UNITED STATES
CONSUMER PRODUCT SAFETY COMMISSION
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Standard Operating Procedure for Determining Lead (Pb) and Its Availability in Children's Metal Jewelry
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This document provides detailed information on two 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 jewelry. The first methodology is used to determine the total lead content of a jewelry item or component. It will be used as a screening test for purposes of the Interim Enforcement Policy issued by the Office of Compliance on February 3, 2005. The second methodology is an acid extraction test. It is used to quantify the amount of lead that may migrate from jewelry and result in human exposure through ingestion.

These methodologies are provided to inform interested parties of the methods used by LSC for assessing the availability of lead for estimating potential human exposure. They are not required to be followed by other laboratories in making such assessments; however, other laboratories should consider using these procedures to ensure they obtain results that are consistent with CPSC's for purposes of the Interim Enforcement Policy announced by the Office of Compliance.

CPSC staff has concluded that these test methodologies are sufficient to make appropriate determinations concerning children's metal jewelry. Accordingly, we intend to use them in lieu of the test methodologies previously followed.

Definitions

1. Sample – The complete package of a product collected by CPSC field staff and submitted to LSC for analysis. A sample generally contains single or multiple identical units of a particular product. The sample will have an official seal with a sample number, inspector name, and date the package was sealed. Each individual item in a sample is identified with the sample number and sub-numbers, if there is more than one item in the sample. As an example, a sample may contain single or multiple items such as necklaces, rings, bracelets, etc.
2. Item – Individual sub-sample within the total sample, such as a necklace, a ring or a bracelet that can be subjected to lead testing. Ideally, the sample should contain only identical items, not a mix of several different items. 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. The IDL for Pb 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, t= 3.14 (99% confidence level for 7 replicates), S= standard deviation. The MDL determined for Pb is 0.01 ppm.
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 1, 5, 10, and 25 ppm of Pb in 3% nitric acid matrix are used for digests and extracts containing high Pb levels. Solutions containing 0.1, 0.25, 0.5, and 1 ppm of Pb in 3% nitric acid matrix are used for digests and extracts containing lower Pb levels. Calibration standards shall be prepared weekly.
9. Laboratory Performance Check Solution (LPC) - A Pb standard used to evaluate the performance stability of the instrument system. One of the calibration standards is generally used.
10. 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.
11. Laboratory Fortified Blank (LFB) – LRBs to which known quantities of Pb are added in the laboratory. The LFB is extracted and analyzed exactly like a sample. Its purpose is to determine whether method performance is within acceptable control limits.

Materials and Reagents: The materials used for sampling and analysis are as follows:

1. Nitric Acid, Trace Metal Grade
2. Hydrochloric Acid, Trace Metal Grade
3. Glass Beakers, 50ml
4. Glass Beakers or Erlenmeyer Flasks - Shall be large enough to contain extract solutions that are 50 times greater than individual jewelry item weight.
5. Water/Shaker Bath
6. Hot Plate
7. Lead-free Insulated Wire.
8. Metal Cutters
9. Parafilm®
10. Distilled Water

I. Screening Test for Total Pb Analysis

Each unique component type from one subsample is analyzed for total Pb content. The procedure for Total Pb Analysis is as follows and is based on methodology found in Canada Product Safety Bureau Method C-02.4:

1. If the children's metal jewelry 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 Association of Official Analytical Chemists (AOAC) standard AOAC 974.02 (Lead in Paint). Care should be taken to remove as little of the substrate metal as possible.
2. Weigh out a 30-50 mg piece of children's metal jewelry in labeled 50ml beaker. Children's metal jewelry items generally weigh several grams, and an aliquot piece (with no paint or similar surface coating) will have to be clipped from item using metal cutters. Samples should be cut into several small pieces or ground to increase the rate of dissolution. If used, grinding apparatus must be thoroughly cleaned to prevent cross-contamination. Record actual weight to the nearest 0.1 mg.
3. Add 8ml of concentrated nitric acid to each beaker and evaporate to approximately 3ml on a hot plate.
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 and gently agitate with stirrer or shaker bath for a minimum of 4 hours.
7. Transfer quantitatively into a 50ml volumetric flask 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.
9. Analyze diluted samples for Pb concentration using ICP spectrometer. High Pb standard calibration curve will be required. Analysis procedure is based on methodology found in ASTM E 1613. (Note: Method C-02.4 describes alternate procedure for analysis by Atomic Absorption Spectroscopy.)

II. Acid Extraction Test

The acid extraction simulates exposure to metal that is ingested into the alimentary tract. The analysis is generally performed on an intact item or component. The procedure for the acid extraction is as follows and is based on methodology found in ASTM C927, C738, D5517, and F963:

1. Suspend the children's metal jewelry item in a flask or beaker using insulated wire so that the item does not touch the bottom or edge of the flask/beaker, but will be submerged by acid.
2. Add 0.07N hydrochloric acid (HCL) solution to cover the jewelry item. The amount of acid solution added should be equivalent to 50 times the weight of the jewelry item. Record the volume of acid solution added. Ensure that the jewelry item is submerged.
3. Extraction is conducted for 1 hour at 37°C in the shaker bath.
4. After the 1 hour extraction period, all the acid extract is taken out, an aliquot saved for analysis, and fresh acid extract is added. The second extraction is conducted for 2 hours at 37°C on shaker bath.
5. After the 2 hour extraction period, all the acid extract is taken out, an aliquot saved for analysis, and fresh acid extract is added. The third extraction is conducted for 3 hours at 37°C on shaker bath.

6. After the 3 hour extraction period, all the acid extract is taken out, and an aliquot saved for analysis. The product has been exposed to a total time of 6 hours (1 + 2 + 3 = 6 hours) of extraction.
7. Each of the three extracted solutions is analyzed for Pb content using an ICP spectrometer. The high lead standard curve is generally required. Analysis procedure is based on methodology found in ASTM E 1613.

ICP Operating Procedures and Quality Control Measures

Analysis

1. Perform wavelength calibration monthly. This can be done prior to igniting plasma. An internal mercury lamp is used for wavelength calibration.
2. Ignite plasma. Set conditions as follows, these are the conditions recommended by the instrument manufacturer:
    a. R.F. Power = 1150 watts
    b. Auxiliary flow = 1 liter /minute
    c. Nebuliser flow = 30.06psi
    d. Pump rate = 100 rpm
    e. Purge Time = 10 seconds
3. Allow the instrument to become thermally stable before beginning. This requires at least 30 minutes of operation prior to doing peak search for Pb.
4. Open the Lead Method for samples requiring high Pb standards or the Low Lead Method for samples requiring low Pb standards.
5. Ensure the following element and wavelength are selected:
    a. Pb 220.353
6. Perform peak search using 5 ppm Pb standard to ensure optimum setting.
7. Perform calibration using calibration blank and 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.
8. Analyze the QCS immediately after the calibration. The analyzed value of Pb should be within ±10% of the expected value. If Pb value is outside the ±10% limit recalibration is required.
9. Analyze the LPC following QCS analysis, after every 10^{th} sample, and at the end of the sample run. The analyzed value for Pb should be within ±5% of its expected value. If Pb value is outside the interval, reanalyze the LPC. If the Pb value is again outside the ±5% limit, recalibrate the instrument. All samples following the last acceptable LPC analysis should be reanalyzed.
10. 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 for the two Pb test procedures are as follows:
    a. Total Pb – 8ml of concentrated nitric acid are placed in a 50ml beaker and heated on a hot plate with samples until concentrated to about 3ml followed by the addition of 2ml of concentrated HCL solution, then diluted to 50ml with deionized water after cooling.

b. Acid – 0.07N HCL solution

11. At least one LFB will be analyzed with each batch of samples. The LFB should be an LRB that is spiked with a known amount of Pb stock solution. LFBs should be prepared so that expected Pb values are within the calibration curve. Analyte recoveries should be within ±20% of expected values. If recoveries are outside this limit, the source of the problem should be identified and resolved before continuing analyses.
12. Dilute any samples that have Pb values exceeding 1.5 times the high calibration standard, and reanalyze.

Calculations and Results Reported

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

1. Total Pb - %Pb (wt./wt.) = 0.10cd/w
   a. c= concentration of Pb detected (in units of ppm)
   b. d= dilution factor (in ml units)
   c. w= weight of aliquot digested (in mg units)

2. Acid Extraction Test - Results for each extraction stage (1, 2, and 3 hour) should be recorded separately as:
   µg Pb extracted = cd
   a. c = concentration of Pb detected (in ppm)
   b. d= dilution factor (in ml)
   - The total weight (in grams) of the jewelry item should be measured

Examples:

Table 1: Total Pb Analysis

	(c)	(d)		(w)	
Item	**ppm Pb**	**Dilution factor**	**Total Pb (µg)**	**Sample wt. (mg)**	**% Pb**
Pendant 1	20	1000	20,000	50	40

Table 2: Acid Extraction Analysis

		(c)	(d)	
Item	**Extraction time (hr)**	**ppm Pb (measured & corrected for blank)**	**Dilution factor**	**Total Pb (µg)**
Ring 1	1	2.0	40	80
	2	1.5	40	60
	3	1.0	40	40
Total				**180**