Guidelines for Testing Metal Cookware for Lead and Other Toxic Metals

Table of Contents

Introduction

The main objective of this protocol is to present a step-by-step process for screening metal cookware for lead and other toxic metals (e.g. cadmium, arsenic, etc) using an XRF device and evaluating the leachability of these metals. The data entry procedures described in this document assume direct entry of information into a series of spreadsheets. However, templates are also available to handwrite results on paper. The handwritten information should then be entered into the spreadsheets.

Reviewers

This protocol has been reviewed by the following individuals:

Gordon Binkhorst | Pure Earth (May, 2024)
Katie Fellows | King County (April, 2024)
Richard Fuller | Pure Earth (May, 2024)
Angela Mathee | SAMRC (April, 2024)
Kate Porterfield | Pure Earth (June, 2024)
Talia Reiss | Pure Earth (July 2024)
Mahbubur Rahman | iccdr,b (May, 2024)
Alfonso Rodriguez | Pure Earth (April, 2024)
Budi Susilorini | Pure Earth (May, 2024)
Renee Street | SAMRC (April, 2024)
Jesmin Sultana | iccdr,b (May, 2024)
Stephen G. Whittaker, Ph.D.| Pure Earth, Hazardous Waste Management Program in King County, Washington/Public Health-Seattle & King County (retired) (April, 2024)

Acronyms

HBA	Home-based assessment
RMS	Rapid Market Screening
XRF	X-ray Fluorescence

Guidelines for Screening Cookware

Introduction

The goal of this document is to provide consistent protocols for the acquisition of data when investigating metal cookware. This document provides guidance on general characterization of cookware, XRF analysis, and leachate testing. Conducting these analyses and reporting the data in a consistent manner will help further our understanding about the hazards associated with lead and other toxic metals in metal cookware.

Screening Cookware: Selection of Items

When analyzing for a Rapid Market Screening (RMS) or Home-Based Assessment (HBA), please reference RMS and HBA protocols regarding the criteria for measuring the total lead content of metal cookware. The main points are summarized below:

Select the most common items used for cooking (e.g., pertinent to a home, school, marketplace) in consideration of the project objectives (e.g., aluminum cookware versus brass or stainless steel).

Preliminary Data

Characterizing the Cookware

This section is designed to record the general characteristics of the cookware to be tested. Please complete as many of the following data fields as possible in the provided template:

Variable	**Data Entry**	**Definition**
Investigator	Free-form	Full name of investigator
OrganizationTesting	Free-form	Organization conducting the analysis
CountryAcquiredFromCode	Dropdown	Alpha-3 code for the country where the cookware was acquired from

Variable	Data Entry	Definition
CityAcquiredFromCode	Free-form	3-digit abbreviation for the city where the cookware was acquired from (UNK if unknown)
CookpotNumber	Dropdown	Assigned cookpot number (001, 002, 003, etc.)
Cookpot_ID	Autogenerated	Autogenerated Cookpot ID from the combination of the previous three fields (for linking to XRF and leachate data)
ManufType	Dropdown	Was the cookpot manufactured by casting molten metal or forged (i.e., shaping of ingots)? UNK if unknown.
CookpotShape	Free-form	Describe the shape of the cookpot (i.e., flat or round bottom, spherical or typical frying pan shape, wok, etc.)
CookpotWidth	Free-form	Average internal width of cookpot (in centimeters)
CookpotDepth	Free-form	Average internal depth of cookpot (in centimeters)
InsideDiffOutside	Dropdown	Is the inside of the pot visibly different from the outside? Yes or No
Photos	Free-form	Photo filenames/links (for pots, components, and labels). For example: 2345.jpg
Manufacturer	Free-form	Manufacturer of cookpot. UNK if unknown.

Variable	Data Entry	Definition
MakeModel	Free-form	Make/Model of cookpot. UNK if unknown.
Volume	Free-form	Volume of pot in quarts or liters (specify). UNK if unknown.
CookpotType	Dropdown	Type of cookpot: pressure cooker, fry pan, sauté pan, saucepan, wok, brazier, stock pot, fryer pot, steamer, caldero, double boiler, kadai, uruli, tadka pan, appam pan, idli maker, tope, handi, dadesen, other
OtherDesc	Free-form	"Other" cookpot description
Description	Free-form	Description of item from the online listing, packaging, or a description of donated items.
Condition	Dropdown	New (purchased locally or online) or Used (donated by the community) or Unknown/UNK
Metal	Dropdown	Primary cookpot metal: Aluminum, Stainless Steel, Hindalium (if noted by the seller of the item), Brass, Other, or Unknown (UNK)
Coating	Dropdown	Yes for an observed non-stick coating, No for no observed coating, UNK for Unknown
Anodized	Dropdown	Yes for manufacturer-noted anodization, No for no mention of anodization, UNK for Unknown

Variable	Data Entry	Definition
Certification	Free-Form	Certification listed on packaging or item (e.g., NSF or UL).
Notes	Free-Form	Additional narrative
Definitions: *Autogenerated* fields are populated automatically based on data entered in other fields *Dropdown* fields restrict data entry to defined choices from a dropdown menu *Free-form* means that the analyst can enter unstructured text, without specific formatting		

Guidelines for XRF Testing

XRF Preparation

Health and Safety

Before operating an XRF analyzer, read and follow the Health and Safety section in the Detailed XRF Guidance in Appendix A of this section.

XRF Calibration

- Inspect the measurement window for damage (rips) or dirt/debris – circled in red below. Replace if needed.

Figure 1. XRF Measurement Window

- Conduct a **calibration verification**. Calibration procedure is determined by the XRF analyzer model in use:
- **If using a *NITON XRF Machine*:**
    - Press the "System Check" icon to initiate the system check process.
    - Once the instrument completes the check, press the "Sample Type" icon, followed by the "Metals" icon, and then the "General Metals" icon.
    - Measure the alloy standard sample: Test the factory supplied alloy standard (or other approved standard).
    - If the standard is correctly identified, and all major elements read within calculated acceptance limits (see factory QC readings), testing may commence.
    - If the standard is not within acceptance limits, turn the device off and on again, and then conduct a second systems check.

        - After the instrument completes the system check, return to “Test” and re-measure the alloy standard as directed above. If it reads correctly, testing may proceed.
    - **Significant deviations from the expected values may indicate a need for recalibration or adjustment of the instrument. Contact your Thermo Scientific Niton Service center for assistance and do NOT proceed with testing.**

- ***If using an OLYMPUS XRF Machine:***
    - Calibration checks (Cal Checks) can be performed in two ways:
        - The docking station provides an automatic Cal Check when inserted.
        - When in the field or away from the docking station, utilize the standardization coupon included in the XRF kit to perform a Cal Check.
    - To perform a manual Cal Check:
        - Navigate to the Test Setup screen
        - Place the supplied Cal Check alloy standard (316 stainless steel) on a flat surface
        - Ensure the analyzer measurement window is flush over the coupon
        - Tap the Cal Check button
        - The message “Cal Check - Passed” indicates that the analyzer is ready for sample testing
    - If the Cal Check fails:
        - Ensure that the alloy standard is positioned correctly beneath the measurement window
        - Confirm that the X-ray indicator blinks during the procedure
        - Restart the analyzer
        - Retry the Cal Check procedure
    - **If the Cal Check fails repeatedly, contact Olympus customer service or a local distributor**

- If you are not using a check sample that was included in the XRF kits, refer to the following standards for each sample type or matrix:

Table 1: XRF Standards by Metal Sample Type

Matrix	Expected Pb conc (ppm)	Lower acceptable range (~25%)	Upper acceptable range (+25%)
MBH-1611X SAC305Q (“Tin Check”)	1000	750	1250

MBH Check Sample R 180-696 (Alternate Tin Standard)	1200	900	1500

- The frequency of calibration checks depends on several factors including the instrument usage, environmental conditions, and regulatory requirements. As a general guideline for analyzing metal cookware, perform the calibration check the XRF machine as follows:
    - Daily or before each analysis session;
    - At the beginning session;
    - At the end of the session;
    - When the instrument has been switched off for 30 minutes;
    - And after analyzing every fifth piece of cookware.
- Record lead measurement result for each calibration standard used.
- Do not proceed if pertinent calibration standard checks are outside of the acceptance limits of the device.

Sample Preparation

The following preparation guidelines should be followed for metal cookware:

- When accessible, samples should be taken from the interior of the cookware, where food would be in contact.
- For curved or irregularly shaped items, analyze the flattest surfaces.
- Retain all samples (properly labeled and secured) for possible additional screening or laboratory testing.

XRF Operation

- Samples should be placed on a hard surface, and **not held in your hand**, when analyzing.
- Select TEST ALL mode on the XRF device. (if applicable)
- Take an XRF reading of the table or surface you will be using to analyze the samples to ensure it does not contain lead, as this could interfere with the readings. If lead is detected, find a new surface.
- Take the following XRF readings; NOTE: XRF readings should be about 30 to 60 seconds long depending on the model used:
    - 6 readings of the interior sides of the cookware, where food would be in contact
    - 6 readings of the interior bottom of the cookware
    - 6 readings of the interior cover/lid of the cookware (if applicable)

    - If applicable, the following readings should be included:
        - 2 reading of each rivet, knob, or other external features (e.g., valves for pressure cookers).
    - Record what part of the item each reading corresponds to.
- If the interior of the cookware is not accessible (e.g., too small), but it is apparent that the interior and exterior materials are similar in makeup, take XRF readings as follows:
    - 6 readings of the exterior sides of the cookware
    - 6 readings of the exterior bottom of the cookware
    - 6 readings of the exterior top of the cookware (if applicable)
    - If applicable, the following readings should be included:
        - 2 reading of each rivet, knob, or other external features of the cookware

XRF Data Documentation

In addition to recording the standard cookware information, please complete as many of the following data fields as possible in the provided template.

Variable	**Data entry**	**Definition**
User	Free-Form	Full name of XRF user
OrganizationTesting	Free-form	Organization conducting the analysis
CountryTested	Dropdown	Country where the cookware was tested: Alpha-3 code
CityTested	Free-Form	3-digit abbreviation for the city where the cookware was tested
XRF_Model	Free-Form	Make and model of XRF analyzer

Variable	Data entry	Definition
XRF_Mode	Free-Form	XRF settings used
Date	Format enforced	Date of XRF measurement
Time	Format enforced	Time of XRF measurement.
Cookpot_ID	Free-form	From Cookpot ID generated in General Dictionary
TestedComponentDesignation	Dropdown	Letter assigned to the cookpot component being tested (a,b,c,d,e, etc. If >26 components, start with aa, then ab, ac, etc.)
SampleID	Autogenerated	Autogenerated Sample ID from the combination of TestedComponentDesignation and Cookpot_ID
XRF_Run_No	Free-Form	XRF run number
InsideXRFMeasure	Dropdown	Is the inside of the pot (i.e., the cooking surface) accessible by the XRF? Yes or No
ReadingLocation	Dropdown	outside lid; inside lid; outside pot base: inside pot base; outside pot wall; inside pot wall; handle; inside steamer insert; outside steamer insert; rivet; vent pipe; other
ComponentMaterialTested	Dropdown	Metal, plastic, glass, or rubber, or other, as determined upon inspection.

Variable	Data entry	Definition
FoodContact	Dropdown	Yes/No whether the component could contribute to lead in food or leachate.
Pb	Free-Form	Concentration detected by the XRF. If non-detected, enter the “<” symbol and enter the error term in the field "Error". Do not enter "0"
Units	Dropdown	XRF concentration units (ppm or %)
Error	Free-form	Error for the measurement, as reported by the XRF
ErrorTerm	Dropdown	Whether the instrument provides the error term as two or three standard deviations.
XRF_Data_File	Free-form	File containing the XRF reading on the instrument
Notes	Free-form	Additional narrative

Definitions:
Autogenerated fields are populated automatically based on data entered in other fields
Dropdown fields restrict data entry to defined choices from a dropdown menu
Format enforced fields restrict data entry to specific formats
Free-form means that the analyst can enter unstructured text, without specific formatting

Data Back-Up

- At the end of each day when XRF readings are taken, download and retain raw data files as .csv or .xls.
- NOTE: Make sure that each XRF reading in the data file corresponds to each sample reading through the XRF Reading Log; otherwise, the data file is not useful.
- In the file name, include the date that the samples were analyzed as DD-MM-YYYY.

Leachate Test

If the average or median of the internal surface XRF readings exceeds the reference value (50 ppm), a leachate test of this item may be warranted depending on the objectives of the particular study.

If samples are to be shipped to a laboratory, use the sample designation system previously outlined.

For guidelines on how to conduct a leachate test, proceed to the next section of this document.

Guidelines for Leachate Testing

Sample Preparation

- Samples should be washed with mild dish soap, rinsed with ultrapure water [1], and allowed to air dry.
- Mark a "fill line" on the cookware's interior at **80% of its total fill capacity**.
    - Note: Mark the fill line in a way that prevents pigment dyes from being introduced to the solution.

Leaching Test

Health and Safety

- The leaching test should be carried out in a laboratory setting following customary lab safety practices, including the use of disposable nitrile (preferred) or latex gloves, eye protection, and protective clothing.

Test Protocol

- Prepare a solution with a 4% volume/volume (v/v) solution of reagent grade acetic acid and ultra-pure water[2]. Please note that the acetic acid concentration used in this procedure may change, depending on the outcome of further investigations. Please contact Pure Earth for updates.
- Add this acetic acid solution to the cookware **up to the 80% capacity fill line**.
- Measure the pH of the solution with a calibrated pH meter.
- Cover cookware with its lid (preferred, if available) or silicone sheet to reduce evaporation, then:
    - If using cookware with a flat bottom, place cookware on an electric hot plate.
    - If using cookware with a rounded bottom, place cookware on a heating mantle such as these to ensure stability and uniform heating. In the absence of a mantle, you may place cookware on a flat pan of sand on top of an electric hot plate.
- Bring the acetic acid solution in the cookware to a simmer, noting the amount of time it took for the solution to come to the desired temperature.

---

[1] If your lab cannot access ultrapure water, you may opt to use deionized or distilled water. In this event, it is important to conduct chemical analysis to determine the concentrations of metals in the water.

[2] See above.

    - If the acetic acid solution does not come to a full simmer, hold cookware at the maximum temperature achieved for the two-hour period. Record the achieved temperature.
    - Check the volume of liquid in the cookware against the fill line **every 15 minutes**. To compensate for evaporation, add additional 4% v/v acetic acid solution to the fill line as needed.
- Take 100 mL samples of the simmering solution using a high-density polyethylene (HDPE)[3] container after:
    - 15 minutes (while hot)
    - 2 hours (while hot)
- After 2 hours of simmering, allow the acetic acid solution to remain at room temperature for 24 hours. Measure the pH of the solution with a calibrated pH meter and collect another 100 mL sample

Cooling and Preservation

- Note: Sample containers should be refrigerated overnight until analysis, if possible.
- As the cookware cools, make note of:
    - The presence or absence of precipitate in the cookware
    - The presence or absence of precipitate in the sample container
    - The color of any precipitate (e.g., black, gray, tan)
- To preserve the sample, add sufficient nitric acid (HNO_3) to achieve a pH of <2. This may be done at the time of collection or after transportation to the lab.

Quality Assurance and Quality Control

Blanks, spikes, and duplicates should be carried throughout the process to confirm the accuracy of the test. At a minimum, this should include:

- Blank: Conduct the leachate test using a cookware sample with a lead concentration of 0 ppm.
- Spike: Add a known quantity of lead to the sample prior to conducting the leachate test.
- Duplicate: Conduct the leachate test on two identical samples with identical concentrations of lead.

[3] LDPE containers may be appropriate, as long as they are of high enough quality to prevent leakage during storage.

Preparation for Analysis

Health and Safety

- Concentrated nitric and hydrochloric acids can irritate the skin and mucous membranes. If available, use a fume hood when handling these reagents. Safety protocol should also include the use of gloves, goggles, and protective clothing.

Digestion

If precipitate is present, ensure that the entire sample is digested to completion.

Analysis

- Samples should be analyzed using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) according to US EPA SW-846 Method 6020.
- An appropriate Pb reporting limit is 1 ppb, but specificity is relative to your laboratory's detection limits.
- ★ **Request a copy of QA/QC procedures and results from the analytical lab.**

Data Recording

This section is designed to record data from the leachate experiments. Please complete as many of the following data fields as possible in the provided template:

Variable	Data entry	Definition
Investigator	Free-form	Full name of investigator
OrganizationTesting	Free-form	Organization conducting the analysis
Cookpot_ID	Free-form	From Cookpot ID generated in General Dictionary

Variable	Data entry	Definition
Date	Format enforced	Date leachate testing initiated
Time	Format enforced	Time leachate testing initiated
AceticAcid%	Free-form	Acetic acid concentration (in percent)
Initial_pH	Free-form	Initial pH of acetic acid at room temperature
AchievesSimmer	Dropdown	Did the acetic acid come to a simmer? Yes/No
AceticTemp	Free-form	If the acetic acid did not come to a simmer, temperature achieved (in Celsius/Centigrade). Otherwise, NA
InitialSimmerTime	Free-form	Simmer (or heating if no simmer) time before first sample (hours)
SecondSimmerTime	Free-form	Simmer (or heating if no simmer) time before second sample (hours)
RT_Time	Free-form	Time at room temperature before final sample (hours)
Final_pH	Free-form	Final pH of acetic acid after cooling to room temperature
Initial_PbConc	Free-form	Analytical Pb result after initial simmering (in micrograms per milliliter - ug/ml)
Second_PbConc	Free-form	Analytical Pb result after second simmering (in micrograms per milliliter - ug/ml)

Variable	Data entry	Definition
RT_PbConc	Free-form	Analytical Pb result after resting at room temperature (in micrograms per milliliter - ug/ml)
Precipitate	Dropdown	Was a precipitate noted in the sample? Yes/No
Notes	Free-Form	Additional narrative

Definitions:
Dropdown fields restrict data entry to defined choices from a dropdown menu
Format enforced fields restrict data entry to specific formats
Free-form means that the analyst can enter unstructured text, without specific formatting

Data Documentation

A downloadable Excel version of the sample data collection table can be found here.

Appendix A: XRF Health and Safety

Correct operation of the XRF is critical for keeping investigators safe and for collecting accurate data.

All investigators operating the XRF should be familiar with the safety information presented in *Chapter 2: Using your analyzer* of Niton XL3 Analyzer User's Guide. The use of XRF is restricted to those people who have taken one of the training courses from one of our providers

XRF (X-ray fluorescence) is a non-destructive analytical technique used to determine the elemental composition of materials. XRF analyzers determine the chemistry of a sample by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. Each of the elements present in a sample produces a set of characteristic fluorescent X-rays ("a fingerprint") that is unique for that specific element. If you are interested in reading more about how the XRF works, read ThermoFisher's XRF Technology in the Field.

Primary radiation is radiation that is produced by the analyzer and emitted out through the measurement window.

- **Always treat radiation with respect.**
- **Do not hold your analyzer near the measurement window during testing. Never point your analyzer at yourself or anyone else when the shutter is open**
- There should always be a sample in contact with the measurement window when the x-ray tube is on.
- The sample will absorb most of the primary-beam radiation unless it is smaller than the instrument's measurement window or of low density and/or thickness. Caution should be taken when analyzing samples that are small, thin, and/or low in density as they may allow much more of the primary beam to escape.

The primary beam is a directed beam out of the front of the analyzer that can have high dose rates. The secondary beam, or scattered beam, has much lower dose rates.

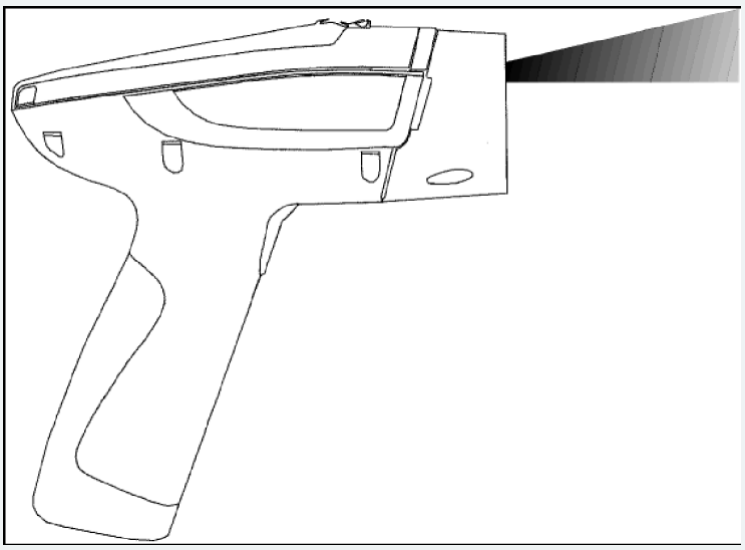

Figure 2. Primary beam

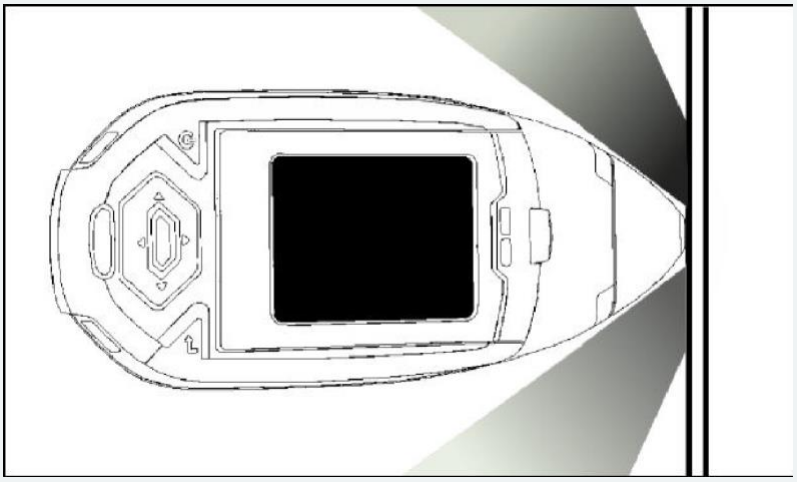

Figure 3. Secondary (scattered) beam

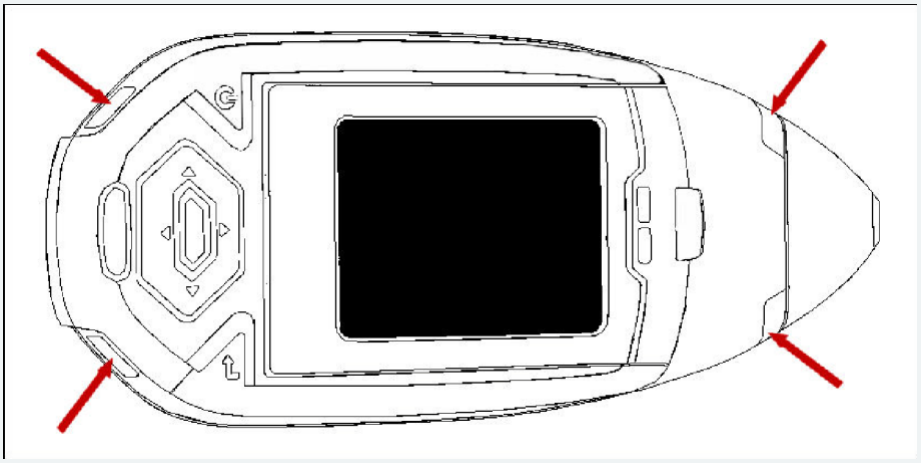

Figure 4. X-ray beam indicator lights