



DEPARTMENT OF  
**ECOLOGY**  
State of Washington

## **Standard Operating Procedure EAP PTP 003, Version 2.0**

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### **Thermo Scientific Fisher Niton XL3t 700 X-Ray Fluorescence Analyzer (XRF)**

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## Purpose of this Document

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The Washington State Department of Ecology develops Standard Operating Procedures (SOPs) to document agency practices related to sampling, field and laboratory analysis, and other aspects of the agency's technical operations.

## Publication Information

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## SOP Revision History

Revision Date	Revision History	Summary of Changes	Sections	Reviser(s)
2/2017	1.0	New	All	S. Sekerak
3/6/2017	1.0	Minor edits	All	B. Kammin
3/27/2017	1.0	Footer, QA approval, minor edits	All	B. Kammin
2/20/2018	1.1	Added Ref. Std., Section 2.4.2, minor edits	All	S. Sekerak
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4/2021	2.0	Procedural edits, new formatting	All	C. Wiseman

## 1.0 Purpose and Scope

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- 1.1 This document serves as the Product Testing (PT) Standard Operating Procedure (SOP) for operating the Thermo Scientific Fisher (Thermo) Niton XL3t 700 X-ray Fluorescence Analyzer (XRF) in TestAll mode.
- 1.2 Warning: The XRF contains an X-ray Tube That Emits ionizing radiation. Thoroughly review and comply with all the safety requirements and recommendations outlined in Section 9.0.

## 2.0 Applicability

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- 2.1 This SOP includes procedures for safety, training, verification, limitations, operation, quality assurance and basic maintenance/troubleshooting of the XRF. The SOP shall be followed when operating the XRF in TestAll mode as a tool to screen for the presence of certain elements in consumer products, raw materials, and other types of product materials.
- 2.2 The manufacturer identifies the following elements as measureable using this XRF instrument:

Chlorine (Cl) ***	Chromium (Cr)	Cobalt (Co) *#
Zinc (Zn)	Bromine (Br) ***	Molybdenum (Mo)
Indium (In)	Barium (Ba)	Gold (Au)
Titanium (Ti) ***	Manganese (Mn)	Nickel (Ni)
Arsenic (As) #	Zirconium (Zr)	Silver (Ag)
Tin (Sn)	Tungsten (W)	Mercury (Hg) #
Vanadium (V)	Iron (Fe)	Copper (Cu)
Selenium (Se)	Niobium (Nb)	Cadmium (Cd) #
Antimony (Sb) #	Platinum (Pt)	Lead (Pb) #

\* Designates elements that were custom calibrated into the instrument.

# designates the PT CSPA target elements.

\*\*\* Designates the additional PT elements of interest.

Note that elements in certain matrices may not be detectable at levels of interest when using the XRF in 'TestAll' mode.

- 2.3 This XRF is operated under a ‘Fundamental Parameters Calibration’ mode that theoretically can see up to a 100% concentration (i.e. pure element) when used in accordance with the manufacturer recommendations and abiding by known x-ray analysis limitations.
- 2.4 Product testing XRF screening data are collected to help select samples for further confirmatory laboratory analysis. This method is designed as a rapid screening tool, and is not accredited.
- 2.5 All product screenings for elements must be initially verified by analysis of calibration verification standards prior to analysis of samples. Identify when the procedure is to be followed.
- The primary of suite of standards (Section 6.5.4 Table 1) covers the PT elements of interest: Cl, Ti, Cr, Co, As, Br, Cd, Sb, Hg, and Pb. Available calibration verification standards and their acceptance limits are displayed in Appendix A.
  - A provisional verification standard acceptance limit of 45% is applied to Co due to the variability observed measuring Co in the available standard. Co data should be used cautiously and any study prioritizing solely on Co should verify instrument performance with a second standard, matrix specific, if available.

### **3.0 Definitions**

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- 3.1 Component - Individual piece or part of a product containing different colors, functions, and/or material (i.e., a sweater may be comprised of several components such as, the woven fabric, a button, and zipper pieces).
- 3.2 Component Sample - Component identified to be screened as a sample using the XRF. Components cataloged in the PTDB receive an alpha-numeric identification (ID) that is used as the XRF component ID (e.g. TG-1-1-1).
- 3.3 Filter - A mechanism built into the instrument that allows modification of the x-ray energy to preferentially enhance the analysis of certain elements in certain matrices.
- 3.4 Fundamental Parameters Calibration – An approach to instrument calibration based upon the theoretical relationship between measured X-ray intensities and the concentrations of elements in the sample. This “standard less” approach is commonly used when there are few to no matrix specific standards available.
- 3.5 Ionizing Radiation - Radiation that carries enough energy to free electrons from atoms or molecules, thereby ionizing them. This type of radiation poses risk due to its potential to alter the chemical structure of living cells.
- 3.6 NDT - Niton Data Transfer. The NDT software is used to download data per section 5.3 from the XRF to the computer.
- 3.7 NDTr - Niton XRF operating software.
- 3.8 Laboratory Sample - Component sample identified for testing by a confirmatory laboratory analysis method (e.g. Environmental Protection Agency (EPA) SW-846 6020).

- 3.9 Limit of Detection (LOD) - The smallest concentration of an element that can be detected with reasonable certainty. It is generally regarded as indicating whether an element is present or not, and does not imply that a value obtained is accurate. The LOD is numerically expressed as two or three standard deviations measured on a sample with none or only a trace amount of the analyte present. Since the individual LODs are based on measurement error, they also improve as a function of the square root of the testing time.
- 3.10 Light Elements - Elements including: Cl, V, Ti, and Cr.
- 3.11 Low Filter - the preferred instrument filter used to fluoresce light elements, e.g. Factory default; set at 10 seconds analysis time.
- 3.12 Main Filter - the preferred instrument filter used to fluoresce the transition elements, which include groups 3-12 on the periodic table. Factory default; set as 50 seconds analysis time.
- 3.13 Primary Beam - The X-ray source directed out of the front of the analyzer. The source containing the highest dose rates of radiation.
- 3.14 Radiation - The emission of energy as electromagnetic waves or as moving subatomic particles, especially high-energy particles that cause ionization.
- 3.15 Shielding -The material that is placed between the analyst and the radiation source (e.g., isolation/shielding box).
- 3.16 TestAll mode - Thermo technology that automatically selects the correct analytical testing sub mode (metal, painted metal, thin metal, plastic, PVC plastic, thin plastic, layered materials, and non-metal) for the operator.
- 3.17 XRF - X-Ray Fluorescence. The emission of characteristic “secondary” x-rays from a substance during exposure to an external source of high-energy x-rays.
- 3.18 X-Rays - The form of radiant energy and component of the electromagnetic spectrum. X-rays originate from the energy loss associated with the interaction of high energy electrons or particles with atoms. Define any words, phrases, or acronyms having special meaning or application. Do not assume the reader has special knowledge of acronyms. Fully state all acronyms before further use.

**4.0 Personnel Qualifications/Responsibilities**

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- 4.1 Always operate the XRF in accordance with this SOP. The SOP is based on the guidance established in the EPA Method 6200 (EPA, 2007) and in accordance with the manufacturer’s instructions and recommendations.
- 4.2 All of the Ecology health and safety guidelines described in Section 9.0 must be followed as specified.
- 4.3 All operators must read and understand the Radiation Safety for Thermo Scientific Niton XRF Analyzers (PDF of Slides by James Blute) available in the PT Prep room, and should review the Thermo Fisher Scientific Niton XL3 Analyzer Version 8.0 User's Guide. (Thermo User’s Guide, 2011)

- 4.4 The XRF analyst will be responsible for verifying the completeness and correctness of data acquisition in accordance with this SOP (PTP003) and any additional guidance pre-established in study-specific QAPP. Errors made during data collection (e.g., sample ID typos, incomplete scans) are recorded in the Error Log and will be corrected prior to upload of the data to the PTDB.
- 4.5 The project manager (PM) will inspect datasets uploaded to the PTDB to verify accuracy, completeness, and adherence to the specific study criteria.
- 4.6 User Training
- 4.6.1 Staff must receive training, perform a successful Initial Demonstration of Capability (IDC) prior to operating the XRF. A qualified operator will provide the training. A qualified operator is a permanent employee that has been trained to operate the XRF by another qualified operator.
- 4.6.2 Permanent employees may also receive training through qualified Thermo technicians and or formal Thermo training opportunities to become a qualified operator.
- 4.6.3 For new analyst training, the overseeing qualified operator will be responsible for supplying the new analyst with:
- The Training Checklist and IDC form available in Product Testing Unit (PTU) SharePoint site
  - A copy of this SOP (PTP003)
  - Copies of or links to the documents listed in Section 4.3
  - Hands on training
  - Administering IDC analysis
  - Continued oversight and review of an analysts first several XRF operation sessions

## **5.0 Equipment, Reagents, and Supplies**

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- 5.1 Thermo Scientific Niton XL3t 700 X-ray Fluorescence Analyzer (XRF).
- 5.2 Isolation/shielding box with leaded self-closing flaps.
- 5.3 Laptop computer with Thermo Scientific NDTTr (v. 8.4.1 or newer) operating software for remote XRF operation and NDT (v. 8.4.2 or newer) software for data downloading, Comma Separated Value (CSV) generation, and spectra review.
- 5.4 XRF Instrument Logbook for recording daily use (study name, date, Res Value, user initials). The logbook is to be used to note poor instrument or software performance, preventive maintenance, repairs, and calibration or verification issues.
- 5.5 XRF Records Logbook to document training records for certified users, DOH X-ray certification, Software, x-ray tube certification preventive maintenance factory records, repairs, calibrations and verifications.
- 5.6 XRF Error Log for recording sample specific errors and to be used for immediate cleanup of data prior to uploading to the PTDB.

- 5.7 “Small Spot Locator” Sample. Not required.
- 5.8 Calibration verification standards containing element(s) of interest.
- 5.9 Current available calibration verification standards with certified values and  $\pm 20\%$  acceptance limits are listed in Appendix A.
- 5.10 Other calibration verification and performance check standards may be used to validate and analyze for additional elements. Standards should be certified according the guidance issued in International Organization for Standardization (ISO) Guides 30-35. The materials selected should be sufficiently homogeneous and be analyzed in an “as is” form.
- 5.11 XRF sample cups (Thermo Part Number (P/N) 187-466) with Mylar<sup>®</sup> film pre-cut circles, 6  $\mu\text{m}$  thickness, (Thermo P/N 187-462) or Polypropylene film, 6  $\mu\text{m}$  thickness.
- 5.12 The 24% ethanol solution, Liquinox<sup>®</sup> detergent, and de-ionized water (DIW) used for tool cleaning reagents. Additional tool cleaning protocols requiring other reagents must be used according to the guidelines set in the Product Collection and Sample Processing Standard Operating Procedure (SOP) SOP# PTP001 and study-specific QAPPs. All applicable chemical specific health and safety protocols shall be followed.
- 5.13 The tools, reagents and supplies described in the current version of the Product Testing Sample Collection and Processing SOP# PTP001 will also be used in the deconstruction and preparation of component samples for XRF screening.

## **6.0 Summary of Procedure**

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- 6.1 Instrument, Measurement and Data Interpretation Limitations, and Potential Sources of Error
- 6.1.1 A visual guide to the basic startup and usage of the XRF instrument is available in PTU SharePoint site.
- 6.1.2 The operation of this XRF has been optimized using the TestAll analysis mode.
- 6.1.3 The physical structure or composition of samples are often the leading cause in the acquisition of inaccurate results.
- 6.1.4 Instrumental limitations of the TestAll mode and sample thickness requirements are detailed in Appendices B and C.
- 6.1.5 Isolation of component samples may be necessary to avoid interference from other surrounding components.
- 6.1.6 Component samples with a heterogeneous composition may produce variable or imprecise results when replicates are performed. Determinations of homogeneity/heterogeneity of a sample is often not clearly visible to the eye, for example, with the compositional metal heterogeneity exhibited in some alloys.
- 6.1.7 Liquid or components in powder form may yield results with more certainty when thoroughly mixed prior to analysis.

- 6.1.8 Use of the XRF as a screening tool does not require homogenization of a component sample (e.g., grinding a solid into a powder). Therefore, data for heterogeneous component samples should be interpreted cautiously.
- 6.1.9 Component samples exhibiting roughness and uneven surfaces may cause decreased intensities of results, especially those of light elements. Use the XL3t 970 GOLDD+ XRF using SOP# PTP004 to optimize screening for light elements.
- 6.1.10 Scanning the smoothest portion of a component sample may reduce potential bias of the results obtained.
- 6.1.11 Irregular shapes or objects with curvature (e.g., wine bottles) may require extra-careful positioning.
- 6.1.12 Several of the same small objects (e.g., earring backings) piled together may lower potential bias of the results.
- 6.1.13 Containing small objects in a prescreened bag or XRF cup with Mylar (or polyethylene) film and scanning them through the bag/film should be used cautiously as the bag/film will decrease the intensity of results, and light elements may go undetected. Bags and film used must be pre-screened to show they do not contain target elements.
- 6.1.14 The thickness of an object can affect accuracy of results. Low density materials such as plastics and fabric require several millimeters up to a centimeter of material thickness as the x-rays necessitate an increased depth of penetration to recover elements accurately. Heavier plastics, like polyvinyl chloride (PVC) would require only a few millimeters thickness, and dense metal objects need only a few micrometers thickness. See thickness recommendations in Appendix C.
- Note: Materials, such as plastic bags and fabrics, should be folded or stacked as recommended above or as thick as possible prior to analysis.
- 6.1.15 A prescreened non-target element containing heavy object (e.g., a rock) can be utilized to compress stacked materials. However, caution should be exercised so that the x-rays do not penetrate the object used to compress the sample.
- 6.1.16 Paint and coatings on materials may lower the intensity, concentration, and ability to detect a target analyte in the underlying material.
- 6.1.17 It is suggested that replicate analyses of an individual component should be performed to assess the within-sample variability.
- 6.1.18 Evaluation of individual component sample spectrum is always advised to verify the presence or absence of a target element to further aid in confirmatory laboratory analysis prioritization and candidacy.
- 6.1.19 Guidance for data review including primary wavelength selection, common matrix interferences, and spectral line overlaps is provided in Appendix D.
- 6.2 Instrument/Analysis Preparations
- 6.2.1 Review study specific QAPP for additional requirements prior to beginning XRF screening analyses.

- 6.2.2 Follow the guidance specified in the PT Sample Collection and Processing SOP (SOP# PTP001) for tool cleaning, glove selection, and product deconstruction protocols. When applicable, follow additional low-level processing and analysis procedures described in SOP# PTP001.
- 6.2.3 Extreme care shall be taken to not introduce contamination or conditions that may affect the product or product components, and the selection of component samples for confirmatory laboratory analysis.
- 6.2.4 Wear gloves when handling products, components, and component samples for XRF screening. At a minimum, change gloves when they become soiled or debris is visible.
- 6.2.5 Use clean tools for deconstruction of the product and components for screening. Follow the guidance specified in the current version of PT Sample Collection and Processing SOP (SOP# PTP001).
- 6.2.6 A specific study's objective, analytes, levels of interest, and/or difficulties encountered due to a product or component matrix or construction may necessitate a more stringent protocol for handling, preparing (e.g. deconstruction), and screening component samples.
- 6.2.7 The isolation/shielding box should be used for most screening. As needed, clean the box (with an ethanol moistened Kim wipe) before the instrument is secured in the test stand and/or between sample analyses when loose debris is deposited on the measurement window (e.g., fine hairs from stuffed animals, glitter, etc.).
- 6.2.8 The XRF is stored in its case nightly in the locked cabinet.
- 6.2.9 The XRF case is to be locked when the XRF is transported out of the PT room.
- 6.2.10 Room access and cabinet keys are issued to PT personnel only to restrict access to the XRF.
- 6.3 Instrument Setup
  - 6.3.1 Inspect the XRF measurement window for damage (i.e., scratches) and for debris. The XRF should not be on during the inspection or window replacement.
  - 6.3.2 Clean the measurement window by blowing air or gently sweeping using KimWipes®. Too much pressure applied while wiping may damage the window, requiring replacement.
  - 6.3.3 If punctured or wrinkled replace the measurement window (P/N 187-1555) as necessary following the instructions found in the "Learning More, Service, and Support" section of the Niton XL3 user's guide (Pages 173-175).
  - 6.3.4 Plug in the USB cable into the mini USB port and the AC cable into the power port. Both ports are located below the XRF LCD screen under the black port cover. Connect the USB to the adjoining laptop and AC cable into an electrical outlet.
  - 6.3.5 The battery should not be in the unit when it is used while plugged in. Refer to the User's Guide for battery charging when the XRF is used in handheld mode.

- 6.3.6 Connect the XRF to the isolation/shielding box with the measurement window pointed into the box and the LCD screen facing toward you. The XRF “clicks” into place when properly installed.
- 6.3.7 The XRF operates in handheld mode as well. However, most screenings should occur with the XRF secured in the isolation/shielding box.
- Note: Place battery into the XRF scanner when using it in hand held mode. It does work while plugged to the laptop however this is not recommended because of fragile connection pins are susceptible to bending.
- 6.3.8 Once the USB cable is connected to the adjoining laptop computer open up the NDTr software.
- 6.3.9 At the XRF analyzer, hold the ON/OFF/ESCAPE button on the XRF control panel until the touch screen comes on. The XRF will take several seconds to start up. The same procedure is followed for turning off the instrument.
- 6.3.10 After the XRF is powered on, all functions for operating the XRF can occur using the LCD touch screen or the NDTr software on the laptop. For ease of use, it is recommended that the XRF be operated from the laptop computer using the NDTr software during normal daily use.
- 6.3.11 Instructions for operation will hereinafter be described in terms consistent with the XRF when controlled by the NDTr software at the laptop.
- 6.3.12 From the NDTr software, turn on the camera by selecting the small >> icon under the HELP tab in the upper right corner. Select the CAMERA icon (TV VIEW). If the XRF is not connecting select to connect and then turn on camera.
- 6.3.13 Select PRESS TO LOGON, select YES to proceed through the radiation “Warning”. Enter in the login password: 1234, select ENTER.
- 6.3.14 With the camera on the measurement window will be illuminated. Look at the camera display on the NDTr software/Laptop, and re-evaluate the window for scratches and debris.
- Note: Verify that the camera image is being saved to the NDT file by selecting System/Camera and both Enable Camera, and Save Image boxes should be checked.
- 6.3.15 Allow the instrument to warm up for at least five minutes before proceeding to the Systems Check.
- 6.3.16 Verify the instrument date and time.
- 6.3.17 From menu select SYSTEM, then DATE & TIME.
- 6.3.18 Adjust to current date and time if necessary, select SAVE to exit the screen or CANCEL if date and time are correct.
- 6.3.19 Select RETURN to get back to Main Screen.
- 6.4 System Check
- 6.4.1 The XRF systems check is used to standardize the detector. It must be performed daily upon use of the XRF.

6.4.2 Perform the XRF systems check by navigating through the main menu. Select SYSTEM CHECK, then select YES.

Note: During analysis and detector calibrations, it is important to ensure that the analyzer is not exposed to strong electromagnetic fields, including those produced by hard drives, cellular telephones, etc. All electronics should be kept at least two feet away.

6.4.3 If the system check is performed adequately the message “System Ok” will be displayed. Select CLOSE to exit.

6.4.4 The system check results will be reported out in the final data exported from the XRF. The value is listed as “Res.” The system check logs a detector calibration value for each occurrence it is performed and reports one sum "Res" value. A detector calibration results “Res value” below 195 is considered to be within manufacturer’s optimum specification.

6.4.5 If an error message is displayed in the System Check dialogue box, consult the User’s Guide for assistance. A RECHECK may be performed if the selection is available (via a pop-up box).

6.4.6 Record any error messages received in the XRF Instrument Logbook. An analysis session shall not proceed if there is not a successful system check performed. Consult Thermo for technical assistance.

6.4.7 At the end of an analysis session record the “Res” value, in the XRF Instrument Logbook.

6.4.8 The “Res” value is located on the NDT file download in the “System Check” sample data. This can be checked during the scanning session by clicking on view data icon and navigating through the readings.

6.4.9 The instrument operation specification values can be reviewed at any time during analysis by navigating to the main menu and selecting SYSTEM, and then SPECS. The display will show the instrument Specifications, including when the last system check was performed, e.g. “Energy Cal: 12/06/16”. Select -> icon to proceed to the diagnostics on page two to view the operating specifications.

## 6.5 Daily Calibration Verification Standards and Sample Screening

6.5.1 Prior to any unknown sample analyses, perform the initial XRF daily calibration verification with certified standards. Matrix specific standards should be analyzed in order to meet the objectives of the study specific QAPPs.

6.5.2 Scan the following suite of standards for CHCC (Chemicals of High Concern for Children’s) metals list: As, Cd, Co, Hg, Sb, and Pb.

- Thermo Scientific Niton Polyethylene (STD-1-1-2)
- MBH Metals Standard (STD-1-1-3)
- Calmetrics Polyethylene Blank (STD-1-2-3)
- Calmetrics PVC Low Standard (STD-1-3-2)

- MBH Metal Standard (STD-1-5-1)
- 6.5.3 The following suite of standards will be analyzed for Flame Retardant Studies of when scanning for light elements like Phosphorus. (Applicable only to the XRF GOLDD+)
- Calmetrics PE Blank (STD-1-6-1)
  - Calmetrics PE Low (STD-1-6-2)
  - Calmetrics PE High (STD-1-6-3)
- 6.5.4 The following suite of standards will be analyzed for Studies scanning for Titanium.
- MBH Metals Standard (STD-1-4-1)
  - MBH Metal Standard (STD-1-5-1)
- 6.5.5 Standard acceptance ranges are  $\pm 20\%$  for all elements. A full list of available standards with certified concentrations and acceptance limits is available in Appendix A.
- 6.5.6 If a target element of interest in a standard fails to meet acceptance criteria at the beginning of the analysis session rescan the specific standard. If this does not work, re-perform the XRF system check (Section 6.4) and reanalyze all of the required standards (Section 6.5.2 -6.5.4).
- If the element fails to meet acceptance criteria for a second time, alert PM via email at the end of the scanning session.
  - Record standard/element failure in XRF Instrument Logbook.
- 6.5.7 The suite of study specific standards listed in 6.5.2 -6.5.4 are to be run at the beginning and end of every XRF scanning session (scanning session is a consecutive time period in which the XRF is run) or as specified in Study QAPP. Table 1 provides an example of Verification Standards selected to represent a variety of matrices for an XRF Scanning session.

Table. 1 Example CHCC XRF Suite of Daily Calibration Verification standards, and Blanks

mm	Matrix	Elements
Std-1-1-2	Polyethylene	As, Cd, Cr, Hg, Pb, Sb
Std-1-1-3	Metal (tin)	Ag, Cd, Cu, Pb
Std-1-2-3	Polyethylene	None (Blank)
Std-1-3-2	PVC	Br, Cd, Cl <sup>+</sup> , Cr, Hg, Pb,
Std-1-5-1	Metal (Si/Al/ Cu)	Cr, Co, Ti

+Certified value for Co is less than XRF LOD.

^Cl does not have a certified value; PVC matrix contains > 15% Cl. PVC/Cl is used to validate the instruments capability to detect and delineate PVC- based plastics.

- 6.5.8 Matrix specific standards should be analyzed in addition to the primary suite of standard, when such standards exist, and as described in study specific QAPPs.
- 6.5.9 Matrix specific element optimization calibrations can be performed when matrix specific standards are available in a set. The set must contain multiple concentration levels and include a blank. Consult the User's Guide for instructions and applicability.
- 6.5.10 Consult study specific QAPPs for additional standards or frequency to perform check standard analyses during an XRF screening session.
- 6.6 Ready to Test
  - 6.6.1 Verify that the camera has been turned on and the System Check has been performed.
  - 6.6.2 Select Sample Type, Consumer Goods and TestAll to navigate to the TestAll mode. All PT screening analyses (and their associated verification standards) will use the Test All mode unless otherwise specified in a study specific QAPP.
  - 6.6.3 In the TestAll mode, from the Ready to Test screen select DATA ENTRY Select the VIRTUAL KEYBOARD to type the standard ID (e.g. STD-1-1-3) into the SAMPLE entry box or use the dropdown arrow to highlight standard.  
  
Note: The suite of standards are pre-programmed into the XRF. Under the VIRTUAL KEYBOARD select the dropdown menu bar to choose the appropriate standard.
  - 6.6.4 Next, select the dropdown arrow under the Model entry box. Highlight the equipment in use (XRF XL3t 700 or the loaner XRF XL3t 700) and select RETURN. The XRF will maintain the model selection for the duration of the scanning session.
  - 6.6.5 Place the required standard into the isolation/shielding box centered over the measurement window. The camera should be used to verify the sample is appropriately placed and the desired area on the component sample will be scanned. Select the Start button on top right to begin scanning.
  - 6.6.6 Once a scanning has stopped click on the return button on the instrument to get back to the Test All screen.
  - 6.6.7 Repeat steps 6.6.3 - 6.6.6 for every standard required in the set.
  - 6.6.8 For scanning component samples click data entry option to get to virtual keyboard select the VIRTUAL KEYBOARD and type the sample component ID into the SAMPLE entry box, select RETURN.
  - 6.6.9 Place the required sample into the isolation/shielding box centered over the measurement window. The camera should be used to verify the sample is appropriately placed and the desired area on the component sample will be scanned. Select the Start button on top left to begin scanning. Select the Start button on top left corner to begin scanning.

- 6.6.10 Use caution when setting small item/s on the XRF screening window; the window is made of thin plastic and can puncture and tear. Placing sample in a thin prescreened bag can accelerate the screening process and prevent damage to the window screen; although it may cause interference.
- 6.6.11 When scanning for elements in the light range (Mg, Al, Si, P, and S) pack samples as thick as possible into XRF Mylar sample cups or place sample directly on XRF window. Scanning through sample bags may cause inaccurate results.
- 6.6.12 Deconstruction of consumer goods and product materials to reduce items in size for placement into the isolation/shielding box is required.
- 6.6.13 Procedures for handling products, components, and component samples for screening by XRF must follow all minimum guidelines specified in this SOP, as well as any specific protocols (e.g., low-level, contamination control) described in the Sample Collection and Processing SOP# PTP001 and/or study specific QAPPs.
- 6.6.14 Once a scan has completed, click on the return button on the instrument to get back to the Test All screen.
- 6.6.15 Repeat for every sample replicate scanned and every new component sample analyzed.  
Note: The small spot 3 mm aperture should be used when co-mingled materials cannot be separated.
- 6.6.16 Record any errors that may occur during analysis in the XRF Error Log for later data review. Errors to note may include:
- Sample ID typos
  - Incomplete scans
  - Wrong samples analyzed
- 6.6.17 If log in mistakes or analysis complication occur create a case narrative based on XRF Error Log notes. Describe discrepancies between the NDT file and the CSV file. Save it as a word document with a standard filename: XRF Case Narrative mm-dd-yyyy ( For example XRF Case Narrative 10-22-2019.docx) Examples of things it can include:
- Analyst name \*
  - XRF screening date \*
  - Screening procedure error descriptions \*
  - Sample analysis complications
  - Possible sources of variability (sample, product, matrix)
  - Samples performed in replicate
  - Items requested by study QAPP
  - Other observations that may aid the PM in selection/prioritization of samples sent for analysis.

(\*Designates required information)

- 6.6.18 Uploaded the case narrative into the PTDB along with the scan results (CSV.) and the NDT file.
- 6.7 Small Spot Calibration and Screening, As Needed
- 6.7.1 The small spot 3 mm aperture should be used when co-mingled materials cannot be separated.
- 6.7.2 As needed, perform a small spot calibration following each replacement of the measurement window.
- 6.7.3 Once the small spot calibration is performed components or objects can be analyzed using the SMALL SPOT (TOGGLE SPOT) mode. For visual guidance on conducting a small spot calibration refer to “Learning More, Service and Support” section of the Niton XL3 User’s Guide (Pages 235-240).
- Note: The instrument and software uses both of the terms SMALL SPOT and TOGGLE SPOT interchangeably. Additional limitations are described in Section 6.1 and Appendices B and C.
- 6.7.4 From the main screen select ADVANCED, scroll down and click on SMALL SPOT CALIBRATION, a popup will ask if you want to reset the center select YES.
- 6.7.5 The small spot target will appear in the instrument camera view. Place the Small Spot Locator Sample in the XRF shielding box so that the copper is in the center of the circle in the camera view. If the sample is not centered for each of the five calibration shots, your calibration will not be valid. Note: During this process the analysis mode will automatically be placed into one of the metals mode (e.g., Electronic Metals or Metals & Ceramics).
- 6.7.6 From the “Ready to Test” screen select DATA ENTRY, select the VIRTUAL KEYBOARD (do not enter/type anything), select RETURN. Select START. A 30 second scan will be performed. A beep will signify the beginning and end of each 30 second scan.
- 6.7.7 For the remaining 4 scans move the Small Spot Locator Sample, centering the copper within each new small spot target position. Take each reading as in 6.7.6.
- 6.7.8 At the end of the calibration, the new calculated center will be located, and a new X, and Y axis point will be reported on the screen. Select YES to accept the new location, the new location should appear to be located in the center of the camera view.
- 6.7.9 Perform a fifth and final analysis of the Small Spot Locator Sample, as in 6.7.6, except enter/type “small spot” into the SAMPLE entry box, select RETURN. Select START to begin analysis. A result will be produced. A Copper (Cu) result of > 950000 ppm (which is equivalent to > 95% recommended by the Thermo Scientific manufacture) is expected.
- 6.7.10 Repeat the entire small spot calibration process if a > 95% result for copper is not obtained.

- 6.7.11 Select the CLEAR/ENTER button to exit from the calibration then select the RETURN icon to return to the main menu.
- 6.7.12 Record that a “valid Small Spot Calibration was performed” in the XRF Instrument Logbook.
- 6.7.13 Record when Small Spot Calibrations were completed due to a polypropylene window replacement.
- 6.7.14 To get back to regular screening select SAMPLE TYPE, CONSUMER GOODS, then select TESTALL mode. All PT screening analyses (and their associated verification standards) will use the TestAll mode unless otherwise specified in a study specific QAPP.
- 6.8 Data Transfer, Review, and Upload
  - 6.8.1 At the end of the analysis session, data acquired by the XRF must be transferred to the NDT software for review and upload into the PTDB.
  - 6.8.2 Close out the NDTr operating software and open the NDT software. The NDTr software must be closed for the data upload to be performed successfully.
  - 6.8.3 Start the data transfer by clicking DOWNLOAD icon from the top ribbon of the NDT software main screen. The Download dialog box will open.
  - 6.8.4 From the Download Readings from XRF Analyzer (pop-up) screen select TEST to test the connection to the XRF. A pop-up window will display if the hardware successfully communicating with the analyzer. Select OK.
  - 6.8.5 If the test fails, there may be a problem with your serial port setup. Navigate to the bottom of the Download dialog box. Verify that there is a valid connection from the laptop to the XRF, as indicated by a green box in the “Connection Status” box. Select CONNECT to establish a new connection. Select SETTINGS to change the associated COM port to properly link the USB cable/data flow from the XRF when necessary. Recheck the connection by selecting TEST.
  - 6.8.6 Select QUERY READINGS. This will return a list of all current readings on your analyzer. The list appears in the large white box in the Download dialog box.
  - 6.8.7 Select the reading(s) for download by checking the boxes next to the individual Reading Types and/or Reading No column headings. Include the “Sample Check” Reading Type.
  - 6.8.8 Enter the path for the file in the Destination Folder field. The default location is the laptop Desktop. It is suggested that a file be saved to the file XRF RAW DATA I.e. XRF raw data 04-05-21 in PT F: Drive - study specific folder as a temporary back-up during the course of a study. Files in the F-drive are purged on an annual basis.
  - 6.8.9 Assign and Enter the File Name in “MM-DD-YYYY” form. If there are more than one file to download on the sample date additional characters should be added for distinction. Commonly there may be a morning data set and an afternoon set, where the suffix “AM” or “PM” would sufficiently differentiate the files. Do not use the characters “#” or “/” as they will cause an error at upload into the PTDB.

- 6.8.10 Select DOWNLOAD from the Download Readings from XRF Analyzer screen to complete the transfer of the data from the XRF into the NDT software. When the progress bar shows all of the readings are downloaded, select DONE. An XRF NDT file (.ndt) will be automatically be generated.
- 6.8.11 Once the .NDT file had been generated click on the Export icon to automatically generate the .CSV File. The PTDB requires a CSV file format in order to upload data.
- 6.8.12 Select the check box “Simultaneous download to MS Excel” in order to automatically generate an Excel file (.exe). This is an option and not a required step.
- 6.8.13 Troubleshoot error messages by following the recommendations in the Connectivity section of the XL3 Analyzer User’s Guide (pages 164-165).
- 6.8.14 Open the XRF NDT file that was just generated in the proceeding steps to review scan session.
- 6.8.15 If cleanup of the NDT file is performed (i.e., to hide rows containing incomplete scans), the file must be saved to preserve these changes. Select SAVE from the upper task bar of the main NDT software screen before exiting the data file.
- 6.8.16 Review the generated CSV file for errors recorded in the XRF Error Log. Delete all incomplete scans (scan time of < 60 seconds) and make simple edits (i.e., to product component sample names) that were recorded during analysis in the XRF Error Log.
- 6.8.17 If additional errors are identified, and edits are made to the .CSV file during review, it is suggested that the details of these modifications are also captured in the XRF Error Log.
- 6.8.18 All corrections made to the file (i.e., deletions or changes; Section 6.6.11) will be documented in a case narrative (Word document) to be saved to the PTDB as an attachment.
- 6.8.19 It is recommended that additional analysis observations, as listed in Section 6.6.12) are additionally recorded in the case narrative.
- 6.8.20 Perform uploads to the PTDB of the CSV file, XRF NDT file, and case narrative, as necessary, per the protocol described in the Product Testing Data Entry and Database SOP# PTP002.
- 6.8.21 The CSV file can be deleted from the F drive Product Testing study folder by, the project manager once the files have been thoroughly reviewed and the data has been uploaded into the PTDB.
- 6.8.22 Data should be deleted from the XRF once the NDT file is saved to the PTDB.
- 6.8.23 Reconnect to the NDTr software and select DATA from the main screen, then ERASE, and finally select ERASE ALL DATA. A confirmation screen asking you “Are you sure?” will appear. Select YES to erase all data from the XRF. Selecting NO will return you to the previous menu.
- 6.8.24 Exit to the main screen by selecting RETURN twice then selecting LOGOFF. It is now safe to turn off the instrument.

- 6.8.25 Hold the ON/OFF/ESCAPE button on the XRF control panel until the touch screen turns off. Remove the USB and AC cable from the XRF then release the instrument from the isolation/shielding box. Return the XRF to its case and store in the appropriate locked cabinet.
- 6.8.26 When verified data has been uploaded into the PTDB the analyst will notify the study specific PM the data is available for a PM review.
- 6.8.27 PMs should review XRF spectra included on the NDT file. Suggested guidelines are available in Appendix D.

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## **7.0 Records Management**

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- 7.1 All PT XRF scanning results will be stored in WA State Department of Ecology's Product Testing Database.
- 7.2 XRF Instrument Logbook is used for recording study name, date, user initials, Res Value, instrument serial number of loaner if in use, instrument performance, model, preventive maintenance, repairs, calibrations and verifications.
- 7.3 XRF Records Logbook is used for keeping training records for certified users, DOH X-ray certification, Software, x-ray tube certification preventive maintenance factory records, Thermo repairs, calibrations and verifications.
- 7.4 XRF Error Log documents sample specific errors and will be used for immediate cleanup of data prior to uploading to the PTDB.
- 7.5 XRF Screening Case Narrative summarizes XRF Error Log and any additional screening notes.
- 7.6 XRF Error Log and case narrative details are outlined in the Summary of Procedure Sections above.
- 7.7 Maintain daily NDT files in the Ecology F: drive/study specific folder.

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## **8.0 Quality Control and Quality Assurance**

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- 8.1 The XRF is calibrated using a fundamental parameters calibration process performed by Thermo Fisher Scientific. Fundamental parameters calibrations are based on the physics of the excitation and emission of x-rays and are programmed into the XRF using mathematical descriptions.
- 8.2 Manufacturer calibrations are designed to eliminate systematic errors or at least make them insignificant. Errors associated with measured results should be considered to be predominantly random in nature and mainly reflect the imprecision of the measurement process (i.e., heterogeneous sample and/or sample analysis process).
- 8.3 The manufacturer has no mandated intervals at which the instrument requires factory recalibration because of the known overall stability of the instrument. However, factory recalibrations can be useful as a measure to try and address any issues before they might adversely affect longevity of intrinsic parts of the instrument.
- 8.4 The manufacturer calibrations will be required only if any one of the following conditions have occurred:

- System check fails
- Calibration Verification Standard (QA/QC) limits are exceeded
- The instrument is sent in for repairs or servicing
- There is a change in the excitation and/or detection conditions, such as a change in detectors, X-ray filters, or processor

- 8.5 In accordance with common industry practices these calibrations certifications are valid for one year from the date of calibration. However this does not mean that the instruments is out of calibration if more than a year has elapsed.
- 8.6 Calibration recertification documents will accompany the XRF each time it is returned to Ecology from the manufacturer. All calibration certificates will be stored in the XRF Records Book and scanned copies saved on the PTU SharePoint.
- 8.7 Instrument system check will be performed at the beginning of each analysis session, when the instrument is powered on, when the batteries are changed (battery only used during hand held mode), and whenever the analyst believes that drift has occurred during analysis (e.g., changes in room temperature, elements in the calibration verification standards fall out of acceptance limits).
- 8.8 The system check validates the energy/voltage requirements necessary for the instrument to perform elemental analyses and is recorded each day.
- 8.9 Instrument blanks are used to verify that no contamination exists in the spectrometer window.
- 8.10 An instrument blank should be analyzed at the beginning and at the end of every scan session or as specified in the study QAPP, and whenever contamination is suspected.
- 8.11 Analysis of calibration verification standards are performed at the beginning and end of every analysis session or as specified in the study QAPP.
- 8.12 Initial lower limits of detection, or LODs, are provided by the manufacturer. However it is not a comprehensive list to cover all elements (see Appendix E).
- 8.13 LODs can vary drastically by element and by matrix, analysis time and level of statistical confidence. Individual element LODs by specific matrices must be performed experimentally.
- 8.14 The analysis time and level of statistical confidence (99.7%) utilized in determining LODs are established as the factory defaults and serve as static contents across all elements and matrix types.
- 8.15 Total analysis time = 60 seconds. Main Filter - the preferred instrument filter used to fluoresce the transition elements, which include groups 3-12 on the periodic table. Factory default; set as 50 seconds analysis time. Low Filter - the preferred instrument filter used to fluoresce light elements. Factory default; set at 10 seconds analysis time.

8.16 If replicate measurements are performed, it is recommended the component sample will be moved to a different location of the same item. It is recommended that a total of five scans are performed. This type of replication will be used to assess variability within a sample.

## **9.0 Safety**

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9.1 Because preparations for the procedure may require the use of hazardous materials, training is required as per the Ecology Chemical Hygiene Plan and Hazardous Material Handling Plan (Ecology, 2011), which includes Laboratory Safety Orientation, Job-Specific Orientation, and Chemical Safety Procedures. The Standard Operating Procedures in Section 16 of the Chemical Hygiene Plan and Hazardous Material Handling Plan for handling chemicals must also be followed.

9.2 The XRF instrument is registered and is under an agreement for use by Ecology through the Washington State Department of Health (DOH) Office of Radiation Protection X-Ray Program under Chapter 246-228 Washington Administrative Code (WAC).

9.3 Under the agreement of use, Ecology agrees to the DOH terms of:

- The unit operating instruction guide must be available for users.
- All users must be trained in proper handling and safe operation of these units. Documentation is required. These records must be available for review. See Section 4.6.
- Any alteration or termination of the XRF use requires immediate notification to the DOH by calling 1-800-299-9729.
- DOH will schedule and perform a site visit every four years to recertify the use of the current Thermo Niton XL3t 700 XRF.

9.4 Safety During Instrument Use

- do not place hands, feet, or other body parts in the radiation field
- do not look into the beam path
- do not point the XRF at anyone
- do not hold the XRF from the front

9.5 Additional safety mechanisms when operating the XRF with the aid of the instrument software and isolation/shielding box include:

- An audible tone will indicate when the instrument begins to emit the x-ray beam and scanning starts, at 30-seconds and again at the commencement of the 60 second scan duration.
- Automatic termination of a scan/x-ray emittance if the object being scanned moves off of the measurement window.

9.6 Protocols for sample preparation safety is discussed in the Sample Collection and Processing SOP PTP001.

## **10.0 References**

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- 10.1 Ecology [Washington State Department of Ecology]. 2019a. Environmental Assessment Program Safety Plan. Washington State Department of Ecology, Olympia.
- 10.2 MEL [Manchester Environmental Laboratory]. 2016. Lab User's Manual, Ninth Edition. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.
- 10.3 Ecology [Washington State Department of Ecology]. 2019. Quality Assurance at Ecology. Environmental Assessment Program, Washington State Department of Ecology, Olympia. <https://ecology.wa.gov/About-us/How-we-operate/Scientific-services/Quality-assurance>.
- 10.4 Wiseman, C., 2020. Product Testing Standard Operating Procedure for Consumer Product Sample Collection and Processing. Olympia, WA. SOP# PTP001 Version 2.1.
- 10.5 Wiseman, C. 2019. Product Testing Database Standard Operating Procedure for Data Entry and Data Entry Quality Assurance. Olympia, WA. SOP# PTP002 Version 2.1
- 10.6 Wiseman, C. 2020. Product Testing Database Standard Operating Procedure of the Thermo Fisher Scientific Niton XL3t 970 GOLDD+ X-ray Fluorescence Analyzer (XRF). Olympia, WA. SOP# PTP004 Version 1.0

## Appendix A

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XRF Calibration Verification Standards summary table.

Standard	Database Component ID	ID from Company
Plastic standard (PE)	STD-1-1-2	Niton 180-619, lot# T-51
Metal standard (Tin)	STD- 1-1-3	MBH 180-606 (batch M)
Metal standard (original)	STD-1-1-1	MBH 180-606 (batch H)*
Calmetrics PE High	STD-1-2-1	PE-H-30A
Calmetrics PE Low	STD-1-2-2	PE-L-27A
Calmetrics PE Blank	STD-1-2-3	PE-05A
Calmetrics PVC High	STD-1-3-1	PVC-H-22A
Calmetrics PVC Low	STD-1-3-2	PVC-L-22A
Calmetrics PVC Blank	STD-1-3-3	PVC-01A
Metal Standard (steel)	STD-1-4-1	MBH 13XPH13800 (batch A)
Metal Standard (Si/Al/Cu)	STD-1-5-1	MBH 55XG02D7 (batch N)
Small Spot Calibration	Small Spot	Small Spot**
Calmetrics PE Blank-FR	STD-1-6-1	PLPE3-4ED-31 (040819DA-1)
Calmetrics PE Low-FR	STD-1-6-2	PLPE3-4ED-31 (040819DA-2)
Calmetrics PE High-FR	STD-1-6-3	PLPE3-4ED-31 (040819DA-3)

\*Standard for backup and troubleshooting only (Pb reads high).

\*\*No certified concentration associated with this standard. Used for camera centering

All PT XRF Calibration Verification Standards with Acceptance Limits

**STD-1-1-1: Metal MBH 180-606 (batch H)\***

Element	Concentration (ppm)	Acceptance Criteria (ppm)
Ag	28,000	22,400-33,600
Cu	4,900	3,920-5,880
Cd	3,500	2,800-4,200
Pb	1,300	1,040-1,560

\*Standard for backup and troubleshooting only (Pb reads high).

**STD-1-1-2: Plastic Niton 180-619, lot# T-51**

Element	Concentration (ppm)	Acceptance Criteria (ppm)
Cd	300	240-360
Cr	104	83-125
Pb	153	122-184
As	53	42-64
Hg	104	83-125
Ba	690	552-828
Sb	100	80-120
Se	203	162-244

**STD-1-1-3: Metal MBH 180-606 (batch M)**

Element	Concentration (ppm)	Acceptance Criteria (ppm)
Ag	30,000	24,000-36,000
Cu	4,600	3,680-5,520
Cd	3,500	2,800-4,200
Pb	1,400	1,120-1,820 <sup>#</sup>

<sup>#</sup>Thermo recommended 30% acceptance at high end.

**STD-1-2-1: PE High PE-H-30A**

<b>Element</b>	<b>Concentration (ppm)</b>	<b>Acceptance Criteria (ppm)</b>
Br	1,100	880-1,320
Hg	1,101	881-1,321
Cr	999	799-1199
Pb	1,200	960-1,440
Cd	302	242-362

**STD-1-2-2: PE low PE-L-27A**

<b>Element</b>	<b>Concentration (ppm)</b>	<b>Acceptance Criteria (ppm)</b>
Br	499	399-599
Hg	200	160-240
Cr	398	318-478
Pb	401	321-481
Cd	101	80.8-121.2

**STD-1-2-3: PE Blank PE-H-30A**

<b>Element</b>	<b>Concentration (ppm)</b>	<b>Acceptance Criteria (ppm)<sup>1</sup></b>
Br	0	0
Hg	0	0
Cr	0	0
Pb	0	0
Cd	0	0

<sup>1</sup>All elemental results all be reported as non-detected on the XRF (<xx, where xx is the 2-sigma instrument detection limit).

**STD-1-3-1: PVC High *PVC-H-22A***

<b>Element</b>	<b>Concentration (ppm)</b>	<b>Acceptance Criteria (ppm)</b>
Br	1,100	880-1,320
Hg	1,100	880-1,320
Cr	1,000	800-1,200
Pb	1,200	960-1,440
Cd	300	240-360

**STD-1-3-2: PVC Low *PVC-L-22A***

<b>Element</b>	<b>Concentration (ppm)</b>	<b>Acceptance Criteria (ppm)</b>
Br	500	400-600
Hg	201	161-241
Cr	399	319-479
Pb	400	320-480
Cd	100	80-120

**STD-1-3-3: PVC Blank *PVC-01A***

<b>Element</b>	<b>Concentration (ppm)</b>	<b>Acceptance Criteria (ppm)<sup>1</sup></b>
Br	0	0
Hg	0	0
Cr	0	0
Pb	0	0
Cd	0	0

<sup>1</sup>All elemental results all be reported as non-detected on the XRF (<xx, where xx is the 2-sigma instrument detection limit).

**STD-1-4-1: Metal 13X PH13800 (batch A)**

<b>Element</b>	<b>Concentration (ppm)</b>	<b>Acceptance Criteria (ppm)</b>
C	386	INFORMATIONAL ^
Si	810	INFORMATIONAL^
S	30	INFORMATIONAL^
P	64	INFORMATIONAL^
Mn	332	± 20 or Study Specific*
Ni	80,400	± 20 or Study Specific*
Cr	125,300	± 20 or Study Specific*
Mo	21,000	± 20 or Study Specific*
Cu	449	± 20 or Study Specific*
Co	220	± 20 or Study Specific*
V	188	± 20 or Study Specific*
Al	10,750	± 20 or Study Specific*
Ti	122	INFORMATIONAL <sup>+</sup>
Sn	51	± 20 or Study Specific*
N	41	INFORMATIONAL^

^ No acceptance criteria; element and concentration provided for material composition assessments.

\* Element can be analyzed for; acceptance criteria is defined in QAPP or QAPP addendum.

+ Below XRF LOD for high Fe alloy matrices.

**STD-1-5-1: Metal Standard (Si/Al/Cu) MBH 55XG02D7 (batch N)**

<b>Element</b>	<b>Concentration (ppm)</b>	<b>Acceptance Criteria (ppm)</b>
Cu	13,500	± 20 or Study Specific*
Mg	3,320	INFORMATIONAL <sup>^</sup>
Si	90,790	INFORMATIONAL <sup>^</sup>
Fe	9,500	± 20 or Study Specific*
Mn	5,020	± 20 or Study Specific*
Ni	1,920	± 20 or Study Specific*
Zn	7,860	± 20 or Study Specific*
Pb	3,110	± 20 or Study Specific*
Sn	1,580	± 20 or Study Specific*
Ti	1,950	1,560-2,640
Cr	481	± 20 or Study Specific*
Co	419	230-608 <sup>+</sup>
V	208	INFORMATIONAL <sup>^</sup>
Be	12	INFORMATIONAL <sup>^</sup>
Sb	39	± 20 or Study Specific*
Cd	22	± 20 or Study Specific*

<sup>^</sup> No acceptance criteria; element and concentration provided for material composition assessments.

\* Element can be analyzed for; acceptance criteria is defined in QAPP or QAPP addendum.

<sup>+</sup> A provisional acceptance range of 45% will be applied due to the observed variability of this standard. An additional verification standard should be used if Co is the primary target element.

**STD-1-6-1: PE Blank PLPE3-4ED-31 (040819DA-1)**

<b>Element</b>	<b>Concentration (ppm)</b>	<b>Acceptance Criteria (ppm)</b>
Br	0	0
Cl	0	0
P	0	0
Sb	0	0

**STD-1-6-2: PE Low PLPE3-4ED-31 (040819DA-2)**

<b>Element</b>	<b>Concentration (ppm)</b>	<b>Acceptance Criteria (ppm)</b>
Br	400	320-480
Cl	400	320-480
P	401	320-480
Sb	400	320-480

**STD-1-6-3: PE High PLPE3-4ED-31 (040819DA-3)**

<b>Element</b>	<b>Concentration (ppm)</b>	<b>Acceptance Criteria (ppm)</b>
Br	1000	800-1200
Cl	1001	800-1200
P	1000	800-1200
Sb	1000	800-1200

## Appendix B

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### Element Limitations

The TestAll mode was designed by Thermo to be a means to quickly and efficiently analyze a variety of matrix types without requiring mode changes by the analyst. It functions by designating a general material identification by comparing the analysis with other general types of materials. The XRF then selects the proper sub-mode for analysis and then the elemental composition of the sample is analyzed. TestAll mode was selected as the default mode for use by Ecology's PT Program for screening analyses.

The TestAll mode encapsulates all available sub modes utilized by other main modes, (e.g., Plastics and Electronic Metals). Below is a list that illustrates PT primary elements not available for detection within each sub-mode.

Sub-Mode	Elements Not Detected
Non-Metals	Cl, As
Painted Metals	Cl, As
Aluminum	Cl, As
Metal -SAC- 305	Cl, As
Plastic	Mo
PVC Type	Mo
Thin Plastic	Mo

## Appendix C

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### Sample Thickness Recommendations

When possible and practical the guidelines in the table below should be followed:

Sub-Mode	Sample Thickness Recommendations
Non-Metals	Low Density Materials: > 9mm
Painted Metals	Dependent on coating material*^
Aluminum	No Value
Metal -SAC- 305	No Value
Plastic	>9mm
PVC Type	>5mm
Thin Plastic	Stack multiple pieces to recommended thickness

\*It is recommended that an area of an object be tested with the paint/coating and without the coating to verify location of presence of target analyte. Coatings may lower the intensity, concentration of ability to detect a target analyte in the underlying material.

^Assessments of only the paint coatings themselves should be performed cautiously as the coating/paint layers are usually not thick enough to analyze appropriately (without detecting the underlying material).

*“Polymers, and plastics in general, unlike metals and soils, are very weak absorbers of x-rays. This is because polymers are composed mainly of very light elements such as carbon and hydrogen. While just half a millimeter of steel will completely stop 23.1 keV energy x-rays of cadmium, for example, it takes at about 10 mm of plasticized PVC and as much as 100 mm of polyethylene (PE) to do so. Fortunately, polymers that may contain cadmium (Cd), lead (Pb) and other restricted elements would also contain considerable quantity of elements such as antimony (Sb), bromine (Br), titanium (Ti), etc. Their presence results in much stronger absorption of x-rays which means that, instead of 100 mm, it takes only about 15 mm of compounded PE to achieve saturation thickness for these x-rays. If the thickness of analyzed polymer sample is less than 5 mm for PVC or less than about 9 mm for a “typical” PE, the measured intensity of x-rays will be a function of both analyte concentration and sample thickness.”*  
(Thermo, 2010)

Thermo recommends the use of the thickness correction for PVC samples under 5 mm in thickness and PE samples less than 9 mm in thickness. Performing this operation is not required however it should be noted those materials registering in the sub-mode of “Thin Plastics” may have an increased error associated with the results. Further discussion including performing thickness corrections, can be found in the User's Guide Chapter 8.

Other non-metal materials should follow similar conventions as described by Thermo for plastic and metals thickness recommendations. Generally, weaker energy absorbing materials like wood and silicone would require a greater thickness than would be required for ceramics or cement.

## Appendix D

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### Spectral Lines and Interferences

Suggested X-ray Lines to Determine Individual Analytes in Polymeric Materials (ASTM, 2015):

Analyte	Preferred Line	Secondary Line
Chromium, Cr	K $\alpha$ 1, K $\alpha$ 2	No Value
Bromine, Br	K $\alpha$ 1, K $\alpha$ 2	K $\beta$ 1, K $\beta$ 3
Cadmium, Cd	K $\alpha$ 1, K $\alpha$ 2	K $\beta$ 1, K $\beta$ 3
Mercury, Hg	L $\alpha$ 1, L $\alpha$ 2	No Value
Lead, Pb	L $\beta$ 1	L $\alpha$ 1, L $\alpha$ 2

For all x-ray line information you can easily find it in NDT. Simply open the program, then under View click on X-Ray Line List. This will reveal a pane on the right side of the program window that has the preferred and secondary lines for confirmation of each element.

X-ray spectrometers may not completely resolve x-ray line pairs for some line combinations (for example, manganese K $\alpha$  and chromium K $\beta$ ; vanadium K $\alpha$  and titanium K $\beta$ ; and phosphorus K $\alpha$  and molybdenum L1). Therefore, care must be exercised in the interpretation of x-ray line intensities when both elements are present. In some cases, alternative x-ray lines without interference can be used (ASTM, 2013). Additional guidance is available in the referenced ASTM method.

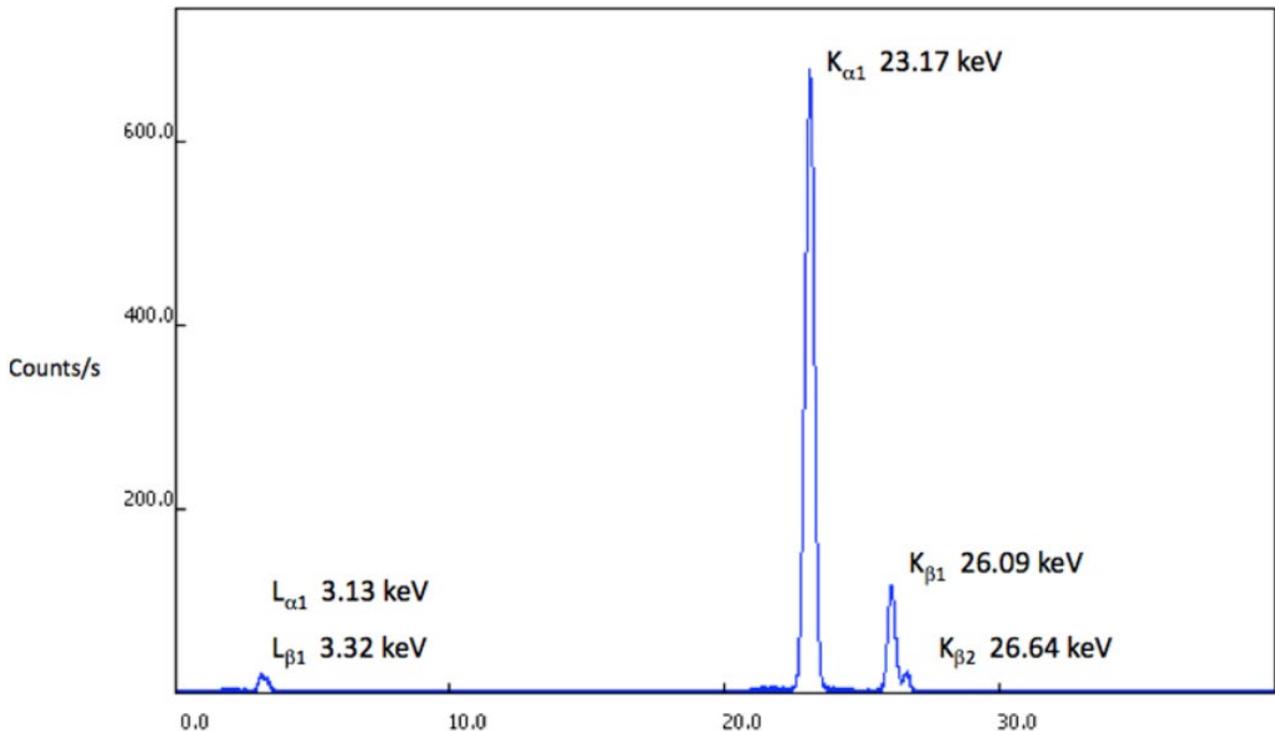
Matrix effects in x-ray spectrometry are caused by absorption and enhancement of x-rays in the s. Primary absorption occurs as the specimen absorbs the x-rays from the source. The extent of primary absorption depends on the composition of the specimen, the output energy distribution of the exciting source, such as an x-ray tube, and the geometry of the spectrometer. Secondary absorption occurs as the characteristic x-ray radiation produced in the specimen is absorbed by the elements in the specimen. When matrix elements emit characteristic x-ray lines that lie on the short-wavelength (high energy) side of the analyte absorption edge, the analyte can be excited to emit characteristic radiation in addition to that excited directly by the x-ray source. This is called secondary fluorescence or enhancement (ASTM, 2014). Additional guidance is available in the referenced ASTM method.

Examples of Additional Matrix Interference Effects in polymeric Material (ASTM 2014)

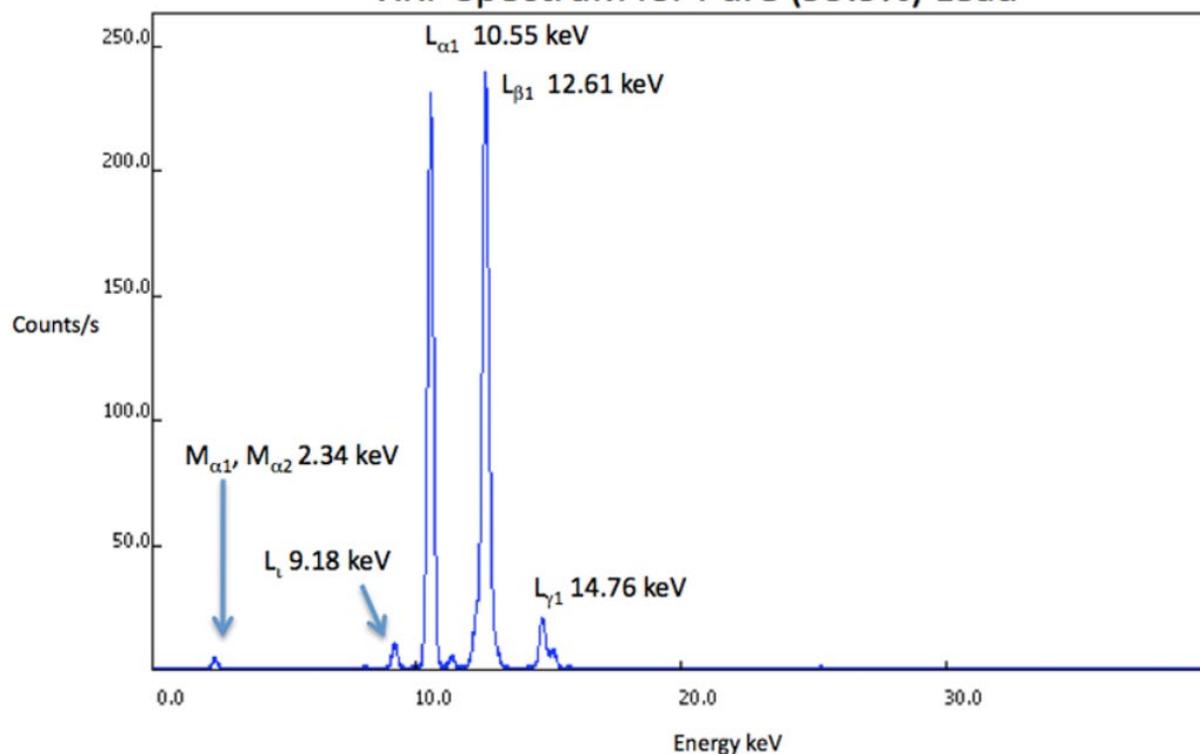
Cause	Effect
Absorption by Cl in PVC	Reduced sensitivity for all analytes as compared to when they are occurring at the same concentration levels in polyolefins
Polymers of similar composition but differences in the relative	Differences in C/H among calibrants and samples may result in biases of a few percent (relative)
Unmeasured elements B, N, O, and F present in the matrix of the polymer for example amide, fluorinated and terephthalate compounds.	If concentrations differ from the calibrants, substantial concentrations of these elements may cause significant changes in both apparent
PBBs, PBDEs, and Sb <sub>2</sub> O <sub>3</sub> Reduction of apparent sensitivity for most analytes	Reduction of apparent sensitivity for most analytes
Absorption of Na, P, S, Ca, Ti, Zn, Mo, Sn, Ba, and other elements included in a formulation as fillers or performance additives	Reduction of apparent sensitivity for most analytes

Example reference spectra of 99.99% Cadmium and 99.9% Lead are displayed below:

**XRF Spectrum for Pure (99.9+%) Cadmium**



## XRF Spectrum for Pure (99.9%) Lead



ASTM, 2013. ASTM E1621-13 Standard Guide for Elemental Analysis by Wavelength Dispersive X-Ray Fluorescence Spectrometry. ASTM International, West Conshohocken, PA: <https://doi.org/10.1520/E1621>

ASTM, 2014. ASTM E1361-02(2014)e1 Standard Guide for Correction of Interelement Effects in X-Ray Spectrometric Analysis. ASTM International, West Conshohocken, PA: <https://doi.org/10.1520/E1361-02R14E01>

ASTM, 2015. ASTM F2617-15 Standard Test Method for Identification and Quantification of Chromium, Bromine, Cadmium, Mercury, and Lead in Polymeric Material Using Energy Dispersive X-ray Spectrometry, ASTM International, West Conshohocken, PA: <https://www.astm.org/f2617-15.html>

# Appendix E

## Manufacturer's Limits of Detection

XRF LODs in metal matrices (Table 1) and polymers (Table 2) were provided by Thermo for a select group of elements (RoHS elements). The following tables denote lower detection limits than have been observed under the XRF settings employed by Ecology's Product Testing. Ecology's Product Testing utilizes the factory default setting of a 60-second total analysis time, 30 seconds for the main filter and 30 seconds for the light filter (Small Spot deactivated and detection of light elements such as phosphorous).

Since LODs are a function of testing time, interference/ matrix, and level of statistical confidence, a decrease in testing time result in an increase the detection limits. In general detection limits improve as a function of the square root of the testing time. All detection limits below are specified following the U.S. EPA protocol of a 99.7% confidence level.

Thermo cited LODs for various metal matrices with a 120-second total analysis time, 60 seconds for the main filter and 60 seconds for the low filter (Small Spot deactivated).

Element	Al	Fe	Sn
Cd	16	57	400
Pb	18	60	120
Hg	25	130	185
Cr	160	150	500
Br	20	30	100

Limits of detection for RoHS Elements in Metal Matrices. All values in the table are represented in ppm (mg/kg)

Thermo cited LODs for various polymer types with a 180-second total analysis time, 120 seconds for the main filter and 60 seconds for the low filter (Small Spot deactivated).

Element	PE Blank	PE+2%Sb	PE+5%Br	PVC
Cd	15	30	40	20
Pb	4	10	55	10
Hg	6	18	35	22
Cr	20	20	25	40
Br	400	500	750	N/A

Limits of detection for RoHS Elements in Polymers. All values in the table are represented in ppm (mg/kg)

Element concentration below the LOD are reported as < LOD followed by the detection limit for that particular element as calculated by the instrument. An indication of an LOD for any individual element in any matrix is to multiply the 2 sigma error on any non-detected elements by 1.5. As an example, if Arsenic read <LOD +/- 12, you can assume that Arsenic is not present in the sample at around 18 ppm.