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State of Washington

Quality Assurance Project Plan

Formaldehyde, Volatile Organic Compounds and Metals in Children's Products

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Publication Information

It is Washington State Department of Ecology policy to have an approved Quality Assurance Project Plan for all Agency-sponsored sampling events. 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 a report of the study to the Internet.

The plan for this study is available on the Department of Ecology's website at http://www.ecy.wa.gov/biblio/1207024.html.

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Quality Assurance Project Plan

Formaldehyde, Volatile Organic Compounds and Metals in Children's Products

April 2012

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HWTR-HQ: Hazardous Waste and Toxics Reduction Program
W2R: Waste 2 Resources Program

Table of Contents

List of Figures and Tables iii
Abstract iv
Background 1
Project Description 3
Sampling Process Design (Experimental Design) 4
    Product Selection 4
    Product Screening 5
    Target Chemicals 5
Organization and Schedule 6
Sample Collection and Preparation 7
Analytical Procedures 9
    Budget 11
Quality Objectives 11
    Measurement Quality Objectives 11
Quality Control Procedures 12
    Field 12
    Laboratory 12
Data Management Procedures 12
Audits 13
Report 13
Data Verification 13
Data Quality (Usability) Assessment 13
References 14
    Appendix A. Chemicals of High Concern to Children 17
    Appendix B. Glossary, Acronyms, and Abbreviations 18

List of Figures and Tables

Figures

Figure 1. Niton Portable XRF 9

Tables

Table 1: Volatile organic compounds reported by the Danish EPA 3
Table 2: State and Federal Criteria for Analytes of Interest 5
Table 3: Specific Volatile Organic Chemicals Included in the Study 6
Table 4: Organization of Project Staff and Responsibilities.....7
Table 5: Proposed Schedule for Completing Field and Laboratory Work and Reports 7
Table 6: Niton Portable XRF LOQs and Expected Range of Results 9
Table 7: Laboratory Methods and Reporting Limits 10
Table 8: Project Budget 11
Table 9: MQOs for Laboratory Analyses 11
Table 10: Quality Control Tests.....12

Abstract

The Washington State Department of Ecology's (Ecology) Hazardous Waste and Toxics Reduction (HWTR) and Waste 2 Resources (W2R) Programs are conducting a study to evaluate presence of formaldehyde, fifteen potential volatile organic compounds and nine hazardous metals in children's products. The study is being conducted to determine compliance with Washington's Children's Safe Product Act (CSPA) and to evaluate the level of formaldehyde, volatile organics and metals in children's products. It is being supported with funding from the Washington State Attorney General's Office.

Formaldehyde and potential volatile organics to be tested under this project include:

Compound	CAS Number
Formaldehyde	50-00-0
n-Butanol	71-36-3
Benzene	71-43-2
Vinyl chloride	75-01-4
Methylene chloride	75-09-2
Carbon disulfide	75-15-0
Methyl ethyl ketone	78-93-3
1,1,2,2-Tetrachloroethane	79-34-5
Hexachlorobutadiene	87-68-3
Ethylbenzene	100-41-4
Styrene	100-42-5
Acrylonitrile	107-21-1
Toluene	108-88-3
1,4-Dioxane	123-91-1
Tetrachloroethylene	127-18-4
Octamethylcyclotetrasiloxane	556-67-2

Metals in this study include:

Metals	
Antimony	Lead
Arsenic	Mercury
Cadmium	Molybdenum
Cobalt	Zinc
Copper	

It is Ecology policy to have an approved Quality Assurance Project Plan (QAPP) for all Agency-sponsored sampling events. The QAPP describes the objectives of the study and the procedures to be followed to achieve those objectives. After completion of the study, a report describing the study results will be posted to the Internet.

Background

Metals

Six metals (molybdenum, arsenic, cobalt, mercury, cadmium and antimony) were identified as chemicals of high concern to children (CHCCs) as defined by the CSPA. Appendix A contains a list of all CHCCs identified in the CSPA. Lead levels in children's products were restricted by the CSPA to 90 ppm; however, subsequent passage of the Consumer Product Safety Improvement Act (CPSIA) Federal legislation substantially pre-empted the state lead limits. (CPSC, 2008) There are some some products for which the state lead and cadmium levels might remain pertinent; therefore, lead is added to the list of metals of concern.

The metals identified as CHCCs have been found to cause cancer (antimony, arsenic, cadmium and copper) and developmental impacts (molybdenum, arsenic, cadmium, cobalt and mercury). (WDOH, 2010) In addition, they have been found in or likely to be found in children's products, which was required before they could be identified as CHCCs.

Two additional metals (copper and zinc) are also being analyzed in children's products. Copper and zinc have been identified as potentially having a major impact upon the Puget Sound (Ecology, 2011). Concerns have been raised about these metals in products as a potential source to the Puget Sound. Copper and zinc are toxic to aquatic species and particularly the development of fish. As indicated in a report from the US Fish and Wildlife Services:

> *Mixtures of zinc and copper are generally acknowledged to be more-than-additive in toxicity to a wide variety of aquatic organisms…'*

The aquatic organisms impacted by zinc and copper include oysters and both marine and freshwater fish among others. (Eisler, 1993)

Formaldehyde

Formaldehyde is used in the manufacture of plastics, particularly amino and phenolic resins like phenol-formaldehyde and urea formaldehyde foam. Phenol-formaldehyde resins are used as adhesives for binding wood products (particle board, fiber board, and plywood), molding compounds (in electrical, automotive, and kitchen parts), phenolic foam insulation, foundry mold binders, decorative and industrial laminates, and binders for insulating materials. Urea-formaldehyde resins are primarily used in foam insulation. (HSDB, 2012)

Formaldehyde is present in the environment as a result of natural processes and from man-made sources. The major source of atmospheric formaldehyde is the photochemical oxidation and incomplete combustion of hydrocarbons (i.e. methane or other gases, wood, coal, oil, tobacco and gasoline). Formaldehyde is mainly used as an intermediate in the chemical industry for the production of resins for the wood, paper and textile processing industries (approx. 40% urea-formaldehyde resins, 10% phenol-formaldehyde resins, 10% polyacetal resins and 5% melamin-formaldehyde resins). (OECD, 2002)

Formaldehyde has been identified as a CHCC in Ecology's rule to implement the CSPA. Formaldehyde is a skin, eye and respirtaory tract irritant and sensitizer. (WDOH, 2010a)

Formaldehyde is classsified as a carcinogen by a number of authoritative sources. Inhalation of formaldehyde is associated with cancer in the respiratory tract in humans and laboratory animals. Oral exposures in animals are also carcinogenic. (WDOH, 2010a)

Volatile Organic Compounds

Fifteen volatile organic compounds are also identified as CHCCs in Ecology's rule to implement the CSPA. These fifteen chemicals were selected for analysis as they are all potential analytes under EPA SW-846 Method 8260B Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS). (EPA, 1996) Although the 15 chemicals are unlikely to be found in all media, it may prove possible to analyze several compounds simultaneously using Method 8260B.

The fifteen volatile organic compounds have a wide range of uses. Two (vinyl chloride and styrene) are monomers used in the production of plastics. The primary plastic produced from vinyl chloride is polyvinyl chloride or PVC. PVC is used in a wide range of consumer products including as a substitute for rubber, in thin pliable sheeting, as a finish for textiles, in non-flammable upholstery, raincoats, tubing, belting, gaskets, shoe soles, piping, pipe fitting and conduits, flooring, windows, siding and other rid structures, swimming pool liners, household products, consumer goods, wire and cable coating, packaging, automobile tops and floor mats and as a popular resin in construction and building industries. (HSDB, 2012)

Styrene is used in numerous plastics both alone (polystyrene including high impact polystyrene or HIPS) and in blends such as acrylonitrile-butadiene-styrene (ABS), styrene-acrylonitrile (SAN), methyl methacrylate-butadiene-styrene (MBS) and others. Plastics made with styrene are used in a wide range of products including packaging, furniture, electrical equipment, industrial moldings, thermal insulation, automobile parts, ventilation pipes, air conditionsing, hobby equipment, tires, radiators, hoses, belts and seals, wire insulation, paper coatings, carpet backings, adhesives, building products, household consumer goods, putty and casting resins.

Uses of the remaining compounds are as extensive and as varied. For the purposes of this QAPP, the individual uses of each compound will not be discussed in more detail. However, the process used to identify chemicals as CHCCs required evidence of carcinogenicity, reproductive toxicicity or endocrine disruption and evidence of a potential for exposure including use in children's products. Table 1 identifies product testing results by the Danish Environmental Protection Agency and other data sources in which the individual chemicals were found in children's products. (Ecology, 2009)

Table 1: Volatile organic compounds reported by the Danish Environmental Protection Agency and other sources where chemicals are found in children's products

Compound	Use
Formaldehyde	Tents and Tunnels (DEPA-46), Baby products (DEPA-90), Hobby products for children (DEPA-93)
n-Butanol	Tents and Tunnels (DEPA-46), Wooden toys (DEPA-60), Slimy toys (DEPA-67), Perfume in toys (DEPA-68)
Benzene	Perfume in toys (DEPA-68), Balloons (DEPA-89)
Vinyl chloride	Children's toys (EU Risk Assessment)
Methylene chloride	Slimy toys (DEPA-67)
Carbon disulfide	Balloons (DEPA-89), Teats and soothers (NL-2002)
Methyl ethyl ketone	Tents and Tunnels (DEPA-46), Slimy toys (DEPA-67), Perfume in toys (DEPA-68)
1,1,2,2-Tetrachloroethane	Baby products (DEPA-90)
Hexachlorobutadiene	Electronics and electrical products (DEPA-32)
Ethylbenzene	Tents and Tunnels (DEPA-46), Slimy toys (DEPA-67), Perfume in toys (DEPA-68), Hobby products for children (DEPA-93)
Styrene	Tents and Tunnels (DEPA-46), Slimy toys (DEPA-67), Perfume in toys (DEPA-68), Baby products (DEPA-90), Plastic toys (NL-2005a)
Acrylonitrile	Children's toys (EU Risk Assessment)
Toluene	Tents and Tunnels (DEPA-46), Wooden toys (DEPA-60), Slimy toys (DEPA-67), Perfume in toys (DEPA-68), School bags and school items (DEPA-84)
1,4-Dioxane	Cosmetics/toiletries (EU Risk Assessment)
Tetrachloroethylene	Tents and Tunnels (DEPA-46)
Octamethylcyclotetrasiloxane	Perfume in toys (DEPA-68), Cosmetics for children (DEPA-88)

All fifteen volatile organic compounds (CAS numbers for these compounds can be found in Table 3) have been identified as being carcinogenic (benzene, vinyl chloride, methylene chloride, 1,1,2,2-tetrachloroethane, hexachlorobutadiene, ethylbenzene, styrene, acrylonitrile, 1,4-dioxane, tetrachloroethylene) or having negative impacts on reproductivity (n-butanol, methylene chloride, carbon disulfide, methyl ethyl ketone, hexachlorobutadiene), mutagenicity/genotoxicity (vinyl chloride, hexachlorobutadiene), neurotoxicity (carbon disulfide, toluene), developmental toxicity (benzene, carbon disulfide, methyl ethyl ketone, hexachlorobutadiene, ethylbenzene, styrene, toluene), endocrine disruptor (octamethylcyclotetrasiloxane) or other systemic impacts (1,1,2,2-tetrachloroethane, styrene, 1,4-dioxane, hexachlorobutadiene). (WDOH, 2010b-p)

Project Description

Ecology's HWTR and W2R Programs will conduct a study to measure formaldehyde, fifteen volatile organics (see Table 3 for a list of chemicals involved) and nine metals (antimony, arsenic, cadmium, cobalt, lead, molybdenum, zinc, copper and mercury) in children's products. The objective of the study is to: determine compliance with the state's CSPA limits for lead and cadmium; determine compliance

with CSPA reporting requirements and to assess the levels of metals and volatile organic compounds in children's products.

Children's products will be purchased and screened for metals with a portable XRF analyzer during the spring and autumn of 2012. Those samples found to contain sufficient metals of interest using the XRF will be sent to Manchester Environmental Laboratory for confirmational analysis. An XRF cannot be used to screen for formaldehyde and volatile organics. Information from a number of sources will be searched to identify potential products containing these compounds. Samples containing volatile organic compounds will be sent to a contract laboratory for analysis.

Sampling Process Design (Experimental Design)

Approximately 200 children's products will be gathered for testing during the two sampling events. For metals, emphasis will be placed upon products intended for children. Liquid products (such as personal care products) and products made of plastics will be selected for volatile organic compounds analysis as they are more likely to contain these compounds and be reported to Ecology during the sampling period.

All product samples will be screened with a portable XRF for the metals of concern to determine if confirmational metals analysis is necessary using EPA approved laboratory methodologies. It is anticipated from the two sampling events that approximately 75 product samples will be forwarded for metals analysis; ten samples will be submitted for formaldehyde analysis; and approximately 5 samples will be submitted for volatile organic analysis. As an XRF cannot detect volatile organic compounds, information on the label, the type of plastic used and other potential sources of information will be used to determine whether a product sample is likely to contain any volatile organics of interest.

Items will be sent to the laboratory if they violate screening criteria (outlined below) during the XRF analysis or are selected for low level analysis. Laboratory analysis will be completed by inductively coupled plasma mass spectroscopy (ICP-MS) (metals), cold vapor atomic absorption (CVAA) (mercury), high performance liquid chromatography (HPLC) (formaldehyde) and gas chromatography-mass spectroscopy (GC/MS) (volatile organic compounds). Alternative methods for formaldehyde are possible and use of other methods will be reviewed and approved by the Project Manager. If alternative methods are identified that provide improved results, Ecology will use the information to update its product testing guidance PQLs.

Product Selection

Screening during the first sampling event will focus on Tier 1 products that are most likely to be mouthed or used by children under three and products identified by other groups as containing one of the chemicals of concern. Under the CSPA Reporting Rule tiered approach, Tier 1 products are those intended to be put into a child's mouth, applied to their skin, or any mouthable product for a child less than 3. Tier 1 products must be reported first. Tiers 2 – 4 include products intended for prolonged direct skin contact, short-duration direct skin contact, and no intended skin contact, respectively. Product analysis will be primarily restricted to Tier 1 products for the samples collected in the spring unless sufficient samples cannot be obtained. Tier 2 products will be given priority for the samples collected in the autumn. Products in other Tiers will then be considered for analysis.

For example, Tier 1 products like lip gloss and other cosmetic and personal care products that, when applied, are likely to be applied to the skin or ingested will be a higher priority than other children's products. Products that are intended to be mouthed by children under 3, such as baby pacifiers, teething rings, and feeding products will also be given priority over other types of children's products.

Product Screening

Products will be screened using a portable XRF analyzer following the XRF manufacturer's recommendations and adaptations of 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*. While ASTM method F 2617-08 is not intended for samples with surface coatings or non-polymeric materials, all samples will be screened following adaptations of the method for qualitative information.

Target Chemicals

Target chemicals proposed for testing along with state and federal criteria are shown in Table 2 and the list of specific organic compounds included in this study is found in Table 3.

Table 2: State and Federal Criteria for Analytes of Interest

Analytes	**Action levels (ppm)**	
	State[=]	**Federal**
VOCs	5.0	Various
Antimony	1.0	60[^]
Arsenic	1.0	25[^]
Cadmium	1.0	75[^]
Cobalt	1.0	-
Copper	-	
Lead	-	90[+]
Mercury	0.5	60[^]
Molybdenum	1.0	-
Zinc	-	

[=] State Limit: Draft practical quantitation limits as defined in the CSPA Rule Reporting Guidance, available at: http://www.ecy.wa.gov/programs/swfa/cspa/pdf/cspaguide_pql.pdf, accessed 1/3/2012.
[^] Federal Limit: ASTM F963-11, Standard Consumer Safety Specification for Toy Safety.
[+] Federal Limit: 16 C. F. R. 1303 restrictions in surface coatings of consumer goods and children's products. Non-soluble portions are limited to 100 ppm in August 2011.

Table 3: Specific Volatile Organic Chemicals Included in the Study

Compound	CAS Number
Formaldehyde	50-00-0
n-Butanol	71-36-3
Benzene	71-43-2
Vinyl chloride	75-01-4
Methylene chloride	75-09-2
Carbon disulfide	75-15-0
Methyl ethyl ketone	78-93-3
1,1,2,2-Tetrachloroethane	79-34-5
Hexachlorobutadiene	87-68-3
Ethylbenzene	100-41-4
Styrene	100-42-5
Acrylonitrile	107-21-1
Toluene	108-88-3
1,4-Dioxane	123-91-1
Tetrachloroethylene	127-18-4
Octamethylcyclotetrasiloxane	556-67-2

For screening purposes, products containing half or more of the state action levels in Table 2 will be forwarded to the laboratory for validation (to the limits of the laboratory budget). It should be noted, criteria under ASTM F963-11 and 16 C.F.R. § 1303 are designed for soluble portions of surface coatings. XRF screening, however, provides results for total metals. In the instance of more detectable levels of metal than the budget will allow, those product samples with the highest concentrations will be sent to the laboratory for additional analysis.

All 9 metals will be analyzed in each sample and forwarded to the laboratory if screening levels for a single metal are violated. In addition to products that exceed the screening levels, multiple samples containing low levels will be forwarded to the laboratory for analysis.

As with metals, samples containing the highest levels of volatile organics determined from available information such as labels, product databases and other readily-available information will be sent to the laboratory for analysis. The exact number of samples will depend upon the availability of applicable products and budgetary constraints.

Organization and Schedule

Table 4 lists the individuals involved in the project and Table 4 contains a schedule.

Table 4: Organization of Project Staff and Responsibilities

Staff	Title	Responsibilities
Joshua Grice, W2R (360) 407-6786	Client	Clarifies scopes of the project. Provides internal review of the QAPP and approves the final QAPP.
John Williams, W2R (360) 407-6940	Client	Clarifies scopes of the project. Provides internal review of the QAPP and approves the final QAPP.
Alex Stone HWTR-HQ Program (360) 407-6758	Project Manager	Writes QAPP, oversees field sampling and transportation of samples to laboratory. Conducts QA review of data, analyzes and interprets data. Writes draft report and final report.
Ken Zarker, HWTR-HQ (360) 407-6698	Manager for Project Manager	Reviews project scope and budget, tracks progress, reviews draft QAPP and approves the final QAPP.
Samuel Iwenofu HWTR-SWRO (360) 407-6964	HWTR QA Officer	Reviews draft QAPP and approves final QAPP.
Carol Kraege, W2R (360) 407-6906	Client	Reviews project scope and budget, tracks progress, reviews the draft QAPP and approves final QAPP and expenditure of funds for implementation of the QAPP.

HWTR-HQ: Hazardous Waste and Toxics Reduction Program-Headquarters.
HWTR-SWRO: Hazardous Waste and Toxics Reduction Program-Southwest Regional Office
QAPP: Quality Assurance Project Plan.
W2R: Waste 2 Resources.

Table 5: Proposed Schedule for Completing Field and Laboratory Work and Reports

Field and laboratory work	Due date	Lead staff
Field work completed	April 2012	Alex Stone
Laboratory analyses completed	December 2012	
Final report		
Author lead / Support staff	Alex Stone	
Schedule		
Draft due to supervisor	November 2012	
Draft due to client/peer reviewer	December 2012	
Final (all reviews done)	February 2013	
Final report due on web	April 2013	

Sample Collection and Preparation

Products will be obtained in person or through internet retailers by HWTR or W2R staff. In addition, products reserved from other Ecology sampling events will be evaluated to determine if they meet the requirements of this QAPP.

Upon collection, products will be removed from their original packaging using pre-cleaned stainless steel implements. Products will be separated into to three fractions. Fraction 1 will consist of the product packaging that will be retained for possible analysis under a separate QAPP. Fraction 2 will comprise the product contents. Fraction 3 will consist of the container used to hold the product ingredients, if appropriate. If necessary, Fractions 2 and 3 may be further broken down into individual components as defined in CSPA rule reporting guidance documents. For example, lipstick might be considered for purchase and testing. Typically lipstick comes packaged in a combination of clear plastic and paper. The lipstick itself is inside a plastic applicator. For the pursposes of this study, the packaging would be the external plastic and paper (fraction 1), the container would be the applicator holding the lipstick (fraction 3), and the product would be the lipstick itself (fraction 2). Similar decisions may be necessary on a case-by-case basis depending upon the product and how it is packaged and presented.

Products in Fraction 1 will be retained for possible analysis during other sampling events. Individual components of the product (Fraction 2) will be screened separately. Items with different colors or base materials will be treated as components. Additionally, individual pieces of products intended to be disassembled will be treated as components.

Components targeted for testing will be removed with stainless steel tools (scissors, pliers, saws, etc.) for further testing. All tools will be cleaned following the sequence identified above. Those samples to be sent for both metals and volatile organic compounds analysis will be divided in half for possible shipment to different laboratories.

Some samples such as those consisting of hard plastic or other unique construction may be sent out for cryomilling to facilitate release of the chemicals of interest from the plastic matrix during extraction and sample preparation. Cryomilling refers to the process of reducing a sample to very small particle sizes by employing cryogenic temperatures and a mechanical mill. Milled samples will be screened by XRF in the stand. Cryomilling decisions will be make on a case-by-case basis. Non-plastic items such as foams, textiles and metals will be reduced in size using a file, drill, dremel tool or scissors. Scrapings will be further ground (if the material allows) by mortar and pestle. Sub-sampled materials (ground, cut or scraped) will be reanalyzed prior to laboratory testing. Ecology will identify a company who can cryomill these samples.

The samples will be screened for metals using the XRF. Samples that contain appreciable levels of metals will be sent to Manchester Laboratory for analysis, where possible. If Manchester is unable to meet the QAPP requirements, the same procedure used for volatile organic chemical analysis will be used to obtain a contract laboratory to conduct the sample analysis.

Product samples will be sent to a contract laboratory for organic analysis. Manchester will be approached first to run the samples. If Manchester declines, laboratories under contract to the state to provide analytical data (State Contract 1807) will be approached for analytical support. If no contract laboratory can conduct the analyses, the Project Manager will solicit qualified laboratories to provide analytical services. The Project Manager will be responsible for the review and evaluation of all laboratory analyses.

Photos and descriptive notes on each product screened such as approximate thickness, surface roughness, material makeup, etc. will be recorded. Other information such as the type of advertisement used to sell the product, where in the store the product was located, etc. may be necessary to prove the product was intended for children that fall within a given age group.

All field and laboratory staff handling the items will wear powder free nitrile gloves. Stainless steel tools used to deconstruct the product or remove it from its products along with the mortar and pestle will be cleaned by the following sequence: hot water scrub with liquinox soap, 10% nitric acid rinse, deionized water rinse, acetone rinse, and hexane rinse.

Analytical Procedures

XRF Analysis

Individual product components will be screened using a Niton XL3t portable XRF analyzer (Figure 1) following the manufacturers recommendations and adaptations of 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*.

Figure 1. Niton Portable XRF

For the initial screening, a reading will be taken for at least 30 seconds on a smooth (or near smooth) area of the packaging large enough to cover the spectrometer's window and at least 2 mm thick. If the item is less than 2 mm thick, it may be folded on to itself until 2 mm depth has been reached (care will be taken to trap minimal air in between folds).

If the screening measurement violates screening criteria, a second longer measurement will be taken (up to 180 seconds). Both measurements will be taken using the appropriate XRF software package (based on sample material). Detection limits are shown in Table 5. After XRF analyses are completed, samples will be placed in pre-cleaned I-Chem jars and forwarded to the appropriate laboratory for testing.

Table 6: Niton Portable XRF LOQs and Expected Range of Results

Element	Expected Range of Results (ppm)	LOQ (ppm)+
Antimony	<LOQ - 300	25
Arsenic	<LOQ - 300	3
Cadmium	<LOQ - 300	15
Cobalt	<LOQ - 300	15
Copper	<LOQ - 300	15

Lead	<LOQ - 300	4
Mercury	<LOQ - 10	6
Molybdenum	<LOQ - 300	*
Zinc	<LOQ - 300	15

ppm = parts per million
LOQ = Limit of Quantitation
[+] Polyethylene blank, 8 mm aperture, 180 second total analysis time
[*] Detection limits are not specified by the manufacturer for these elements

All samples screened will be assigned a unique identifier and results from the XRF will be transferred to Microsoft Excel spreadsheets.

Laboratory

Table 7 describes digestion and analysis methods along with estimated LOQ's. Metals samples will be prepared following EPA 3052 (microwave complete digestion) and measured using ICP-MS or CVAA (mercury).

Volatile organic compounds will be measured by a contract laboratory using GS-MS. Sample extraction and analysis methods used by the contract laboratory will be approved by the Project Manager. All sample extraction methods, however, must effect complete digestion of the sample and minimize potential loss of volatile organic compounds during analysis.

Table 7: Laboratory Methods and Reporting Limits

Analyte	Digestion Method	Instrumentation	Method	RL (ppm)
Antimony	EPA 3052	ICP-MS	EPA 6020	1.0
Arsenic	EPA 3052	ICP-MS	EPA 6020	1.0
Cadmium	EPA 3052	ICP-MS	EPA 6020	1.0
Chromium	EPA 3052	ICP-MS	EPA 6020	1.0
Cobalt	EPA 3052	ICP-MS	EPA 6020	1.0
Copper	EPA 3052	ICP-MS	EPA 6020	1.0
Lead	EPA 3052	ICP-MS	EPA 6020	1.0
Molybdenum	EPA 3052	ICP-MS	EPA 6020	1.0
Mercury	EPA 3052	ICP-MS	EPA 6020	0.1
Zinc	EPA 3052	ICP-MS	EPA 6020	1.0
Formaldehyde	*	HPLC	EPA 8315	5.0
VOCs**	*	GC-MS	EPA 8260	1.0
n-Butanol	*	GC-MS	EPA 8260	5.0
Carbon disulfide	*	GC-MS	EPA 8260	10.0
Hexachlorobutadiene	*	GC-MS	EPA 8260	30.0
Tetrachloroethylene	*	GC-MS	EPA 8260	0.5
Octamethylcyclotetrasiloxane	*	GC-MS	EPA 8260	10.0

ICP-MS = Inductively-coupled plasma/mass spectrometry
CV AA = Cold vapor atomic absorption

GC-MS = Gas chromatography/mass spectroscopy
RL = Reporting Limit
* Method will be approved by Project Manager but will be inline with CSPA PQL guidance.
** PQL for all VOCs not specifically called out will be 1 ppm

Budget

The project budget is included in Table 8.

Table 8: Project Budget

	# of Samples	Cost per sample	Total
New Samples	100	$5.00	$500.00
Metals	38	$200.00	$7,6000.00
Formaldehyde	10	$350.00	$3,500.00
VOCs	75	$350.00	$26,500.00
Total			**$38,100.00**

Quality Objectives

Quality objectives for this project are to obtain data of sufficient quality so that the amount of metals and volatile organic compounds in children's products can be determined. These objectives will be achieved through careful attention to the sampling, sample processing, measurement, and quality control (QC) procedures described in this plan.

Measurement Quality Objectives

An XRF reading will be taken every 25 samples on standards provided by the manufacturer. Since the XRF analysis is being used as a screening tool only, no measurement quality objectives (MQOs) are outlined. Performance of the portable XRF has been determined in a previous EAP report (Publication No. 12-03-009), which proves the efficacy of using XRF as a screening tool, particularly for metals. The conclusions from the report will be implemented in this work where possible and all screening will be done using a stand to minimize error.

MQOs for laboratory analysis of metals and volatile organic compounds are shown in Table 9. It is expected that MEL and contract laboratories will meet these criteria. MQOs falling outside of the acceptance limits will be reviewed by the Project Manager for their usability.

Table 9: MQOs for Laboratory Analyses

	Laboratory Control Samples	Matrix Spikes	Duplicates[+]	Method Blanks*
	(recovery)	(recovery)	(RPD)	(ppm)
Antimony	85- 115%	75-125%	±20%	1.0

Arsenic	85- 115%	75-125%	±20%	1.0
Cadmium	85- 115%	75-125%	±20%	1.0
Cobalt	85- 115%	75-125%	±20%	1.0
Lead	85- 115%	75-125%	±20%	1.0
Mercury	85- 115%	75-125%	±20%	0.1
Molybdenum	85- 115%	75-125%	±20%	1.0
VOCs**	70- 130%	70-130%	±20%	30.0

* Metals reporting limits were established by raising soil limits by a factor of 10
** Special consideration may be necessary for methylene chloride which is often used to clear glassware in analytical laboratories; however, as the detection lmit is high, the amount of remaining contamination is unlikely to have a major impact upon analytical results.
+ Matrix spike duplicates and split duplicates
RPD – Relative Percent Difference
ppm = parts per million

Quality Control Procedures

Field

No field quality control procedures are anticipated for this project.

Laboratory

Table 10 shows laboratory QC samples planned for the project. Split duplicate samples will be used to assess variability in the data due to sample preparation and laboratory procedures.

Table 10: Quality Control Tests

	Laboratory Control Samples	Matrix Spikes	Matrix Spike Duplicates	Laboratory Duplicates	Split Duplicates†	Method Blanks	Surrogate Recovery*
Elements	1/batch	1/batch	1/batch	1/batch	1/batch	1/batch	every sample

† Dependent on amount of sample available

* PBDEs only

Data Management Procedures

XRF data from the screening portion of the project will be transferred to Microsoft Excel spreadsheets and managed by the Project Manager.

Data packages from MEL and any lab contracted selected for sample analysis will include case narratives discussing any problems encountered with the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. The narrative should address condition of the samples on receipt, sample preparation, methods of analysis, instrument calibration, recovery data,

and results on QC samples. This information is needed to evaluate the accuracy of the data and to determine whether the MQOs were met.

Audits

MEL and any contracted laboratory must participate in performance and system audits of their routine procedures. Results of these audits must be made available on request.

Report

A final report detailing the findings of the study will be completed. The final report will include:

- Categorical descriptions of the products screened with the XRF (some information such as brands, product names, etc. will not be included).
- Comparison of laboratory results with XRF screenings, where applicable.
- Assessment of products test results from children's products for metals and volatile organic compounds.
- Determination of whether measurable levels of volatile organic compounds are found in children's products.
- Data on specific children's products and product components and whether the levels of metals found would violate standards in the CSPA legislation.

Data Verification

The Project Manager will conduct a review of all laboratory data generated by MEL and contract laboratories. The Project Manager will verify that methods and protocols specified in this QAPP were followed, that all calibrations, checks on quality control, and intermediate calculations were performed for all samples, and that the data are consistent, correct, and complete, with no errors or omissions. Evaluation criteria will include the acceptability of procedural blanks, calibration, matrix spike recoveries, labeled compound and internal standard recoveries, ion abundance ratios, duplicates, laboratory control samples, and appropriateness of data qualifiers assigned.

A case narrative will meet the requirements for a data verification report for MEL's chemical data.

Data Quality (Usability) Assessment

The Project Manager will examine the data reviews, case narratives, and data packages to assess the usability of the data. To determine if project MQOs have been met, results for laboratory control samples, sample duplicates, matrix spikes, and labeled compound recoveries will be compared to QC limits. The method blank results will be examined to verify there was no significant contamination of the samples. To evaluate whether the targets for reporting limits have been met, the results will be examined for "non-detects" and to determine if any values exceed the lowest concentration of interest. Based on these assessments, the data will be either accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

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Appendices

Appendix A. Chemicals of High Concern to Children

CAS	Chemical
50-00-0	Formaldehyde
62-53-3	Aniline
62-75-9	N-Nitrosodimethylamine
71-36-3	n-Butanol
71-43-2	Benzene
75-01-4	Vinyl chloride
75-07-0	Acetaldehyde
75-09-2	Methylene chloride
75-15-0	Carbon disulfide
78-93-3	Methyl ethyl ketone
79-34-5	1,1,2,2-Tetrachloroethane
79-94-7	Tetrabromobisphenol A
80-05-7	Bisphenol A
84-66-2	Diethyl phthalate
84-74-2	Dibutyl phthalate (DBP)
84-75-3	Di-n-Hexyl Phthalate
85-44-9	Phthalic Anhydride
85-68-7	Butyl Benzyl phthalate (BBP)
86-30-6	N-Nitrosodiphenylamine
87-68-3	Hexachlorobutadiene
94-13-3	Propyl phthalate
94-26-8	Butyl phthalate
95-53-4	2-Aminotoluene
95-80-7	2,4-Diaminotoluene
99-76-3	Methyl phthalate
99-96-7	p-Hydroxybenzoic acid
100-41-4	Ethylbenzene
100-42-5	Styrene
104-40-5	4-Nonylphenol; 4-NP and its isomer mixtures including CAS 84852-15-3 and CAS 25154-52-3
106-47-8	para-Chloroaniline
107-13-1	Acrylonitrile
107-21-1	Ethylene glycol
108-88-3	Toluene
108-95-2	Phenol
109-86-4	2-Methoxyethanol
110-80-5	Ethylene glycol monoethyl ester

CAS	Chemical
115-96-8	Tris(2-chloroethyl) phosphate
117-81-7	Di-2-ethylhexyl phthalate (DEHP)
117-84-0	di-n-octyl phthalate (DnOP)
118-74-1	Hexachlorobenzene
119-93-7	3,3'-Dimethylbenzidine and Dyes Metabolized to 3,3'-Dimethylbenzidine
120-47-8	Ethyl phthalate
123-91-1	1,4-Dioxane
127-18-4	Perchloroethylene
131-55-5	Benzophenone-2 (Bp-2); 2,2',4,4'-Tetrahydroxybenzophenone
140-66-9	4-tert-Octylphenol; 1,1,3,3-Tetramethyl-4-butylphenol
140-67-0	Estragole
149-57-5	2-Ethylhexanoic Acid
556-67-2	Octamethylcyclotetrasiloxane
608-93-5	Benzene, pentachloro
842-07-9	C.I. Solvent Yellow 14
872-50-4	N-Methylpyrrolidone
1163-19-5	2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether; BDE-209
1763-23-1	Perfluorooctanyl sulphonic acid and its salts; PFOS
1806-26-4	Phenol, 4-octyl-
5466-77-3	2-Ethyl-hexyl-4-methoxycinnamate
7439-97-6	Mercury & mercury compounds including methyl mercury (22967-92-6)
7439-98-7	Molybdenum & molybdenum compounds
7440-36-0	Antimony & Antimony compounds
7440-38-2	Arsenic & Arsenic compounds including arsenic trioxide (1327-53-3) & dimethyl arsenic (75-60-5)
7440-43-9	Cadmium & cadmium compounds
7440-48-4	Cobalt & cobalt compounds
25013-16-5	Butylated hydroxyanisole; BHA
25154-52-3	Nonylphenol
25637-99-4	Hexabromocyclododecane
26761-40-0	Diisodecyl phthalate (DIDP)
28553-12-0	Diisononyl phthalate (DINP)

Appendix B. Glossary, Acronyms, and Abbreviations

Acronyms and Abbreviations

Following are acronyms and abbreviations used frequently in this report.

CDC	Center for Disease Control and Prevention
CHCC	Chemicals of High Concern to Children
e. g.	For example
Ecology	Washington State Department of Ecology
et al.	And others
HQ	Headquarters
HWTR	Hazardous Waste and Toxics Reduction Program
i. e.	In other words
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
PBT	persistent, bioaccumulative, and toxic substance
QA	Quality assurance
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedures
SRM	Standard reference materials
SWRO	Southwest Regional Office
W2R	Waste 2 Resources Program

Units of Measurement

ng	nanogram, a unit of mass equal to one millionth of a gram
mg	milligram, one thousandth of a gram
g	gram, a unit of mass
kg	kilograms, a unit of mass equal to 1,000 grams.
meter	meter, a unit of distance
mm	millimeter, a unit of distance equal to one thousandth of a meter
Liter	liter, a unit of volume
mL	milliliter, equal to one thousandth of a liter
ppm	parts per million
mg/kg	milligrams per kilogram (parts per million)
ng/g	nanograms per gram (parts per billion)
ng/kg	nanograms per kilogram (parts per trillion)
mg/L	milligrams per Liter (parts per million)
ng/L	nanograms per Liter (parts per trillion)
s.u.	standard units