UNITED STATES
CONSUMER PRODUCT SAFETY COMMISSION
DIRECTORATE FOR LABORATORY SCIENCES
DIVISION OF CHEMISTRY
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Test Method: CPSC-CH-E1001-08

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

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This document provides detailed information on test methods that will be used by the U.S. Consumer Product Safety Commission's (CPSC) testing laboratory (LSC) in the analysis of children's metal products for lead (Pb) content. The methods described determine the total lead content of metal items such as, but not limited to, children's metal jewelry.

CPSC staff has concluded that these test methods are sufficient to determine lead content in most metal and metal alloy consumer product component parts. Adjustments may be necessary for products made from certain metal alloys, and should be based on sound chemistry and materials science knowledge as well as appropriate acids for the alloy matrix. Test methods selected should be those that best demonstrate that they can achieve total digestion of the sample material being analyzed. Test methods should 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 completely in a combination of hot, concentrated nitric and hydrochloric acids; and analyze by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES).

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 analytical 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 a bead, a hook, and a pendant, with those component parts individually analyzed.
3. Instrument Detection Limit (IDL) – 3 times the standard deviation of 10 replicate measurements of reagent blank. The IDL for Pb on the Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) currently used by LSC is 0.01 ppm.
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% confidence level for 7 replicates) and S = standard deviation. The MDL determined based on current LSC staff practices and equipment for Pb is 0.01 ppm.
5. Laboratory Reagent Blank (LRB) – An aliquot of the digestion reagents that is treated exactly as a sample including exposure to glassware, digestion media, apparatus and conditions used for a particular Pb test, but with no added metal sample. 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 (in nitric acid) purchased from reputable commercial source, used to prepare calibration standards. Replace before expiration date.
8. Calibration Standard – 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 should be prepared weekly from the stock solution.
9. Quality Control Sample (QCS) – Solutions containing Pb that are used to evaluate the performance of the analytical instrument system. QCSs are obtained from a source external to the laboratory and are not made from the Stock Standard Solution.
10. Certified Reference Material (CRM) – CRMs are materials with similar matrices as test samples with known lead levels. The CRMs are used to verify digestion and analysis methods. For example, standard reference materials (SRMs) are CRMs that are available from the National Institute of Standards and Technology (NIST), such as those listed in the Equipment and Supplies section below.

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 (glass or plastic suitable for the digestion conditions)
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 Leaded Metals (such as NIST SRM 53e, 54d, 1129, 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 of Sample

When preparing a sample, the laboratory should 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 must be analyzed for total Pb content. LSC uses either of two methods for determining lead content in metal items.

One method used by LSC is a hot block digestion, based on methodology found in Canada Product Safety Bureau Method C-02.4.[1] 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[2] (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 the 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, the coating should 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 aliquot of a component part in a labeled 50ml digestion vessel. Component parts of children's products including metal jewelry items generally weigh

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

several grams 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 dissolution rate. If a grinding apparatus (such as a rotary grinding tool with disposable grinding bits) is used, then any contaminated parts must be thoroughly cleaned or disposed of between uses to prevent cross-contamination. Record the actual weight of the aliquot of the ground up component part 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 to below 50°C, add 2ml of concentrated hydrochloric acid and stir.
5. Dilute with distilled water, washing the side of the beaker, to 20ml.
6. Warm up the solution to at least 60°C without boiling and gently agitate on an 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 the calibration range of the instrument. Generally a 1:50 dilution is sufficient.

B. Microwave Method

1. If the item is coated with paint or a similar surface coating, the coating should 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 an 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, 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 dissolution rate. If a grinding apparatus (such as a rotary grinding tool with disposable grinding bits) is used, then any contaminated parts must be thoroughly cleaned or disposed of between uses to prevent cross-contamination. Record the actual weight of the aliquot of ground up component part to the nearest 0.1mg.
3. In a chemical fume hood, add 4.5ml of concentrated nitric acid and 1.5ml of concentrated hydrochloric acid to each vessel. Wait for the 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 microwave digester manufacturer's directions.
4. The microwave method should involve increasing the temperature of each sample to 175±5°C in approximately 5.5 minutes, and holding at 175±5°C for 4.5 minutes.
5. Allow the samples to cool for a minimum of 5 minutes before removal of the vessels from the microwave. Vent the microwave vessels in fume hood before uncapping.
6. Quantitatively transfer the sample to a 50ml volumetric flask or disposable volumetric digestion cups. Dilute to 50ml with deionized water.

II. Total Pb in Metals - Analysis of Sample Using ICP Method

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[3]. ICP-MS may also be employed with appropriate procedures, such as EPA 6020A[4]. 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 3 standards appropriate to the concentration of the analyte and instrument, such as 0.25, 0.5, 1.0 and 5.0 µg/ml. 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 ±10% of the expected value. If the Pb value is outside the ±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, 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 but without added sample.
7. At least one certified reference material (CRM) should be analyzed with each batch of samples. The CRM should be similar material as the test specimen with a known amount of Pb. Analyte recoveries should be within ±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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[3] 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

[4] Inductively Coupled Plasma-Mass Spectrometry

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 1000 µg/mg)] x 100% where:

C = concentration of Pb detected (in units of µg/ml)
D = dilution factor (in ml units)
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% 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	1000	20,000	50	40