Produced from Foam Plastic (Borling et al., 2006).
- Survey, Emission and Health Assessment of Chemical Substances in Baby Products (Tonning et al., 2008).
- Quality Assurance Project Plan for Chemicals of High Concern to Children in Children's Clothing, Footwear and Accessories (Mathieu and McCall, 2014).
- Metals and Phthalates in Tier 3 Children's Products (Mathieu and Bookter, 2014).
- Evaluation of XRF as a Screening Tool for Metals and PBDEs in Children's Products and Consumer Goods (Furl et al., 2012).
- Ecology's CSPA manufacturer reporting database.

4.4 Target population

Products made from PVC plastic, often marketed as vinyl, and polyurethane plastic and foam will be targeted for this study. The variety of products collected, purchased, and sent to the laboratory for the analysis of mercury will be limited to novelty, children's novelty and children's only products.

For the purpose of this study, there will be three categories of product types investigated for the presence of mercury, defined by which law regulates the product type: novelty products (Mercury Law), children's novelty products (Mercury Law and CSPA) and children's only products (CSPA). Children's only products refer to children's products that are not considered novelty items, such as changing pads or car seats. The three categories will be collectively referenced as novelty and children's products, when the delineation of each specific category provides no additional value.

4.5 Study boundaries

Ecology staff will purchase products "off the shelf" from stores in the Puget Sound area and through online retailers. Large chain retailers and discount stores will be targeted. The practice of statewide distribution by most of the retail chain stores ensures that products purchased in the Puget Sound area are representative of products sold across the state. Internet purchases will also be considered representative, because all Washington residents can obtain these same products via the Internet.

4.6 Tasks required

Tasks to be performed for this study are:

- Researching Internet for novelty and children's products made from PVC and polyurethane.
- Purchasing novelty and children's products made from PVC and polyurethane.
- Screening products, using the XRF analyzer, for the presence of mercury and chlorine.
- Processing products into samples and submitting samples to MEL.
- Laboratory performed preparation method study.
- Laboratory analysis of mercury.
- Data validation and verification.
- Entering data into the Product Testing Database (PTDB).
- Reviewing QC of data entered into PTDB.
- Submitting the data to Ecology's Compliance Officers.
- Developing the final project report.

4.7 Practical constraints

The only foreseeable constraint anticipated is in locating and purchasing the desired numbers of samples made of PVC and polyurethane.

4.8 Systematic planning process

This Quality Assurance Project Plan constitutes the systematic planning process.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

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

Table 1. Organization of Project Staff and Responsibilities.

Staff	Title	Responsibilities
Ian Wesley HWTR Phone: 360-407-6747	Client	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.
Ken Zarker HWTR Phone: 360-407-6724	Client's Section Manager	Reviews the draft QAPP and approves the final QAPP.
Sara Sekerak Toxic Studies Unit SCS, EAP Phone: 360-407-6997	Project Manager	Writes the QAPP. Coordinates with laboratory. Prepares samples and sends samples to laboratory. Conducts QA review of data, analyzes and interprets data. Writes the draft report and final report.
Samuel Iwenofu HWTR Phone: 360-407-6346	HWTR Quality Assurance Coordinator	Reviews and approves the draft QAPP and the final QAPP.
Christina Wiseman HWTR Phone: 360-407-7672	Sampling Lead	Purchases products, conducts XRF screening of products. Enters data into the Product Testing Database.
Dale Norton Toxic Studies Unit SCS, EAP Phone: 360-407-6765	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Will Kendra SCS, EAP Phone: 360-407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Joel Bird Manchester Environmental Laboratory Phone: 360-871-8801	Director	Reviews and approves the final QAPP.
William R. Kammin Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP.

HWTR: Hazardous Waste and Toxics Reduction Program
SCS: Statewide Coordination Section
EAP: Environmental Assessment Program
QAPP: Quality Assurance Project Plan

5.2 Special training and certifications

Ecology's published Product Sampling Procedure will be followed for product selection and documentation, product tracking, sample preparation and XRF analysis (van Bergen, 2014). Ecology staff conducting the XRF analysis will follow the manufacturer's standard operating procedure as defined in the XL3 Analyzer Version 8.0.0 Users Guide (Abridged) Revision A November 2011.

5.3 Organization chart

See Tables 1 and 2.

5.4 Project schedule

Table 2. Proposed Schedule for Completing Product Collection and Laboratory Work, Data Entry into Product Testing Database (PTDB), and Reports.

Field and laboratory work	Due date	Lead staff
Product collection completed	04/2015	Christina Wiseman
XRF screening completed	05/2015	Christina Wiseman
Laboratory analyses completed	07/2015	
Product Testing Database (PTDB) database		
	Due date	Lead staff
Lab data loaded	09/2015	Christina Wiseman
PTDB QA review	10/2015	Sara Sekerak
Data entry complete	11/2015	Christina Wiseman
Final report		
Author lead / Support staff	Sara Sekerak (lead) / Christina Wiseman	
Schedule		
Draft due to supervisor	10/2015	
Draft due to client/peer reviewer	11/2015	
Final (all reviews done) due to publications coordinator	12/2015	

5.5 Limitations on schedule

No schedule limitations are expected for the project.

5.6 Budget and funding

Proposed cost estimate for product collection, processing, and laboratory analysis totals $53,915. Table 3 shows the estimated costs for this project.

An additional $9,400 will be spent from the general Consumer Product Testing budget, separate from the project budget, to perform a preparation study on PVC and polyurethane matrices. Table 4 shows the budget for the preparation study. Table 5 shows the entire budget and funding allocation associated with this project plan.

Table 3. Project Budget and Funding.

Product/Parameter	Number of Samples	QC Samples*	Cost per Sample	Subtotal	
Product Collection^	266	---	$15	$3,990	---
				Product Collection Total:	$3,990
Cryomilling	266	---	$100	$26,600	---
Mercury	266	45	$75	$23,325	---
				Laboratory Analysis Total:	$49,925
				Project Total:	$53,915

*QC samples in this table include those that are not provided free of charge (matrix spikes, duplicates, and cryomill rinseates).
^ Product collection spending is allocated from a separate budget from project budget.

Table 4. Preparation Method Study Budget and Funding.

Procedure	Analyte	Number of Samples to Process	QC Samples	Cost per Sample	Subtotal
Cryomilling	--	10	---	$100	$1,000
MEL Method	Hg	20	4	$75	$1,800
CPSC^{+} Method	Hg	20	4	$75	$1,800
Addit. Microwaving Ramp Cycles$^{\blacklozenge}$	--	80	16	$50	$4,800
				Study Total:	$9,400

$^{+}$ Method modeled after the Consumer Product Safety Commission (CPSC) method for total lead in non-metal children's products.
$^{\blacklozenge}$Includes maximum possible cycles.

Table 5. Total Project and Study Budget and Funding Allocation.

Study	Number of Samples to Process	Subtotal
Preparation Method Study	10	$9,400
Hg in PVC and Polyurethane Novelty and Children's Products Project	266	$53,915
	Total:	$63,315

6.0 Quality Objectives

6.1 Decision Quality Objectives (DQOs)

Decision quality objectives are not necessary for this project.

6.2 Measurement Quality Objectives

MEL is expected to meet all QC requirements for this project. Table 6 lists the specific measurement quality objectives (MQOs), including the lowest concentration of interest. MEL will evaluate all collected data and report any discrepancies to the listed MQOs.

Table 6. Measurement Quality Objectives for Laboratory Analysis.

Analyte	Bias		Precision	Sensitivity
	LCS (% recov.)	Matrix Spikes (% recov.)	Matrix Spike Duplicates (RPD)	Lowest Concentration of Interest
Mercury	85 - 115%	75 - 125%	≤ 20%	0.02 ppm

6.2.1 Targets for precision, bias, and sensitivity

6.2.1.1 Precision

Precision is a measure of the variability in the results of measurements due to random error. There is no plan to purchase products in replicate for this project. Laboratory precision will be assessed through laboratory duplication of product samples. The project manager will select 3 samples to be analyzed in duplicate by MEL. See Table 6 for MQOs.

6.2.1.2 Bias

Bias is the difference between the population mean and the true value. Assessments of laboratory bias will be determined by analysis of laboratory control samples (LCSs) and matrix spiked samples. See Table 6 for MQOs.

6.2.1.3 Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance. The lowest concentrations of interest are listed in Table 6.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

Product samples will be purchased, processed, scanned by XRF and submitted to the laboratory consistent with the methods described in Ecology's Product Sampling Procedure (van Bergen, 2014). The aforementioned process will ensure comparability between all product testing projects.

6.2.2.2 Representativeness

Ecology staff will purchase a large number of products (approximately 266) to help ensure that products collected are representative of those available to consumers. Staff will visit major retailers in the area to obtain a wide variety of types of products.

6.2.2.3 Completeness

The project manager will consider the study to have achieved completeness if 95% of the samples are analyzed acceptably.

7.0 Sampling Process Design (Experimental Design)

7.1 Study design

To characterize levels of mercury in PVC or polyurethane, approximately 266 products will be purchased from retailers in the Puget Sound area and through Internet retailers selling to Washington consumers. Of these, a target goal of 44 products will be made from PVC and 222 products will be made from polyurethane.

A majority of the PVC and polyurethane merchandise will be in the form of children's novelty products. Purchased products in the novelty children's product category will include items such as games and toys, or items that are intended mainly for personal or household enjoyment or adornment, and are marketed for or used by children. Purchased products in the novelty category will include, but are not limited to, items of apparel, decorations, figurines, and other similar products not designed or intended for use by a child. Purchased products in the children's products category will include any product designed or intended for use by a child, regardless of designed purpose or use. All children's products will meet the CSPA RCW 70.240.010 definition of a *Children's Product* (Washington, 2008).

Products will be purchased by Ecology staff and brought back to Ecology headquarters. Product data will be entered into the PTDB. The products will be scanned by the XRF analyzer. The products will be reduced as necessary, placed into sample containers, and sent to MEL for mercury analysis.

Table 7. 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	5	34	5	56	111	55	266

7.1.1 Field measurements

Not applicable.

7.1.2 Sampling location and frequency

Products will be purchased from online sources and Puget Sound retailers over a two-week period in April.

7.1.3 Parameters to be determined

See Table 3 for a list of parameters to be determined.

7.2 Maps or diagram

Not applicable.

7.3 Assumptions underlying design

PVC and polyurethane products were chosen because a mercury compound may possibly be used during the manufacturing of these materials. Mercury is used as an effective catalyst for producing the vinyl chloride monomer used to make polyvinyl chloride (PVC), and it is used as a catalyst in the production of polyurethane plastic and foam. Catalysts facilitate an accelerated chemical reaction and functionally are not intended to remain in the final product.

With a sampling of products in the marketplace, we will assess the presence of mercury, in support of Washington's Mercury Law and Children's Safe Product Act Reporting Rule.

7.4 Relation to objectives and site characteristics

Not applicable.

7.5 Characteristics of existing data

Ecology's previous studies on chemicals in products were designed to look at a wide range of toxic chemicals and product types. This study will narrow the focus of study to products made of either PVC or polyurethane and sold for use as novelty and children's products.

8.0 Sampling Procedures

8.1 Field measurement and field sampling SOPs

Product collection will follow the Product Sampling Procedure (van Bergen, 2014).

8.2 Containers, preservation methods, holding times

Samples will be stored in 8-oz glass jars with no preservation. No holding times have been established for product matrices.

8.3 Invasive species evaluation

Not applicable.

8.4 Equipment decontamination

Due to the low level of quantification, additional measures to those covered in Ecology's Product Sampling Procedure (van Bergen, 2014) will be performed for equipment decontamination. Stainless steel tools (e.g., scissors or knives) will be used for separating components and reducing samples. Tools will be decontaminated at the beginning of the day, after each use, and at the end of the day. The cleaning protocol will consist of an initial scrubbing of the tools with Liquinox® and rinsing with tap water, followed by a 10% nitric acid rinse and a deionized water rinse.

Staff wearing powder-free nitrile gloves will prepare samples on a clean bench that is lined with aluminum foil.

8.5 Sample ID

Product samples will be labeled with component IDs generated by the Product Testing Database and a sample ID based on the MEL work order. The mass of the sample will be written on the outside of the jar. Specific details of sample ID generation and tracking are described in the Product Testing Procedure (van Bergen, 2014).

8.6 Chain-of-custody, if required

A chain of custody will be maintained throughout sample processing, screening, shipment, and laboratory analysis.

8.7 Field log requirements

Upon return from purchasing events, staff will record and store photographs, receipts, and store information in the Product Testing Database.

8.8 Other activities

Product Collection

Products made entirely of PVC or polyurethane will be targeted. Collected products will include products made partially of−or have a component made of− PVC or polyurethane. Each product is required to have a minimum sample weight of 2 grams when reduced.

Staff will record information such as the type of advertisement used to sell the product and the area in the store where the product was found; this will help ensure the product is marketed for children. Staff will take photos at the time of purchase of products and include the adjacent area when there is ambiguity about whether the product is intended for children.

After staff collect all products, they will return to Ecology headquarters and assign a unique product identification number. Photos and descriptive notes will be recorded.

Product Isolation

Products that are made with multiple components will be separated, and only parts made of PVC or polyurethane will be tested. Staff will reduce large products or components by selecting small portions from different areas to make a composite sample representative of the whole product or component. Component isolation of children's products will follow the CSPA Reporting Rule guidelines (Ecology, 2011b).

XRF Screening

Staff will screen all PVC and polyurethane samples, using a Niton XL3 XRF for mercury and chlorine. Procedures for screening samples will follow those outlined in the Product Sampling Procedure (van Bergen, 2014) and the XRF manufacturer user manual. Staff will also reference the ASTM Method F 2617-08 *Standard Test Method for Identification and Quantification of Chromium, Bromine, Cadmium, Mercury, and Lead in Polymeric Material Using Energy Dispersive X-ray Spectrometry* (ASTM, 2008).

Laboratory Preparation Method Study

Samples will be initially submitted to MEL for the purpose of performing pre-treatment and preparation method study. There is currently very little published information on lab preparation methods for consumer products. Consumer products vary widely in their design and composition and can be challenging to analyze. The objective of this study is to determine the best method to facilitate a complete digestion and total dissolution of PVC and polyurethane

matrices. Complete digestion is desired to ensure that the analyte of interest has been fully extracted into aqueous solution and is available for quantification by instrumental analysis. Ten samples will be prepared by Ecology HQ staff, according to the processing procedures described in Ecology's Product Sampling Procedure (van Bergen, 2014). These samples will be submitted to MEL. These samples will consist of five PVC samples and five polyurethane samples taken from a previously completed project. The samples study will be performed before the main project plan begins, and it will serve to determine how the 266 PVC and polyurethane samples should be processed. The project manager and MEL staff will evaluate the results of the samples study and determine the best practice to apply to the main project plan samples.

MEL will split the ten received samples into two portions. One of the split portions will receive the cryomill treatment and the other portion will not undergo a cryomill treatment prior to the microwave digestion step. The non-cryomilled portion will receive a snipping treatment to reduce the sample to 2 mm x 2 mm or less. After the initial treatments, each split portion, cryomilled and non-cryomilled, will be split again into two additional fractions. The final splitting of the samples results in two portions of cryomilled samples and two portions of non-cryomilled samples.

The pre-treated samples will be processed by one of two regimens of acid-assisted microwave digestion methods. The variables of this step include: acid types, acid concentrations, sequence of acid addition, and microwave (heat and pressure) program set-ups. All four sample sets will receive the initial digestion acid(s) and sit overnight (8 -12 hours) prior to undergoing the first microwaving cycle. Following the initial microwaving cycle, as necessary, additional cycles of microwaving may be employed to facilitate a complete digestion of the samples.

The first microwave digestion preparation method is based on the EPA 3052 method. The samples will each receive 9 mL nitric acid and 3 mL hydrochloric acid. They then will be microwaved at settings recommended by the microwave's manufacturer (CEM). This is the process currently being used by MEL to digest samples of similar matrices. One set of cryomilled samples and one set of non-cryomilled samples will undergo this course.

The second microwave digestion preparation process will be modeled after a Consumer Product Safety Commission (CPSC) method process for digesting plastic materials, such as polyethylene and PVC (CPSC, 2012). The samples will receive an initial 10 mL of nitric acid prior to the microwaving step and an additional 3 mL hydrochloric acid addition after all microwaving cycles have been completed. One set of cryomilled samples and one set of non-cryomilled samples will undergo this course.

Each of the four sample sets will be visually evaluated after each microwave digestion cycle. Additional microwaving cycles will be performed as necessary. Appearance of the samples will be annotated after each cycle and used to confirm complete digestion.

Instrumental analysis of all four variations of preparation techniques will be performed in an identical manner according to EPA 6020. One quality control sample of each of these will be included with each sample set: Matrix Spike, Matrix Spike Duplicate, Method Blank and Blank Spike (LCS). These quality control samples will be assessed in accordance with the guidelines established for measurement quality, as presented in Section 6.2.

We will assess and compare all sample sets to determine effectiveness of each procedure. We will then select the most appropriate pre-treatment and method to apply to PVC- and polyurethane-based products.

9.0 Measurement Methods

9.1 Field procedures table/field analysis table

Not applicable.

9.2 Lab procedures table

Table 8. Laboratory Procedures.

Analyte	Samples (number/arrival date)	Expected Range of Results	Matrix	RL (ppm)	Preparation Method	Analysis Method	Analysis Instrument
Mercury	266, 5/15/15	<0.02 - 500 ppm	PVC	0.02	3052 or CSPC	EPA 6020	ICP-MS
			PU	0.02	3052 or CSPC	EPA 6020	ICP-MS

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 mercury in all and any form will be of interest to this study. Analysis method EPA 6020 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.

9.2.3 Number of samples

See Table 7.

9.2.4 Expected range of results

The expected level of mercury in PVC and polyurethane products is less than 0.02 ppm to 500 ppm.

9.2.5 Analytical method

EPA Method 6020 will be used to analyze the mercury in PVC and polyurethane polymer products.

9.2.6 Sensitivity/Method Detection Limit (MDL)

See Table 6.

9.3 Sample preparation method(s)

After XRF screening, staff at Ecology HQ will reduce the purchased products before submitting them to MEL for analysis. For large products, staff will select small portions from different areas to make a composite sample representative of the whole purchased product. Composite samples and smaller products will be further reduced to approximately 8 mm x 8 mm pieces using stainless steel tools (e.g., scissors or snips). The final reduced samples will be placed into labeled 8-oz. jars, and the mass of contained sample will be recorded on the jar. A chain-of-custody will be recorded throughout sample processing, screening, shipment, and laboratory analysis. Detailed product processing procedures are described in Ecology's Product Sampling Procedure (van Bergen, 2014)

Pending the outcome of the preparation study performed by MEL, samples necessitating a cryomill treatment will be cryomilled prior to processing by microwave preparation. The cryomilling process uses cryogenics temperatures achieved with liquid nitrogen to assist in mechanical milling of sample matrices down to final fineness of 5 µm or less. MEL will conduct cryomilling, using the latest version of the MEL standard operating procedure.

An acid-assisted microwave digestion of the samples will be performed in accordance with either current EPA 3052 method or the CPSC-based method investigated in the Laboratory Preparation Method Study, as described in Section 8.8. The microwave digestion method will be determined based on the outcome of the preparation study.

9.4 Special method requirements

When cryomilling is performed, cryomill rinseate blanks will be collected and analyzed to assess any sample-to-sample carryover during the cryomill process. After each sample is cryomilled, the cryomill grinding jar, grinding ball, and Teflon gasket will be scrubbed with Citranox® five times and rinsed thoroughly with deionized water. The final aliquot of deionized rinse water will be collected and acidified with nitric acid for use as the cryomill rinseate blank; all rinseate blanks will be kept through the end of the project. One rinseate from each batch of twenty samples will be randomly selected and analyzed. The analyst will assess the rinseate blanks and sample results for the presence of mercury and run any additional rinseate blanks as necessary to determine possible carryover.

9.5 Lab(s) accredited for method(s)

MEL will conduct all analyses for mercury. MEL is accredited for method EPA 6020.

10.0 Quality Control (QC) Procedures

10.1 Table of field and lab QC required

Table 9 outlines the quality control tests that MEL will perform. MEL will run cryomill rinseate blanks, 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. MEL will follow applicable SOPs as described in the *Manchester Environmental Laboratory Quality Assurance Manual* (MEL, 2014).

Table 9. Quality Control Tests.

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

10.2 Corrective action processes

MEL will document and report any discrepancies to the listed MQOs in Table 6. The project manager shall be promptly notified of issues with sample amounts, cryomilling, or sample digestion processes for direction of further recourse.

11.0 Data Management Procedures

11.1 Data recording/reporting requirements

All project data will be stored in Ecology's Product Testing Database. The database will hold product descriptions, purchase receipts, photos of products, and laboratory data and case narratives. The data will be available to the public through an external search application at: https://fortress.wa.gov/ecy/ptdbpublicreporting/.

11.2 Laboratory data package requirements

MEL will provide a standard deliverable package after completing their work. All quality control data will be included with the package. MEL will discuss any problems encountered with the analyses, corrective action taken, changes to the requested analytical method, and a glossary for data qualifiers.

The narrative will include:

- Printed reports with QA summaries for all results.
- Explanations of any difficulties encountered during cryomilling, digestion or analysis.

11.3 Electronic transfer requirements

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.

11.4 Acceptance criteria for existing data

Not applicable.

11.5 EIM/STORET data upload procedures

Not applicable. Section 11.1 describes the database where data will be stored for this project.

12.0 Audits and Reports

12.1 Number, frequency, type, and schedule of audits

MEL and contracted laboratories must participate in performance and system audits of their routine procedures. No audits are planned specifically for this project.

12.2 Responsible personnel

As per Table 2.

12.3 Frequency and distribution of report

A report summarizing findings for this project will be published at the end of the study. The final report will include:

- General descriptions of products purchased.
- Descriptions of product categories.
- A brief discussion of the preparation study findings.
- Results of laboratory analyses.
- Statistical summaries of laboratory results.
- Summary of laboratory data collected and data gathered by XRF for mercury.

12.4 Responsibility for reports

See Section 5.1.

13.0 Data Verification

13.1 Field data verification, requirements, and responsibilities

Not applicable.

13.2 Lab data verification

Case narratives from MEL will be sent to the project manager as a summation of laboratory data quality. The narrative will include MEL's assurance that the QA Project Plan, methods, and SOPs were followed and all data quality objectives were met. The project manager will review the QC sample results for precision, bias, and accuracy and will determine whether quality assurance criteria have been met.

13.3 Validation requirements, if necessary

Independent data validation is not planned for this project.

14.0 Data Quality (Usability) Assessment

14.1 Process for determining whether project objectives have been met

After the project data has been reviewed and verified, the project manager will evaluate and determine if the study objectives were met.

14.2 Data analysis and presentation methods

The final report will include a statistical summary of the results. Summary statistics, such as minimum, maximum, median, and frequency of detection will be presented in a table.

14.3 Treatment of non-detects

Laboratory data will be reported down to the reporting limit, with an associated "U" or "UJ" qualifier for non-detects.

14.4 Sampling design evaluation

The number and type of samples collected will be sufficient to meet the objectives of this project.

14.5 Documentation of assessment

Documentation of assessment will occur in the final report.

15.0 References

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16.0 Figures

Not applicable.

17.0 Tables

See the Table of Contents for a list of tables in this report.

18.0 Appendix: Acronyms, Abbreviations, and Glossary

Ecology	Washington State Department of Ecology
CPSC	Consumer Products Safety Commission
CSPA	Children's Safe Product Act
e.g.	For example
EPA	U.S. Environmental Protection Agency
et al.	And others
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
PBT	persistent, bioaccumulative, and toxic substance
PTDB	Product Testing Database
PVC	Polyvinyl chloride
PU	Polyurethane
QA	Quality assurance
RCW	Revised Code of Washington
RPD	Relative percent difference
SOP	Standard operating procedures
SRM	Standard reference materials
WAC	Washington Administrative Code

Units of Measurement

ppm	parts per million

Quality Assurance Glossary

Accreditation: A certification process for laboratories, designed to evaluate and document a lab's ability to perform analytical methods and produce acceptable data. For Ecology, it is "Formal recognition by (Ecology)…that an environmental laboratory is capable of producing accurate analytical data." [WAC 173-50-040] (Kammin, 2010)

Accuracy: The degree to which a measured value agrees with the true value of the measured property. USEPA recommends that this term not be used, and that the terms precision and bias be used to convey the information associated with the term accuracy. (USGS, 1998)

Analyte: An element, ion, compound, or chemical moiety (pH, alkalinity) which is to be determined. The definition can be expanded to include organisms, e.g., fecal coliform, Klebsiella. (Kammin, 2010)

Bias: The difference between the population mean and the true value. Bias usually describes a systematic difference reproducible over time, and is characteristic of both the measurement system, and the analyte(s) being measured. Bias is a commonly used data quality indicator (DQI). (Kammin, 2010; Ecology, 2004)

Blank: A synthetic sample, free of the analyte(s) of interest. For example, in water analysis, pure water is used for the blank. In chemical analysis, a blank is used to estimate the analytical response to all factors other than the analyte in the sample. In general, blanks are used to assess possible contamination or inadvertent introduction of analyte during various stages of the sampling and analytical process. (USGS, 1998)

Calibration: The process of establishing the relationship between the response of a measurement system and the concentration of the parameter being measured. (Ecology, 2004)

Check standard: A substance or reference material obtained from a source independent from the source of the calibration standard; used to assess bias for an analytical method. This is an obsolete term, and its use is highly discouraged. See Calibration Verification Standards, Lab Control Samples (LCS), Certified Reference Materials (CRM), and/or spiked blanks. These are all check standards, but should be referred to by their actual designator, e.g., CRM, LCS. (Kammin, 2010; Ecology, 2004)

Comparability: The degree to which different methods, data sets and/or decisions agree or can be represented as similar; a data quality indicator. (USEPA, 1997)

Completeness: The amount of valid data obtained from a project compared to the planned amount. Usually expressed as a percentage. A data quality indicator. (USEPA, 1997)

Continuing Calibration Verification Standard (CCV): A QC sample analyzed with samples to check for acceptable bias in the measurement system. The CCV is usually a midpoint calibration standard that is re-run at an established frequency during the course of an analytical run. (Kammin, 2010)

Control chart: A graphical representation of quality control results demonstrating the performance of an aspect of a measurement system. (Kammin, 2010; Ecology 2004)

Control limits: Statistical warning and action limits calculated based on control charts. Warning limits are generally set at +/- 2 standard deviations from the mean, action limits at +/- 3 standard deviations from the mean. (Kammin, 2010)

Data Integrity: A qualitative DQI that evaluates the extent to which a data set contains data that is misrepresented, falsified, or deliberately misleading. (Kammin, 2010)

Data Quality Indicators (DQI): Commonly used measures of acceptability for environmental data. The principal DQIs are precision, bias, representativeness, comparability, completeness, sensitivity, and integrity. (USEPA, 2006)

Data Quality Objectives (DQO): Qualitative and quantitative statements derived from systematic planning processes that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions.
(USEPA, 2006)

Data set: A grouping of samples organized by date, time, analyte, etc. (Kammin, 2010)

Data validation: An analyte-specific and sample-specific process that extends the evaluation of data beyond data verification to determine the usability of a specific data set. It involves a detailed examination of the data package, using both professional judgment, and objective criteria, to determine whether the MQOs for precision, bias, and sensitivity have been met. It may also include an assessment of completeness, representativeness, comparability and integrity, as these criteria relate to the usability of the data set. Ecology considers four key criteria to determine if data validation has actually occurred. These are:

- Use of raw or instrument data for evaluation.
- Use of third-party assessors.
- Data set is complex.
- Use of EPA Functional Guidelines or equivalent for review.

Examples of data types commonly validated would be:

- Gas Chromatography (GC).
- Gas Chromatography-Mass Spectrometry (GC-MS).
- Inductively Coupled Plasma (ICP).

The end result of a formal validation process is a determination of usability that assigns qualifiers to indicate usability status for every measurement result. These qualifiers include:

- No qualifier, data is usable for intended purposes.
- J (or a J variant), data is estimated, may be usable, may be biased high or low.
- REJ, data is rejected, cannot be used for intended purposes (Kammin, 2010; Ecology, 2004).

Data verification: Examination of a data set for errors or omissions, and assessment of the Data Quality Indicators related to that data set for compliance with acceptance criteria (MQOs). Verification is a detailed quality review of a data set. (Ecology, 2004)

Detection limit (limit of detection)**:** The concentration or amount of an analyte which can be determined to a specified level of certainty to be greater than zero. (Ecology, 2004)

Duplicate samples: Two samples taken from and representative of the same population, and carried through and steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variability of all method activities including sampling and analysis. (USEPA, 1997)

Field blank: A blank used to obtain information on contamination introduced during sample collection, storage, and transport. (Ecology, 2004)

Initial Calibration Verification Standard (ICV): A QC sample prepared independently of calibration standards and analyzed along with the samples to check for acceptable bias in the measurement system. The ICV is analyzed prior to the analysis of any samples. (Kammin, 2010)

Laboratory Control Sample (LCS): A sample of known composition prepared using contaminant-free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern. It is prepared and analyzed in the same batch of regular samples using the same sample preparation method, reagents, and analytical methods employed for regular samples. (USEPA, 1997)

Matrix spike: A QC sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias due to interference or matrix effects. (Ecology, 2004)

Measurement Quality Objectives (MQOs)**:** Performance or acceptance criteria for individual data quality indicators, usually including precision, bias, sensitivity, completeness, comparability, and representativeness. (USEPA, 2006)

Measurement result: A value obtained by performing the procedure described in a method. (Ecology, 2004)

Method: A formalized group of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, data analysis), systematically presented in the order in which they are to be executed. (EPA, 1997)

Method blank: A blank prepared to represent the sample matrix, prepared and analyzed with a batch of samples. A method blank will contain all reagents used in the preparation of a sample, and the same preparation process is used for the method blank and samples. (Ecology, 2004; Kammin, 2010)

Method Detection Limit (MDL): This definition for detection was first formally advanced in 40CFR 136, October 26, 1984 edition. MDL is defined there as the minimum concentration of an analyte that, in a given matrix and with a specific method, has a 99% probability of being identified, and reported to be greater than zero. (Federal Register, October 26, 1984)

Percent Relative Standard Deviation (%RSD): A statistic used to evaluate precision in environmental analysis. It is determined in the following manner:

$$\%RSD = (100 * s)/x$$

where s is the sample standard deviation and x is the mean of results from more than two replicate samples (Kammin, 2010)

Parameter: A specified characteristic of a population or sample. Also, an analyte or grouping of analytes. Benzene and nitrate + nitrite are all "parameters." (Kammin, 2010; Ecology, 2004)

Population: The hypothetical set of all possible observations of the type being investigated. (Ecology, 2004)

Precision: The extent of random variability among replicate measurements of the same property; a data quality indicator. (USGS, 1998)

Quality Assurance (QA): A set of activities designed to establish and document the reliability and usability of measurement data. (Kammin, 2010)

Quality Assurance Project Plan (QAPP): A document that describes the objectives of a project, and the processes and activities necessary to develop data that will support those objectives. (Kammin, 2010; Ecology, 2004)

Quality Control (QC): The routine application of measurement and statistical procedures to assess the accuracy of measurement data. (Ecology, 2004)

Relative Percent Difference (RPD): RPD is commonly used to evaluate precision. The following formula is used:

[Abs(a-b)/((a + b)/2)] * 100

where "Abs()" is absolute value and a and b are results for the two replicate samples. RPD can be used only with 2 values. Percent Relative Standard Deviation is (%RSD) is used if there are results for more than 2 replicate samples (Ecology, 2004).

Replicate samples: Two or more samples taken from the environment at the same time and place, using the same protocols. Replicates are used to estimate the random variability of the material sampled. (USGS, 1998)

Representativeness: The degree to which a sample reflects the population from which it is taken; a data quality indicator. (USGS, 1998)

Sample (field): A portion of a population (environmental entity) that is measured and assumed to represent the entire population. (USGS, 1998)

Sample (statistical): A finite part or subset of a statistical population. (USEPA, 1997)

Sensitivity: In general, denotes the rate at which the analytical response (e.g., absorbance, volume, meter reading) varies with the concentration of the parameter being determined. In a specialized sense, it has the same meaning as the detection limit. (Ecology, 2004)

Spiked blank: A specified amount of reagent blank fortified with a known mass of the target analyte(s); usually used to assess the recovery efficiency of the method. (USEPA, 1997)

Spiked sample: A sample prepared by adding a known mass of target analyte(s) to a specified amount of matrix sample for which an independent estimate of target analyte(s) concentration is available. Spiked samples can be used to determine the effect of the matrix on a method's recovery efficiency. (USEPA, 1997)

Split Sample: The term split sample denotes when a discrete sample is further subdivided into portions, usually duplicates. (Kammin, 2010)

Standard Operating Procedure (SOP): A document which describes in detail a reproducible and repeatable organized activity. (Kammin, 2010)

Surrogate: For environmental chemistry, a surrogate is a substance with properties similar to those of the target analyte(s). Surrogates are unlikely to be native to environmental samples. They are added to environmental samples for quality control purposes, to track extraction

efficiency and/or measure analyte recovery. Deuterated organic compounds are examples of surrogates commonly used in organic compound analysis. (Kammin, 2010)

Systematic planning: A step-wise process which develops a clear description of the goals and objectives of a project, and produces decisions on the type, quantity, and quality of data that will be needed to meet those goals and objectives. The DQO process is a specialized type of systematic planning. (USEPA, 2006)

References for QA Glossary

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