DEPARTMENT OF
ECOLOGY
State of Washington

Quality Assurance Project Plan

Phthalates and Metals in Tier 3 Children's Products

April 2013

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Publication Information

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/1303108.html

Data for this project will be available upon request, provided it is not enforcement sensitive.

Ecology's Activity Tracker Code for this study is 14-002.

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Signatures are not available on the Internet version.
EAP: Environmental Assessment Program
W2R: Waste 2 Resources

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Abstract

The Washington State Department of Ecology (Ecology) is conducting a study to measure phthalates and metals in children's products purchased from Washington retailers to determine compliance with the state's Children's Safe Products Act (CSPA) legislation. The CSPA legislation limits the amount of phthalates, lead, and cadmium allowed in children's products sold in Washington and also requires manufacturers to report to Ecology if their products contain certain chemicals. Ecology will test children's products for a subset of these chemicals – eight phthalates and seven metals – in 2013.

Ecology will collect approximately 200 children's products in the Tier 3 category of the CSPA Reporting Rule, with a focus on toys intended for children ages 3 to 12 years old. Products will be pre-screened for metals with an X-ray fluorescence (XRF) analyzer. Up to 35 product samples will be sent to a laboratory for metals analysis based on XRF measurements, and 40 samples will be forwarded to a laboratory for phthalates analysis.

A final report summarizing findings is anticipated to be published in December 2013.

Background

Washington State passed the Children's Safe Products Act (CSPA) in 2008[1]. Part of this law prohibited the sale of a children's product, or product component, containing phthalates (greater than 1,000 ppm, individually or in combination), lead (greater than 90 ppm), or cadmium (greater than 40 ppm). Another part of this law required the Departments of Ecology (Ecology) and Health (DOH) to develop a list of chemicals of high concern for children (CHCC). Beginning August 2012, manufacturers must report to Ecology if a product contains a chemical from this list. For more information on the CSPA legislation, visit http://www.ecy.wa.gov/programs/swfa/cspa/.

The CSPA Reporting Rule requires manufacturers to report on CHCCs in products on a phased-in schedule according to the type of product and size of manufacturer[2]. Manufacturers are separated into size categories by gross annual sales of children's products. The largest manufacturers started reporting in August 2012 on Tier 1 products. Reporting for Tier 2 products began in February 2013. Tier 3 products are next in line to be reported (August 2013) by the largest manufacturers. Tier 4 products will not be reported on, except by amendment of the reporting rule based on a case-by-case evaluation. See Table 1 for product types included in the Tier system.

Table 1. Product Type by Tier as Defined in WAC 173-334.

Tier	Children's Product Type	Example
1	Products intended to be put into a child's mouth or applied to the child's body, or any mouthable product intended for children who are age 3 or under.	Teethers, pacifiers, lotions, shampoos, creams, toys for ages 3 and under
2	Products intended to be in prolonged (>1 hr) direct contact with a child's skin.	Clothes, jewelry, bedding
3	Products intended for short (<1 hr) periods of direct contact with child's skin.	Most toys for children ages 3 to 12 years
4	Product components that during reasonable and foreseeable use and abuse of the product would not come into direct contact with the child's skin or mouth.	Inaccessible, internal components for all children's products

[1] Chapter 70.240 of the Revised Code of Washington (RCW)
[2] Washington Administration Code (WAC) 173-334

Ecology began independent testing of CHCCs in Tier 1 and Tier 2 products in 2012 to assess compliance with the CSPA Reporting Rule (Stone, 2012a). Analytes included the six metals on the CHCC list (antimony, arsenic, cadmium, cobalt, mercury, and molybdenum) copper, lead, zinc, and eight phthalates (DEP, DBP, DHP, BBP, DEHP, DnOP, DIDP, and DINP[3]). Several other Ecology studies were initiated in 2012 to test consumer products for various contaminants (Stone, 2012b, Stone, 2012c, Stone, 2012d).

Project Description

Ecology's Environmental Assessment Program will conduct a study in 2013 to measure phthalates and metals in children's products that are subject to Tier 3 reporting as part of the CSPA Reporting Rule. The goals of the study will be to determine compliance with the state's CSPA legislation by assessing levels of phthalates and metals in children's products.

In spring 2013, Ecology will purchase children's products from major retailers in the Puget Sound area and through internet retailers. Products collected from the Puget Sound area represent products available statewide. All products will be pre-screened using an X-ray fluorescence (XRF) analyzer for the metals included in this study. Based on XRF results, samples containing metals concentrations at or above predetermined selection criteria (Table 4) will be forwarded to Manchester Environmental Laboratory (MEL) for analysis. Products, or product components, that appear to have the potential to contain phthalates (e.g., items with soft plastic) will also be sent to the laboratory for analysis.

[3] DEP = Diethyl phthalate; DBP = Dibutyl phthalate; DHP = Di-n-hexyl phthalate; BBP = Butyl benzyl phthalate; DEHP = Di-2-ethylhexyl phthalate; DnOP = Di-n-octyl phthalate; DIDP = Diisodecyl phthalate; DINP = Diisononyl phthalate.

Organization and Schedule

Table 2 lists the people involved in this project. All are employees of the Washington State Department of Ecology. Table 3 presents the proposed schedule for this project.

Table 2. Organization of Project Staff and Responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Josh Grice W2R Program Phone: 360-407-6786	EAP Client	Clarifies scopes of the project. Provides internal review of the QAPP and approves the final QAPP.
Callie Mathieu Toxics Studies Unit SCS, EAP Phone: 360-407-6965	Project Manager	Writes the QAPP. Oversees project timeline. Conducts QA review of data, analyzes and interprets data. Writes the draft report and final report.
Andy Bookter Toxics Studies Unit SCS, EAP Phone: 360-407-6060	Field Lead	Leads sample collection, processing, and shipment to laboratory. Conducts XRF analysis. Assist with QAPP, data analysis, result interpretation, and report writing.
Dale Norton Toxics 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	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.

EAP: Environmental Assessment Program
QAPP: Quality Assurance Project Plan
SCS: Statewide Coordination Section
W2R: Waste 2 Resources

Table 3. Proposed Schedule for Completing Field and Laboratory Work, Data Entry, and Reports.

Field and laboratory work	Due date	Lead staff
Field work completed	April 2013	Andy Bookter
Laboratory analyses completed	June 2013	
Final report		
Author lead / Support staff	Callie Mathieu / Andy Bookter	
Schedule		
Draft due to supervisor	September 2013	
Draft due to client/peer reviewer	October 2013	
Final (all reviews done) due to publications coordinator	November 2013	
Final report due on web	December 2013	

Sampling Process Design (Experimental Design)

Approximately 200 children's products will be purchased from retailers in the Puget Sound area and through internet retailers selling to Washington State consumers. The majority of large Washington state retailers distribute the same children's products throughout the state from central distribution centers (Mathieu, 2013). The practice of statewide distribution indicates that products purchased from Puget Sound area stores are representative of products sold across the state. Internet retailers sell products representative of products available statewide.

Products will be brought back to Ecology headquarters and deconstructed into separate components. Ecology staff will screen all individual components using an XRF analyzer. Metals samples will be sent to an analytical laboratory if they (1) violate the screening criteria outlined in Table 4 during the XRF analysis or (2) are selected for low level analysis. Because an XRF analyzer cannot screen for phthalates, samples selected for phthalate analysis by the laboratory will be determined based on (1) information on the label, (2) the type of plastic used (e.g., soft plastics), and (3) other potential sources of information. Detailed product processing and XRF screening procedures are described in Appendix B.

Product Selection

Products selected for purchase will focus on those that fall within the Tier 3 product definition under the CSPA Reporting Rule (Table 1). This includes children's products intended for short-duration (less than one hour) of skin contact. Tier 3 products include most toys intended for children ages 3 to 12 years old. Product selection will be based on existing product information for phthalates and metals from a variety of sources. For example, the Danish Environmental Protection Agency has completed multiple studies regarding the chemicals present in children's products (Hoibye et al., 2011). For phthalates analysis, soft plastic toys will be given priority.

Product Screening

All products will be screened using a portable XRF analyzer following the 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* (ASTM, 2008). Individual product components will be isolated and screened in a bench-top stand.

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.

Ecology previously conducted two studies to evaluate the usefulness of XRF technology as a screening tool for metals in consumer products (Furl, 2011; Furl et al., 2012). The studies concluded that XRF measurements on isolated components of products using a bench-top stand compared well with laboratory results for metal analytes subject to CSPA legislation and may be used as a screening tool to identify products that warrant further laboratory analysis. Recommendations from the studies included the isolation of individual product components prior

to XRF analysis and the use of a bench-top stand to hold the component to improve the accuracy of measurements and reduce false positive results.

Target Analytes and Screening Levels

Phthalates and metals to be tested in this study are presented in Tables 4 and 5. Table 4 displays the state and federal regulatory limits for phthalates and metals. In addition, the state-required practical quantification limits (PQLs), the concentrations at which reporting is required by manufacturers under the CSPA guidance, are shown in Table 4. These criteria informed the selection of the XRF screening levels used to determine which product samples are sent for laboratory analysis.

Table 4. State and Federal Criteria for Target Analytes.

Analytes	Action levels (ppm)			
	State PQL*	State Limit**	Federal Limit	XRF Screening Level
Phthalates	5.0	1,000	6,000[a]	NL
Antimony	1.0	NL	60^	50
Arsenic	1.0	NL	25^	50
Cadmium	1.0	40	75^	20
Cobalt	1.0	NL	NL	50
Lead	NL	90	90+	45
Mercury	0.5	NL	60^	NL
Molybdenum	1.0	NL	NL	50

* Draft practical quantitation limits (PQL) as defined in the CSPA Rule Reporting Guidance.
** Maximum concentrations as defined by CPSA (Chapter 70.240 RCW)
http://apps.leg.wa.gov/RCW/default.aspx?cite=70.240

a Consumer Products Safety Improvement Act, establishes a total of 1,000 ppm for each of six phthalates.
^ Federal Limit: ASTM F963-07, Maximum allowable amounts in surface coatings of toys.
NL: no limit specified.

Samples with XRF-measured concentrations of metals at or above the XRF screening levels shown in Table 4 will be forwarded to the laboratory for analysis. If more samples are subject to forwarding to the laboratory than the budget will allow, then the samples with the highest metals concentrations will be sent for laboratory analysis.

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

All eight phthalate esters outlined in Table 5 will be analyzed in each sample forwarded for laboratory phthalate analysis.

Table 5. Specific Phthalate Esters Included in this Study.

Phthalate	CAS Number
Diethyl phthalate (DEP)	84-66-2
Dibutyl phthalate (DBP)	84-74-2
Di-n-Hexyl Phthalate (DHP)	84-75-3
Butyl Benzyl phthalate (BBP)	85-68-7
Di-2-ethylhexyl phthalate (DEHP)	117-81-7
Di-n-octyl phthalate (DnOP)	117-84-0
Diisodecyl phthalate (DIDP)	26761-40-0
Diisononyl phthalate (DINP)	28553-12-0

Sample Collection and Preparation

Ecology staff will purchase approximately 200 products at stores in the Puget Sound area, and through internet retailers selling to Washington State consumers. Upon collection, products will be brought back to Ecology headquarters and assigned a unique sample identification number. Photos and descriptive notes will be recorded. Information such as the type of advertisement used to sell the product and where in the store the product was located will also be recorded to help ensure the product was intended for children within a given age group.

Products will be removed from their original packaging and separated into individual components for separate screening. Packaging will be retained for potential analysis under another quality assurance project plan (Stone, 2012d). Items with different colors or base materials, different functions, or individual pieces intended to be disassembled will be treated as separate components. Components will be removed with stainless steel tools for further testing.

Sample preparation will be done on a clean bench lined with aluminum foil by staff wearing powder-free nitrile gloves. The stainless steel tools used to deconstruct the products will be cleaned at the beginning of each day with hot water and soap (Alconox), and then rinsed with deionized water. The stainless tools will be cleaned between samples using isopropyl alcohol.

Individual component samples may need to be reduced in size depending on the material of the sample and laboratory requirements. When necessary, staff will reduce the product part in size by cutting into smaller pieces using stainless steel tools (such as scissors or snips). All tools used for size reduction will be cleaned between samples with isopropyl alcohol.

Chain-of-custody will be recorded throughout sample processing, screening, shipment, and laboratory analysis. Detailed product processing procedures are described in Appendix B.

Measurement Procedures

XRF Screening

Individual product components will be screened for metals using a Niton XL3 portable XRF analyzer. All screening measurements will be made using a bench-top stand to hold the sample and XRF analyzer in place. Measurements will be taken for 120 seconds on a representative area large enough to cover the spectrometer's window. Soft materials must be at least 2 mm thick for XRF screenings. If the component is less than 2 mm thick, it may be folded onto itself until 2 mm depth has been reached.

The XRF analyzer will be used as a screening tool for metals. After XRF screening is complete, samples with metals concentrations at or above the screening levels (Table 4) will be forwarded to the laboratory for analysis. If more than 35 samples contain metals above the selection criteria, then samples will be prioritized for analysis based on the highest metals concentrations. Samples with detectable levels of lead and cadmium will be given first priority.

Detailed XRF screening procedures are described in Appendix B.

The limits of quantitation (LOQ), or detection limits, for the XRF analyzer are the minimum metals concentrations the instrument is capable of measuring. The XRF LOQs are greater than the state-required PQLs shown in Table 4. The XRF LOQs relate to the initial product screening. The PQLs will be compared to analytical laboratory results. The XRF analyzer LOQs are displayed in Table 6.

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

Ppm: parts per million
LOQ: Limit of Quantitation
+ Polyethylene blank, 8 mm aperture, 120 second total analysis time.
* Detection limits are not specified by the manufacturer for this element.

Laboratory Analysis

Manchester Environmental Laboratory (MEL), or an accredited contract laboratory, will conduct the phthalates and metals analyses described in Table 7. Project reporting limits are also included in the table. Chain-of-custody will be recorded throughout sample processing, screening, shipment, and laboratory analysis.

Metals samples will be digested via EPA Method 3052 (complete microwave digestion without hydrofluoric acid) and measured using ICP-MS following EPA Method 200.8. Mercury will be analyzed by CVAA following EPA Method 245.5.

Phthalates will be measured using GC-MS following Method CPSC-CH-C1001-09.3 (CPSC, 2010)[4]. This guidance allows for several different extraction and analysis methods. MEL is currently developing analytical procedures for the analysis of phthalates. Proposed sample methods include EPA 3546 for digestion and EPA 8270D for analysis.

Samples consisting of material such as hard plastic may need to be cryomilled prior to analysis. Cryomilling is the process of reducing a sample to very small particle sizes by lowering the product to cryogenic temperatures and mechanically milling it. This process provides a homogenous, finely divided solids sample necessary for efficient extraction. When necessary, a contract laboratory will carry out the cryomilling.

Table 7. Laboratory Methods and Reporting Limits.

Analyte	Digestion Method	Instrumentation	Method	RL (ppm)
Phthalates	EPA 3546*	GC-MS	EPA 8270D*	5.0
Antimony	EPA 3052^	ICP-MS	EPA 200.8	1.0
Arsenic	EPA 3052^	ICP-MS	EPA 200.8	1.0
Cadmium	EPA 3052^	ICP-MS	EPA 200.8	1.0
Cobalt	EPA 3052^	ICP-MS	EPA 200.8	1.0
Lead	EPA 3052^	ICP-MS	EPA 200.8	1.0
Molybdenum	EPA 3052^	ICP-MS	EPA 200.8	1.0
Mercury	EPA 245.5	CVAA	EPA 245.5	0.1

*Or equivalent methods allowed under CPSC-CH-C1001-09.3.
^ Alternate digestion method without hydrofluoric acid.
RL: Reporting Limit
EPA: Environmental Protection Agency
GC-MS: Gas Chromatography-Mass Spectroscopy
ICP-MS: Inductively Coupled Plasma-Mass Spectroscopy
CVAA: Cold Vapor Atomic Absorption

[4] United States Consumer Product Safety Commission Standard Operating Procedure for Determination of Phthalates

Budget

The product collection and laboratory costs estimated for this project totals $35,000. Table 8 shows the product collection and laboratory cost breakdown. Sample numbers are approximate.

Table 8. Project Budget.

Products	Number of Samples	QA	Cost per Sample	Subtotal
Product Collection	200		$10	$2,000
Cryomilling	75		$100	$7,500
Phthalates	40	6	$375	$17,250
Metals	35	6	$200	$8,200
			Total	$34,950

Quality Control Procedures

Laboratory

Table 9 outlines the laboratory quality control (QC) samples planned for this project. QC tests will include a laboratory control sample, matrix spike, matrix spike duplicate, and method blank per analysis batch of 20 samples or less.

Laboratory QC procedures for cryomilling preparation will include: (1) rinsing the cryomill with deionized water and reagents specified by the laboratory between each sample and (2) testing a rinse blank per batch of 20 samples processed.

Table 9. Quality Control Tests.

Analyte	Laboratory Control Samples	Matrix Spikes	Matrix Spike Duplicates	Laboratory Duplicates	Method Blanks
Phthalates	1/batch*	1/batch	1/batch	1/batch	1/batch
Metals	1/batch	1/batch	1/batch	1/batch	1/batch

*A batch equals 20 samples or less.

Quality Objectives

Quality objectives for this project are to obtain data of sufficient quality for confident quantification of phthalates and metals in products and to ensure that results are comparable between product matrices. Objectives will be achieved through careful attention to the sampling, sample processing, measurement, and quality control procedures described in this plan.

Measurement of Quality Objectives

XRF measurements will include measurement of duplicates and standards (provided by the manufacturer) after every 25 samples. Since the XRF analysis is being used as a screening tool only, no XRF measurement quality objectives (MQOs) are outlined in this project plan.

MQOs for laboratory analysis of phthalates and metals are shown in Table 10. MEL, or a contract laboratory, will be expected to meet these criteria. If the QC test MQOs are not met, then the analytical laboratory will reanalyze the samples in question in an attempt to conform to the MQOs. Quality control tests falling outside of MQO acceptance limits, and related data batches, will be reviewed by the project manager for their usability.

Table 10. Measurement Quality Objectives for Laboratory Analyses.

Analyte	Laboratory Control Samples (recovery)	Matrix Spikes (recovery)	Matrix Spike Duplicates (RPD)	Laboratory Duplicates (RPD)
Phthalates	50 - 150%	50 - 150%	≤ 40%	≤ 40%
Metals	85 - 115%	75 - 125%	≤ 20%	≤ 20%

Data Management Procedures

All project data will be stored on the shared Ecology Y:\ drive.

Product notes, purchase receipts, and photos of products will be stored by the project manager. XRF screening data will be transferred to Microsoft Excel spreadsheets and managed by the project manager.

Laboratory data and case narratives will be stored with the project manager. No publicly-available database currently exists for analytical data on products tested by Ecology. This type of data storage is anticipated for future development. In the interim, data for this project will be available upon request to the project manager, provided the data is not enforcement-sensitive.

Audits and Reports

Audits

MEL and contracted laboratories must participate in performance and system audits of their routine procedures. Results of these audits will be available upon request.

Report

A report summarizing findings for this project will be published after an internal review period. The final report will include:

- Categorical descriptions of the products screened with XRF (some information such as brands, product names, and retailers will not be included).
- XRF results (product names will not be associated with the result).
- Laboratory results of phthalates and metals analyses (product names will not be associated with the result).
- Statistical summary of laboratory results.
- Assessment of levels found that would violate standards in the CSPA or the reporting rule. Some data may be reserved until any compliance issues are resolved.

Data Verification and Validation

MEL will verify that (1) methods and protocols specified in this project plan were followed, (2) all calibrations, QC tests, and intermediate calculations were performed for all samples, and (3) the data are consistent, correct, and complete, with no errors or omissions. Evaluation criteria will include the acceptability of procedural blanks, calibration, ion abundance ratios, QC tests, and appropriateness of data qualifiers assigned.

MEL will provide case narratives to the project manager, describing the quality of MEL and contract laboratory data. Case narratives should include any problems encountered with the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. Narratives will also address the condition of samples on receipt, sample preparation, methods of analysis, instrument calibration, and results of QC tests.

Data Quality (Usability) Assessment

The project manager will assess the quality of the data, based on case narratives and data packages, to determine whether MQOs were met for this study. The project manager will determine whether the data should be accepted, accepted with additional qualification, or rejected and re-analysis considered. Data quality and usability will be discussed in the final report.

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Appendices

Appendix A. Acronyms and Abbreviations

Acronyms and Abbreviations

CPSC	Consumer Product Safety Commission
CSPA	Children's Safe Products Act
CVAA	Cold Vapor Atomic Absorbance
e.g.	For example
EAP	Environmental Assessment Program
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
et al.	And others
GC-MS	Gas Chromatography – Mass Spectrometry
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
LOQ	Limit of Quantitation
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
PQL	Practical Quantification Limit
RCW	Revised Code of Washington
RL	Reporting Limit
QC	Quality Control
WAC	Washington Administrative Code
XRF	X-ray fluorescence

Units of Measurement

ppm	parts per million

Appendix B. Product Sampling Standard Operating Procedure (SOP) - *Draft*

Product Sampling Procedure

Product Selection and Documentation

1. **Select products for potential analysis** by consulting the QAPP for the project. Select products that:
    - Are regulated by law being enforced.
    - Are likely to contain the chemicals of concern being targeted by the project.
    - Do not exceed a value of $300 (per Ecology inventory policies).

    Tip: Keep products in store bags for ease of identification of purchase location when cataloging items.

2. **Photograph the shelf space** around the product to document how the product is marketed if there is any ambiguity about whether the product is intended for children. Store photos according to Ecology's photo storage policies.
3. **Save and log the receipt from the purchase**. When you return to the office, scan the receipt. Save the file with the naming convention "yy-monthname-day-storename" in the RTT Product Testing SharePoint folder. Give the original paper receipt to the Fiscal Office for credit card expense tracking purposes.

Product Tracking

1. **Assign an identification number** (ID#) to the product. The ID# will be used to reference all future actions to which the sample is subjected. Use the format "XX000-X00" for the ID#.

    - The first two letters in the code represent a two letter designation given to each retail outlet.
    - The following three digit number, starts at 000, for the first product from the store and goes up by one for each product.
    - The third letter represents either
        - a = all (entire product)
        - c = component of product
        - p = packaging
        - b = both a product component and packaging
        - f = flame retardants
        - d = duplicate sample.
    - The final two digit number, starts at 00 and goes up by one for each sample of the same kind (so if there were two components of a product they would be c00 and c01).
    - Put the ID# on a label and affix label to the sample bag. If the product is too large for a Ziploc bag, label with cotton string tag or place label on box.

2. **Photograph the product** before dismantling begins.
3. **Use the Product Tracking Log (Product Testing Data)** to record as much of the following product information as possible:
    - Product ID#
    - Product component use
        - Intended to be put in child's mouth
        - Mouthable
        - Intended to be applied to child's body
        - Intended to be in prolonged (more than 1 hour) direct contact with child's skin
        - Intended for short (less than 1 hour) periods of direct contact with child's skin
        - No direct contact with mouth or skin during reasonably foreseeable use and abuse
    - Product Category
    - Product category or brick, if known (see Ecology's CSPA reporting rule guidance on product categories)
    - Brick #
    - Age recommendation
    - Primary QAPP
    - Date of Purchase
    - Retailer
    - Brand Name
    - Associated websites
    - Manufacturer and address
    - Distributor and address
    - Importer and address
    - Date of Manufacture
    - Manufacture location
    - Item/component description
    - Filenames and URL in PIMS database for any photographs
    - Filename and SharePoint URL for scan of purchase receipt
    - Particular notes about product.
4. **Prepare the product for XRF screening** as identified below in the "XRF Analysis" section.

Packaging

1. **Remove the packaging and packaging components from the product**. The definition of *packaging* and *packaging component* is very broad and includes everything except the actual product itself. This includes all of the following:
    - Any container providing a means of marketing, protecting or handling a product and shall include a unit package, an intermediate package and a shipping container.
    - Unsealed receptacles such as carrying cases, crates, cups, pails, rigid foil and other trays.
    - Wrappers and wrapping films.
    - Bags.
    - Tubs.
    - Interior or exterior blocking, bracing, cushioning, waterproofing.
    - Exterior Strapping.
    - Coatings.
    - Closures or ties.
    - Inks.
    - Labels.
    - Hangers or other means of displaying or storing a product.
2. **Place the packaging and packaging components into a plastic bag** if possible and label the bag with the Product ID#. If not possible, place as many items into a bag as possible and, for those portions too large, attach a label with the ID#. If you need to separate the packaging between what can be contained in a plastic bag and what cannot, make sure to attach the same ID# to both portions. For the large pieces, it may be necessary to use a string label with the ID# written on the paper portion.
3. **Store the packaging** with the Toxics in Packaging Enforcement Coordinator (Alex Stone).

XRF Analysis

1. **XRF Standard Operating Procedure.** Review the manufacturer's standard operating procedures as defined in the XL3 Analyzer Version 8.0.0 User's Guide (Abridged) Revision A November 2011. This will define how the instrument is to be operated to obtain the desired data. http://teams/sites/W2R/rtt/ProductTesting/Niton%20XL3%20Documentation/Niton%20XL3%20User%27s%20Guide%20(Abridged)%20v.8.0.0.pdf
2. **Set up the XRF analyzer, laptop, and bench-top test stand**. The analyzer must be properly mounted in the bench-top test stand. Plug in the analyzer's AC adapter to ensure battery life for extended periods of use. Make sure that the analyzer is communicating properly with the NDTr software such that it can be operated using the laptop's mouse and keyboard.
    a. If you have trouble connecting to the XRF, verify the correct USB port is being queried.
3. **Prepare the XRF analyzer for use**. The logon password is 1234. Under the *Data* menu, go to Erase > Erase readings to clear data from earlier sampling event(s) from the analyzer.
4. **Perform a system check.**
    a. Note: System check as the first data point saved and retrieved maintains a consistent output when downloading data from the analyzer.
5. **Allow the XRF analyzer to warm-up.** The manual advises a 10-minute warm-up before taking readings.
6. **Screen the manufacturer-provided standards**. Go to Sample Type > Consumer Goods > TestAll. Name the measurement "plasticstd" or "metalstd". Conduct a 2-minute scan. Repeat this standard analysis once every 20 scans and at the end of a session of readings.
7. **Prepare the product component** for screening using the XRF analyzer.
    - Make sure the product can physically fit inside the bench-top test stand.
    - If individual components of the product cannot be isolated for screening within the test stand:
        - Separate the sample into its components, using the procedures described in the *Sample Preparation* section.
        - Remove the analyzer from the test stand and conduct a handheld scan.
    - If screening a liquid, gel, or any other product that may leave residue, take great care not to contaminate the analyzer's sample window. For most liquids, a sample can be placed into a small plastic bag for analysis. The XRF can detect the sample through the thin plastic bag without appreciably impacting results.
        - To verify the bags being used do not contain any of the target elements, scan the plastic bag alone before attempting use. It is likely the bag will need to be folded several times to obtain sufficient thickness for analysis.
        - For verification that the bag is not hindering screening, place the metal and plastic standards within a plastic bag and scan separately using the XRF. Compare these results to the two standards without the plastic bag.
    - Ensure that a smooth area of the component is large enough to cover the spectrometer's window and at least 2 mm thick. If the component is less than 2 mm thick, it may be folded onto itself until 2 mm depth has been reached. Take care to minimize the air trapped in between folds.

8. **Enter identifying information into the data fields in the XRF analyzer**. At a minimum, enter the product ID# into the *Sample* field. If a product is separated into several components, differentiate each component by incrementing the final two numbers for each sample.
9. **Scan the component using the XRF analyzer.** Perform an initial screen of 2 minutes. Approximately once every 20 samples, conduct a duplicate scan (scan the same component twice). Add "dup" to the end of the name of the measurement.
10. **Download the data from the XRF analyzer at the end of every session.**
    a. Close the XRF scan program and open the software used to download. Save the file in the NDT format and also check the box for *Simultaneous Download to MS Excel*. Use the file naming convention "yy-monthname-day-XRF". Upload both files to the RTT Product Testing SharePoint folder.

Sample Preparation

1. **Make sure you have access** to all of the items on the supplies checklist in **Appendix I**. Not all of these items may be needed for every sample preparation event; however, most may be necessary at one point or another in the process, depending upon the type of sample involved.
2. **Clean all needed tools** as described in **Appendix II**. Tools most likely to be needed include scissors, scrapers, lab spatulas and knives or box cutters.
    - Plastic tools are not recommended for samples to be analyzed for phthalates as cross-contamination is possible. Plastic tools are fine for analyses of metals, parabens, and other chemicals unlikely to be present in plastic.
    - Use of stainless steel tools are not an issue for metals analysis as iron and the main components of stainless steel are not among the metals being tested.
3. **Place absorbent pads** on a flat surface. This protects samples from any potential contamination during sample preparation process. Place a Chem-wipe on top of the absorbent pads and replace Chem-wipes after each sample and absorbent pads as necessary.
4. **Refer to Appendix III for details on specific product procedures**. Separate a product into components using cleaned tools. A product may contain multiple components in addition to any portion of the product that meets the definition of packaging. If a product is separated into several components, differentiate each component by adding an appropriate letter to the Product ID# and incrementing the number on the end of the Product ID#. Record in the Sample Log (Product Testing Data) a description of each individual component and the letter extension added to differentiate between the product components. Each product component needs to be evaluated separately and placed into individual containers for potential analysis.
    - For example, a tube of lip gloss can be separated into the product (lip gloss itself) and the container used to hold and apply the lip gloss (the external plastic tube). In this example, a scraper would be necessary to remove the lip gloss product from the plastic tube. A "*1"* would be assigned to the lip gloss itself and a "2" for the plastic container.
    - Another possible product is a compact for applying makeup. The compact is likely to contain powder, a puffy applicator, a mirror, and the plastic container to hold all of the other components. Each item would be separated into potentially individual parts or components of the product.
5. **Perform an XRF screen** on any components that could not be screened before the product was separated into components (see the "XRF Analysis" section).
6. **Label each sample**.
    - Using the white labels that make each component with the Product ID# used in the XRF scan results.
    - Place items in sample containers if they are being sampled for more than just metals.
    - If the presence of metals is the determination of whether a lab sample is necessary, then either view results on XRF screen or determine whether a sample needs to be taken and placed in a separate bag labeled with the product's ID#.
    - Analyze XRF data for the presence of metals of concern.
    - Using the sample labels that come with the containers, label each sample that is destined for lab analysis.
    - At the end of each day of sampling, place samples in a cooler.

- Fill out a red chain-of-custody sticker and seal cooler.
- Place cooler in chain-of-custody cooler in the basement for safe overnight storage.

7. **Ship samples for lab analysis.**
    - **Fill out a chain-of-custody form**. Be sure to complete all necessary fields.
    - For samples to be sent to Analytical Laboratory Services, use the "Chain of Custody for General Testing" form from their website: http://www.caslab.com/Forms-Downloads/
        - Instructional video on Chain of Custody: http://www.caslab.com/Video/
    - For any samples that are sent to Manchester Environmental Laboratory, use the "Laboratory Analyses Required" form: http://aww.ecology/programs/eap/forms/Labanalysis_10_05.pdf
    - Place forms in a plastic bag.
8. **Place the sample into a bubble wrap bag** for storage. The bubble wrap is to protect the samples from potential breakage.
9. Place ice packs in cooler with samples.
10. Fill voids in cooler with extra packing material.
11. Place chain-of-custody forms inside cooler.
12. Fill out and apply the security seals. The seals are applied over the container which holds the sample vials. They prevent access to the samples without breaking the seal. They are necessary to maintain chain-of-custody and to protect the integrity of the sample within.
13. **Sample Shipment:** Samples may be analyzed either by Manchester Laboratory or a contract laboratory; shipment to each lab follows a different procedure. Based on which laboratory is being used, follow these practices when preparing the samples for shipment:
    - **Manchester:**
        - Place the samples in the sample storage refrigerator – either in a cage or a clearly marked cooler if there are too many samples to fit in a cage.
        - Seal the cage with a numbered key or secure the cooler using security tape. Keys and security tapes can be found on the bench in the sample storage room. The keys are typically found in a large plastic container on the bench and security tape is found in the same area.
        - Place a completed chain-of-custody (COC) form in the box on the lab bench. The location of the samples must be clearly marked on the COC. If the samples are placed in a cage, identify which cage is being used and the number of the security key. The key number must be clearly identified on the COC.
        - The samples will be picked up by Manchester staff and delivered to the laboratory for analysis.
    - **Contract Laboratory:**
        - Place the samples into either a bubble wrap bag or wrap and tape samples in bubble wrap to minimize the chance for breakage.
        - Place the samples into a cooler, making sure the glass containers are well protected to prevent possible breaking. Use additional bubble wrap if necessary. Disposable Styrofoam coolers may be used for shipment.
        - Add several blue ice containers. Blue ice can be found in the freezers across from the ice machine in the sample storage room.
        - Place a completed chain-of-custody (COC) form within the cooler before sealing. The COC should be sealed in a plastic bag to prevent possible moisture damage.

- Seal the cooler with shipping tape to prevent accidental release of samples during shipment.
- Add the laboratory shipping address. Take the samples to the Ecology shipping office. You will need to provide your name, phone number and the project SIC. SICs that may be appropriate for these projects include:
    1. NMATT – Mattel Attorney General grant
    2. NNEPD – NEP Flame Retardant grant
    3. M1630 – HWTR Program Packaging Testing funds
- If the samples are not to be shipped within a short period of time, place the samples back in the sample storage refrigerator until just before shipping.
- Ship the samples using over-night services to minimize the time in transit.

SOP Appendix I

Supplies checklist

Sterilizing tools

- ☐ Alconox (cleaning agent)
- ☐ Jars to store Alconox solution
- ☐ Scrub/bottle brush
- ☐ Aluminum foil (to wrap sterilized tools)
- ☐ Chem-wipes (to dry sterilized tools)
- ☐ Metal bowl (to hold Alconox solution for tool cleaning)

Sampling

- ☐ Sample log (can be done on computer)
- ☐ Alcohol pads (for sterilization/cleaning)
- ☐ Absorbent pads
- ☐ Chem-wipes
- ☐ Sample containers (40 mL, 2 oz, 4 oz, 8 oz, ½ L)
- ☐ Labeling stickers
- ☐ Fine tip marker
- ☐ Latex gloves
- ☐ Lab spatula
- ☐ Razor blade/carpet knife
- ☐ Scissors
- ☐ Plastic bag(s) to hold sample
- ☐ Needle nose pliers
- ☐ Standard pliers
- ☐ Various other tools that may come in handy

Shipment

- ☐ Chain-of-Custody seals
- ☐ Chain-of-Custody forms
- ☐ Sealable bubble wrap bags
- ☐ Bubble wrap/packing material
- ☐ Sample labels

Tools

- ☐ Hammer
- ☐ Saw
- ☐ Needle nose pliers
- ☐ Pliers
- ☐ Clamps
- ☐ Drill

SOP Appendix II

Tool cleaning

1. Clean tools at least once per day of sampling. During a sampling event (<1 day) clean the tools in between samplings, using moistened alcohol wipes. Exceptions do apply. If cleaning thoroughly with an alcohol wipe is entirely too impractical, then a more thorough cleaning will need to be conducted via the below description.
2. Place sufficient absorbent pads on a flat surface.
3. On the pads, place strips of aluminum foil that will be used to wrap the utensils used during the sample preparation. The aluminum foil strips must be large enough to encapsulate the items being cleaned. It is recommended that care be taken with the strips to prevent any potential contamination. For example, only wrap the utensils in the side of the strips that have not come in contact with the absorbent pads. You may place the strips on top of one another as long as you are careful to avoid contamination.
4. Using the directions on the container, mix a liter or an appropriate amount of Alconox solution as directed on the container. Use only de-ionized water found in the sample preparation room. Mix the solution in clean, unused glass sampling containers. Any unused Alconox solution can be retained for future cleaning activities.
5. Place an appropriate amount of the Alconox solution into a clean metal bowl.
6. Put on clean latex gloves.
7. Clean only one utensil at a time to minimize potential for cross-contamination.
8. Using a scrubber, clean the utensil with Alconox solution. It is recommended that the cleaning take place so that Alconox solution does not drip back into the original bowl. Clean until all material has been removed or Alconox has come in contact with all portions of the utensil.
9. Using de-ionized water, rinse the utensil three times or with sufficient water to remove all the Alconox solution.
10. Using a clean Chem-wipe, dry the utensil. Use only wipes that are directly from the box and cannot have been contaminated. Dispose of the wipe once the item has been dried.
11. Using a prepared strip of aluminum foil, wrap the tool in foil. Make sure that all surfaces are covered by foil and that only the internal, clean side of the foil comes in contact with the tool.
12. Place the cleaned tool aside to prevent contamination from work done on other utensils.
13. Continue with the above process until all tools are ready for use.

SOP Appendix III

Sample Type Guidelines

1. Packaging
    a. Phthalates
        i. Mainly used as plasticizers (substances added to plastics to increase their flexibility, transparency, durability, and longevity). They are used primarily to soften polyvinyl chloride (PVC).
        ii. Soft plastics (often clear) will be targets for this type of testing. An example is the clear plastic zipper bag many bedding sets are sold in.
        iii. Sampling
            1. Plastics
                a. Use sterilized scissors to cut into small pieces.
    b. Metals
        i. Scan all metal and plastic items with the XRF.
            1. Note: glass such as wine bottles could contain lead.
            2. Violations constitute any product which contains greater than 100 ppm lead, cadmium, or mercury cumulatively.
        ii. Sampling
            1. Thin
                a. Use snips to cut into small pieces.
            2. Small in size (e.g., zipper pull).
                a. Send for Cryomilling.
2. Children's Products
    a. Parabens
        i. A class of chemicals widely used as preservatives by cosmetic and pharmaceutical industries. Parabens are preservatives in many types of formulas. These compounds, and their salts, are used primarily for their bactericidal and fungicidal properties. They can be found in shampoos, commercial moisturizers, shaving gels, personal lubricants, topical/parenteral pharmaceuticals, spray tanning solution, makeup, and toothpaste.
        ii. Parabens, if present, can be listed on ingredients list on the product's container.
        iii. Sampling
            1. Liquids
                a. If a sample is only being tested for parabens and not volatile organic compounds, no special care is needed for samples, other than to minimize contamination and ensure enough volume for proper testing.
            2. Several small samples.
                a. If a product contains multiple small samples, for example an eye shadow palette, make a composite sample to maximize sample volume.

    b. Volatile Organic Compounds

i. Generally from cosmetic or hygiene products.
ii. Organic samples should go directly from the original container to the sample container.
iii. Sampling
    1. Liquids, Gels, Powders.
        a. If the sample is less than the volume of the container, sometimes it is best to forgo XRF measurements or only use a very small amount to measure.
        b. Once a sample has been XRF'd, it has been exposed to the environment too long to be an ideal organic sample. Therefore, use different bits of the sample for XRF and organic sampling.
        c. Minimal headspace is very important when sampling for the organic compounds. In particular, keep this in mind when purchasing samples. Purchase duplicates if necessary.
        d. The smallest volume sample container (40 mL) is usually the best option.
        e. When ample amounts of a component are available, fill the sample container full enough that a meniscus of excess is at the top. Also put enough sample into the lid of the container to coat the bottom surface of the cap.
        f. Carefully tilt lid and container together and screw shut. The goal is to have as little air in the sample container as possible.
        g. There should be excess sample expelling from the lid and container seam if done properly.
        h. Use a Chem-wipe to clean the outside of the sample container.
            i. Using a sticky label, indicate which sample the container holds and be sure to enter it into the Sample Log (Product Testing Data).

c. Formaldehyde
    i. Formaldehyde releasers are often used as an antimicrobial preservative in cosmetics. Examples that might be found in ingredients lists include:
        1. **Quaternium**-15
        2. Imidazolidinyl urea (**Germall** 115)
        3. Diazolidinyl urea (Germall II)
        4. DMDM hydantoin (Glydant)
        5. **2-Bromo-2-nitropropane-1,3-diol** (Bronopol)
        6. Tris(hydroxymethyl) nitromethane (Tris Nitro)
        7. Hydroxymethylglycinate (Suttocide A)
    ii. Formaldehyde may also be present in wrinkle-free clothing.
    iii. Sampling
        1. Fabric
            a. Cut into small pieces using scissors or rotary cutter and mat.
        2. Liquids
            a. See above (in Organics).

d. Metals
    i. See above (in Packaging)
    ii. Note: The XRF readings of cobalt are unstable; do not rely on its output in this parameter to determine testing of cobalt.
        1. Cobalt is often in blue products such as blue jeans.
    iii. Sampling
        1. See Packaging Section above.
e. Phthalates
    i. See Packaging section above.

3. Flame Retardants

a. May be present in plastics and textile applications, e.g., electronics, clothes, and furniture. This includes, but not exclusively, plastic covers of television sets, carpets, paints, upholstery (internal foam), and domestic kitchen appliances.
b. The lab has requested at least 15 grams of product. Therefore the ½ liter or 8-oz jars are recommended, depending on the density of the sample material.
c. Foam samples (presumably from furniture) will need to be Cryomilled. However, fabric samples should not need to be Cryomilled. Plastics should be broken into pieces.
d. Sampling
    i. Foams
        1. Collect about 15 grams for cryomilling
    ii. Plastics
        1. Break down into smaller pieces for cryomilling.
    iii. Fabrics
        1. See Formaldehyde section above.