UNITED STATES
CONSUMER PRODUCT SAFETY COMMISSION
DIRECTORATE FOR LABORATORY SCIENCES
DIVISION OF CHEMISTRY
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ROCKVILLE, MD 20850

Test Method: CPSC-CH-E1001-08.3

Standard Operating Procedure for Determining Total Lead (Pb) in Children's Metal Products (Including Children's Metal Jewelry), Revision

November 15, 2012[*]

This document provides detailed information on test methods that will be used by the U.S. Consumer Product Safety Commission's (CPSC's) testing laboratory (LSC) in the analysis of children's metal products for lead (Pb) content. The set of methods described here is used to determine the total lead content of metal items, such as, but not limited to, children's metal jewelry. This revision recognizes the use of X-ray Fluorescence Spectroscopy (XRF) measurement techniques to analyze certain homogeneous materials with certain limitations and acceptable ranges, and it replaces the previously issued Test Method CPSC-CH-E1001-08.2.

CPSC staff has concluded[1] that these test methods are sufficient to determine lead content in most metal consumer products. Adjustments may be necessary for products made from certain alloys, and they should be based on sound chemistry knowledge and appropriate acids for the matrix. Test methods selected should demonstrate best that they can achieve total digestion of the sample material being analyzed. Test methods shall not be used if they are inconsistent with the specified application of the test method or do not demonstrate the best performance or proficiency for achieving total digestion of the sample material.

The methods apply to metal and metal alloy components and have not been recommended by CPSC staff for other materials that will not dissolve under the conditions specified below, or when combined with the specified acid(s), result in an inappropriate combination of materials that would be inconsistent with safe laboratory practices.

The general approach is to grind any accessible component part of a sample to a powder; digest the powder completely in a combination of hot, concentrated nitric and hydrochloric acids; and then analyze the digested metal by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES).

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[*] This is a revision of Test Method CPSC-CH-E1001-08.1. This document was prepared by CPSC staff, has not been reviewed or approved by, and may not necessarily reflect, the views of the Commission.

[1] US CPSC. *Study on the Applicability of X-ray Fluorescence Spectrometry for Measuring Lead in Metal and Glass Substrate, Jan 2012.* (Tab C in http://www.cpsc.gov/library/foia/foia12/brief/tprequirements.pdf)

Other analytical methods, such as Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) and Flame Atomic Absorption Spectroscopy (FLAA) and Graphite Furnace Atomic Absorption Spectroscopy (GFAA), may be used under appropriate conditions as an alternative to ICP-OES, using applicable, recognized analytical techniques for the alternative method.

Alternately, section III (below) describes how XRF spectroscopy can be used, with limitations, to determine lead content in homogeneous metal substrates. The general approach in that case is to consider any XRF result to be indeterminate and in need of digestion and ICP analysis if that result falls within 30 percent of the Consumer Product Safety Improvement Act (CPSIA) limit.

Definitions

1. Sample–an individual consumer product or a group of identical consumer products from a batch to be tested.
2. Component Part–individual subunit within the total sample. An item such as a bracelet may be broken into its component parts, such as a bead, a hook, a pendant, with those component parts individually analyzed.
3. Instrument Detection Limit (IDL)–three times the standard deviation of 10 replicate measurements of laboratory reagent blank.
4. Method Detection Limit (MDL)–reagent blank fortified with 2–3 times the IDL. Seven replicate measurements are made. Calculate the MDL as follows: MDL = t x S, where t = 3.14 (99 percent confidence level for 7 replicates) and S = standard deviation.
5. Laboratory Reagent Blank (LRB)–extraction or digestion media used for a particular Pb test. LRB data are used to assess contamination from the laboratory environment.
6. Calibration Blank–deionized water acidified with nitric acid (3 ml concentrated nitric acid diluted to 100 ml with deionized water).
7. Stock Standard Solution–1,000 ppm solution of Pb purchased from a reputable commercial source, used to prepare calibration standards. Replace before expiration date.
8. Calibration Standard–solutions containing 0 to 25 ppm of Pb in a 3 percent nitric acid matrix are used. A minimum of 4 calibration standards are used. Calibration standards shall be prepared bi-weekly, at a minimum.
9. Quality Control Sample (QCS)–a solution containing Pb that is used to evaluate the performance of the instrument system. QCS is obtained from a source external to the laboratory and to the Stock Standard Solution.
10. Certified Reference Material (CRM)–CRMs are materials with similar matrix as test samples with known lead levels. The CRMs are used to verify digestion and analysis methods. Examples of CRMs are listed in the Equipment and Supplies section below, but are not limited only to the ones listed.

Equipment and Supplies: The materials used for sampling and analyses are as follows:

1. Nitric Acid, Trace Metal Grade
2. Hydrochloric Acid, Trace Metal Grade
3. Digestion Vessels, 50ml
4. Hot Block Digester (such as Environmental Express HotBlock)

5. Metal Cutters
6. Distilled Water
7. Microwave Digestion Apparatus
8. Rotary Grinder (such as Dremel Tool) with carbide burr grinders
9. Orbital Shaker
10. CRMs for Metals with known lead content such as NIST SRM 54d, 1728.
11. Internal Standard (such as yttrium, from a stock standard solution of that element, appropriate to the instrument parameters of the ICP used for the analysis)

I. Total Pb in Metals - Digestion of Sample

When preparing a sample, the laboratory should make every effort to ensure that the aliquot removed from a component part of a sample is representative of the component to be tested and is free of contamination.

Each unique, accessible component part from a sample is analyzed for total Pb content. CPSC laboratory staff uses either of two methods for determining lead content in metal items.

One method used by CPSC staff is a hot block digestion, based on methodology found in Canada Product Safety Bureau Method C-02.4.[2] This method is equivalent to the procedure referred to as *I. Screening Test for Total Pb Analysis,* given in the *CPSC Standard Operating Procedure for Determining Lead (Pb) and its Availability in Children's Metal Jewelry* dated February 3, 2005 (http://www.cpsc.gov/businfo/pbjeweltest.pdf). Note that the second part of the referenced procedure for determining acid extractability of Pb is not applicable for the determination of total lead content.

The other method used by LSC is a microwave digestion method based on EPA method 3051A[3] (http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3051a.pdf), with modifications as described below.

Modifications of these methods may be necessary for certain alloys, taking into account appropriate acids for digestion. Certified reference materials that closely match the alloy of the tested product should be used to verify accuracy of the digestion and analysis methods.

SAMPLE PREPARATION METHODS

Either of two methods outlined below have been found by LSC staff to be suitable for preparation of metal samples within the scope of this document for subsequent elemental analysis.

A. Hot Block Method

1. If the item is coated with paint or a similar surface coating (it may contain Pb), the coating shall be removed and analyzed separately from the base metal for lead content,

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[2] Determination of Total Lead in Metallic Consumer Products.
[3] Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils.

as described in the CPSC Standard Operating Procedure for Determining Lead (Pb) in Paint (http://www.cpsc.gov/businfo/leadsop.pdf). Care should be taken to remove as little of the substrate metal as possible.

2. Weigh out 30–100mg of a component part in labeled 50ml digestion vessel. Component parts of children's products, including metal jewelry items, generally weigh several grams or more, and an aliquot (with no paint or similar surface coating, but including any electroplated coating that is considered to be part of the substrate) will have to be obtained. Samples should be cut or ground into many small pieces to increase the rate of dissolution. If used, grinding apparatus (such as a rotary grinding tool with disposable grinding bits) must be cleaned thoroughly to prevent cross-contamination. Record actual weight to the nearest 0.1mg.
3. In a chemical fume hood, add 8ml of concentrated nitric acid to each beaker, and evaporate to approximately 3ml on a hot block digester at 105±3°C.
4. After cooling, add 2ml of concentrated hydrochloric acid, and stir.
5. Dilute with distilled water, washing the side of the beaker, to 20ml.
6. Warm up solution to at least 60°C, and gently agitate on orbital shaker, or with a stirrer or shaker bath for a minimum of 4 hours.
7. Transfer quantitatively into a 50ml volumetric flask or disposable volumetric digestion cups, and dilute to 50ml with distilled water.
8. Dilute samples so that Pb results are within calibration range of instrument. Generally, a 1:50 dilution is sufficient.

B. Microwave Method

1. If the item is coated with paint or a similar surface coating (it may contain Pb), the coating shall be removed and analyzed separately from the base metal for lead content, as described in the CPSC Standard Operating Procedure for Determining Lead (Pb) in Paint (http://www.cpsc.gov/businfo/leadsop.pdf). Care should be taken to remove as little of the substrate metal as possible.
2. Weigh out a 30–100mg piece of metal item into appropriate microwave vessel equipped with a controlled pressure relief mechanism. Component parts of children's products, including metal jewelry items, generally weigh several grams or more, and an aliquot (with no paint or similar surface coating) will have to be obtained. Samples should be cut or ground into many small pieces to increase the rate of dissolution. If used, grinding apparatus (such as a rotary grinding tool with disposable grinding bits) must be cleaned thoroughly to prevent cross-contamination. Record actual weight to the nearest 0.1mg.
3. Add 4.5ml of concentrated nitric acid and 1.5ml of concentrated hydrochloric acid to each vessel. Wait for initial reaction of acid and sample at room temperature to be complete (to the point of no obvious fuming or bubbling) before sealing vessels. Seal vessels in accordance with the manufacturer's directions.
4. The microwave method should involve increasing the temperature of each sample to 175°C in approximately 5.5 minutes, and holding at 175°C for 4.5 minutes.
5. Allow the samples to cool for a minimum of 5 minutes before removal from the microwave. Vent the microwave vessels in fume hood before uncapping.
6. Quantitatively transfer the sample to 50 ml volumetric flask or disposable volumetric digestion cups. Dilute to 50 ml with deionized water.

Caution: The analyst should wear protective gloves and face protection. This document does not address all safety concerns; additional safety precautions are necessary for all steps. This method is not to be used except by qualified, properly trained workers.

II. Total Pb in Metals Analysis

Analyze diluted samples for Pb concentration, using an ICP spectrometer (or Atomic Absorption spectrometer). Analysis procedures for ICP-OES and FLAA and GFAA are based on the methodology in ASTM E1613-04.[4] ICP-MS may also be employed with appropriate procedures, such as EPA 6020A.[5] (Note: Method C-02.4 describes an alternate procedure for analysis by Atomic Absorption Spectroscopy.) Calculate total lead concentration in the component part from that of the diluted sample, accounting for all dilution, and reported as percent by weight of the component part itself.

ICP Operating Procedures and Quality Control Measures

Analysis

1. Ignite plasma. Perform wavelength calibration or torch alignments per instrument manufacturer's recommendations.
2. Allow the instrument to become thermally stable before beginning.
3. Ensure the following element and wavelength are selected in analytical method:
    a. Pb 220.353.
    b. One other Pb line, such as Pb 217.00, to ensure spectral interferences are not occurring during analysis.
4. An internal standard, such as 2 µg/ml yttrium, is used.
5. Perform calibration using calibration blank and at least three standards. Calibration shall be performed a minimum of once a day when used for analysis, or each time the instrument is set up. Results for each standard shall be within 5 percent of the true value, and the calibration blank should be < 5 times MDL. If the values do not fall within this range, recalibration is necessary.
6. Analyze the QCS after the calibration and before any samples. The analyzed value of Pb should be within ±10 percent of the expected value. If Pb value is outside the ±10 percent limit, recalibration is required.
    a. At least one LRB must be analyzed with each sample set. If the Pb value exceeds 10 times the MDL, then laboratory or reagent contamination should be expected. The source of the contamination should be identified and resolved before continuing analyses. The LRBs should be the same acid concentrations as added to the sample and should be taken through the same digestion procedure.
7. At least one certified reference material (CRM) should be analyzed with each batch of samples. The CRM should be similar material as test specimen with a known amount of Pb. Analyte recoveries should be within ±15 percent of expected values. If recoveries

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[4] Standard Test Method for Determination of Lead by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Flame Atomic Absorption Spectrometry (FAAS), or Graphite Furnace Atomic Absorption Spectrometry (GFAAS) Techniques.

[5] Inductively Coupled Plasma-Mass Spectrometry.

are outside this limit, the source of the problem should be identified and resolved before continuing analyses.

8. Dilute any samples that have Pb values exceeding 1.5 times the high calibration standard and reanalyze.

Calculations and Results Reported

Results for the Pb test methods are calculated and reported as follows:

Total Percentage Pb: % Pb (wt./wt.) = C x D / W x 100% /1000 µg/mg

a. C= concentration of Pb detected (in units of µg/ml)
b. D= dilution factor (in ml units)
c. W= weight of aliquot digested (in mg units)

Example:

A 50 mg aliquot of a component part was digested and diluted to 1000 ml in order to analyze by ICP. The ICP analysis found 20 µg/ml of lead in the solution, which showed that the original component part contained 40 percent Pb by weight.

	(C)	**(D)**		**(W)**	
Component	**Concentration Detected on ICP (µg/ml Pb)**	**Dilution Factor (ml)**	**Total Pb (µg)**	**Sample wt. (mg)**	**% Pb**
Pendant 1	20	1,000	20,000	50	40

III. Total Pb in Metals Determined by X-ray Fluorescence Spectrometry

A. Identification and Quantification of Pb in Homogeneous Metal Materials Using Energy Dispersive XRF Spectrometry Using Multiple Monochromatic Excitation Beams

Alternately, Energy Dispersive XRF Spectrometry Using Multiple Monochromatic Excitation Beams (HDXRF) can be used to determine quantitatively the amount of Pb in homogeneous metal materials by following ASTM F2853-10e1,[6] with limitations. ASTM F2853-10e1 is applicable only for homogeneous metal materials and for XRF instruments meeting the requirements given in the ASTM method. The following limitations apply:

1. This method is applicable only for analysis of homogeneous materials. It is not suitable for testing electroplated metal alloys.
2. Multiple measurements on different locations of the sample component part should be performed to ensure some degree of spatial homogeneity, unless the component part is

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[6] Standard Test Method for Determination of Lead in Paint Layers and Similar Coatings or in Substrates and Homogenous Materials by Energy Dispersive X-Ray Fluorescence Spectrometry Using Multiple Monochromatic Excitation Beams.

small enough that distinct different measurements could not be made. If the relative standard deviation (the standard deviation divided by the mean) of three or more XRF measurements of a sample component part exceeds 30 percent, analysis using wet chemical procedures (after preparing a homogenized aliquot by grinding sufficient sample) should be done before determining the items meet CPSIA requirements for lead. If each of the 3 or more XRF measurements taken is below 50 percent of the limit (*i.e.*, below 50 ppm) this limitation on relative standard deviation shall not apply, but the remaining limitations still hold.

3. Any XRF measurement of lead concentration, where the interval comprised of the reported result, plus or minus the instrument's reported 95 percent uncertainty, includes the range with 30 percent above or below the CPSIA limit shall be considered "inconclusive." An average of at least three measurements, none of which is "inconclusive," as defined in this paragraph, should be obtained in order to have a "conclusive" result.[7]
4. For "inconclusive" results, additional testing is necessary in order to make a determination, such as by digestion and ICP analysis per sections I and II.

B. Identification and Quantification of Pb in Homogeneous Metal Materials Using Other Forms of XRF Spectrometry

Other types of XRF spectrometers that do not meet the requirements of ASTM F2853-10 can be used to determine quantitatively the amount of Pb in homogeneous metal materials with limitations. The following limitations apply, in addition to those outlined in Section I-B for HDXRF:

1. Follow sampling, testing, calibration, quality control guidelines described in section 6 of International Electrotechnical Commission (IEC) Method 62321 ED 1.0 B[8].
2. A set of at least four calibration standards should be used to validate that the instrument is suitable for testing for Pb for each material or metal type (*e.g.*, aluminum base, zinc base, iron base) to be tested. The calibration standards should cover the applicable range to certify that the sample meets CPSIA lead content requirements (0−2000 mg/kg). At least one standard in each calibration set should have a lead concentration less than 100 mg/kg.
3. Verify the instrument performance daily by analyzing one or more reference materials of the same matrix or metal type as the materials on which analyses will be performed. The lead concentration of the reference material should be in the range of 50–300 mg/kg, and the determined concentration from the measurement must be in agreement

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[7] For example, if the XRF instrument reports a result of 65 ppm lead with an uncertainty of 10 ppm lead for a material subject to the CPSIA limit of 100 ppm lead content, this measurement would be considered inconclusive because 65 ppm +10 ppm = 75 ppm which is less than 30 percent below the applicable limit of 100 ppm. A reported result of 60 ppm with a reported uncertainty of 8 ppm would be a conclusive measurement of a material subject to the CPSIA limit of 100 ppm as 68 ppm is more than 30 percent below the applicable limit of 100 ppm.

[8] Electrotechnical products – Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers).

with the known or certified value. The measured result with the given uncertainty (at 95 percent confidence) should overlap with the reported certified values and the given uncertainty of the reference materials.

4. The limit of detection (LOD) for lead in each material or metal type should be determined following guidelines in section 6 of IEC 62321. The lead LOD shall be equal to or less than 30 mg/kg for the specific material or metal type tested. Some types of XRF spectrometers may not have the sensitivity to obtain sufficient LOD for certifying to lead requirements.

Summary of Changes in Revision CPSC-CH-E1001-8.1

1. Page 1, revised test method # and date.
2. Page 2, removed IDL and MDL CPSC lab values; not relevant to method and new instruments will have different values.
3. Page 2, definition 10, last sentence revised to allow other sources for CRMs.
4. Page 3, changed CRMs recommended, removed NIST 53e and 1129 (not certified for Pb), and added 1728 (new NIST SRM with 545 ppm Pb in Tin matrix).
5. Page 4, changed microwave temperature requirements from "175±5" to "at least 175."

Summary of Changes in Revision CPSC-CH-E-1001-8.2

1. Page 1, revised test method # and date.
2. Page 2, changed to biweekly from weekly minimum time between calibration standard preparations.
3. Page 2, added paragraph stating X-Ray Fluorescence (XRF) Spectroscopy can be used with limitations to determine lead content in homogeneous metal substrates.
3. Page 5, **Analysis** step 5, added statement that calibration blank should be < 5 times MDL.
4. Page 5, **Analysis** step 6, removed "immediately" after QCS and added "and before any sample" after calibration.
5. Page 5, **Analysis** step 6a, changed "the LRB shall not exceed 3 times MDL" to "the LRB shall not exceed 10 times MDL." This change reflects lower MDLs achieved on some instruments in particular ICP-MS and the difficulty in LRB meeting three times MDL.
6. Page 6, added section III **Total Pb in Metals Determined by X-ray Fluorescence Spectrometry.**

Summary of Changes in Revision CPSC-CH-E-1001-8.3

1. Page 7, limitation number 2 for XRF use, added statement allowing use of XRF for samples with lead readings below 50 percent of limit, in certain circumstances with >30% RSD, and made allowance for component parts which are too small for multiple distinct measurements.