



**UNITED STATES  
CONSUMER PRODUCT SAFETY COMMISSION  
DIRECTORATE FOR LABORATORY SCIENCES  
DIVISION OF CHEMISTRY  
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**Test Method: CPSC-CH-E1001-8.1  
Standard Operating Procedure for Determining Total Lead (Pb) in Metal  
Children's Products (including Children's Metal Jewelry), Revision  
June 21, 2010\***

This document provides detailed information on test methodologies that will be used by the U.S. Consumer Product Safety Commission's testing laboratory (LSC) in the analysis of children's metal products for lead (Pb) content. The set of methods described are used to determine the total lead content of metal items such as but not limited to children's metal jewelry. This version replaces the previously issued Test Method CPSC-CH-E1001-08. The changes are mainly editorial in nature.

CPSC staff has concluded 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 should be based on sound chemistry knowledge and appropriate acids for the matrix. Test methods selected shall be those that best demonstrate 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) results in an inappropriate combination of materials that would not be consistent with safe laboratory practices.

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

\*This is a revision of CPSC Test Method CPSC-CH-E1001-08. This document was prepared by CPSC staff, has not been reviewed or approved by, and may not necessarily reflect the views of the Commission

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.

### **Definitions**

1. Sample – An individual consumer product or a group of identical consumer products from a batch to be tested.
2. Component part – Individual sub-unit within the total sample. An item such as a bracelet may be broken into its component parts such as bead, hook, pendant, with those component parts individually analyzed.
3. Instrument Detection Limit (IDL) – 3 times the standard deviation of 10 replicate measurements of 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:  $MDL = t \times S$ ,  $t = 3.14$  (99% confidence level for 7 replicates),  $S$  = 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 – 1000 ppm solution of Pb purchased from reputable commercial source, used to prepare calibration standards. Replace before expiration date.
8. Calibration Standards - Solutions containing 0 to 25 ppm of Pb in 3% nitric acid matrix are used. A minimum of 4 calibration standards are used. Calibration standards shall be prepared weekly.
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 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 to only 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 Hot Block)
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, etc.
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**

When preparing a sample, the laboratory shall make every effort to assure 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 use 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.<sup>1</sup> 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 2/3/2005 (<http://www.cpsc.gov/businfo/pbjeweltest.pdf>). Note that the second part of the reference procedure for determining acid extractability is not applicable for the determination of total lead content.

The other method used by CPSC staff is a microwave digestion method based on EPA method 3051A<sup>2</sup> (<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 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 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

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<sup>1</sup> Determination of Total Lead in Metallic Consumer Products

<sup>2</sup> Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils

or more, and an aliquot (with no paint or similar surface coating, but including any electroplated coating which 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 thoroughly cleaned to prevent cross-contamination. Record actual weight to the nearest 0.1 mg.

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  $105 \pm 3^\circ\text{C}$ .
4. After cooling, add 2ml of concentrated hydrochloric acid and stir.
5. Dilute with distilled water, washing side of beaker, to 20ml.
6. Warm up solution to at least  $60^\circ\text{C}$  and gently agitate on orbital shaker or with 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 30-100 mg 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 thoroughly cleaned to prevent cross-contamination. Record actual weight to the nearest 0.1 mg.
3. Add 4.5 ml of concentrated nitric acid, and 1.5 ml 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 manufacturer's directions.
4. The microwave method should involve increasing temperature of each sample to at least  $175^\circ\text{C}$  in approximately 5.5 minutes, and holding at  $175^\circ\text{C}$  for 4.5 minutes.
5. Allow the samples to cool for a minimum of 5 minutes before removal from 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.

## **II. Total Pb in Metals Analysis**

Analyze diluted samples for Pb concentration using ICP spectrometer (or Atomic Absorption spectrometer). Analysis procedures for ICP-OES and FLAA and GFAA are

based on methodology found in ASTM E 1613-04<sup>3</sup>. ICP-MS may also be employed with appropriate procedures, such as EPA 6020A<sup>4</sup>. (Note: Method C-02.4 describes 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 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 is used 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 3 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% of the true value. If the values do not fall within this range, recalibration is necessary.
6. Analyze the QCS immediately after the calibration. The analyzed value of Pb should be within  $\pm 10\%$  of the expected value. If Pb value is outside the  $\pm 10\%$  limit recalibration is required.
  - a. At least one LRB must be analyzed with each sample set. If the Pb value exceeds 3 times the MDL, the 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 (CR) will be analyzed with each batch of samples. The CR should be similar material as test specimen with a known amount of Pb. Analyte recoveries should be within  $\pm 15\%$  of expected values. If recoveries 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.

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<sup>3</sup> 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

<sup>4</sup> Inductively Couple Plasma-Mass Spectrometry

## Calculations and Results Reported

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

Total Percentage Pb:  $\%Pb \text{ (wt./wt.)} = C \times D / W \times 100\% / 1000 \mu\text{g/mg}$

- a. C= concentration of Pb detected (in units of  $\mu\text{g/ml}$ )
- b. D= dilution factor (in ml units)
- c. W= weight of aliquot digested (in mg units)

Example:

Table 1: Total Pb Analysis

A 50mg aliquot of a component part was digested and diluted to 1000ml in order to analyze by ICP. The ICP analysis found 20 $\mu\text{g/ml}$  of lead in the solution, which showed that the original component part contained 40% Pb by weight.

	(C)	(D)		(W)	
	Concentration Detected on ICP ( $\mu\text{g/ml Pb}$ )	Dilution factor (ml)	Total Pb ( $\mu\text{g}$ )	Sample wt. (mg)	% Pb
Component					
Pendant 1	20	1000	20,000	50	40

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

1. Page 1 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) added 1728 (new NIST SRM with 545 ppm Pb in Tin matrix)
5. Page 4, changed microwave temperature requirements from “175 $\pm$ 5” to “at least 175”