UNITED STATES
CONSUMER PRODUCT SAFETY COMMISSION
DIRECTORATE FOR LABORATORY SCIENCES
DIVISION OF CHEMISTRY
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Test Method: CPSC-CH-E1002-08
Standard Operating Procedure for Determining Total Lead (Pb) in Non-Metal Children's Products*
February 1, 2009

This document provides detailed information on the test method that will be used by the U.S. Consumer Product Safety Commission's testing laboratory (LSC) in the analysis of non-metal children's products for lead (Pb) content. This method is divided into three sections. The first section describes how to digest samples to determine the total lead content in crystal, ceramic, and other siliceous materials. The second section describes how to digest samples to determine the total lead content in polymeric (including natural and synthetic polymers) or plastic materials, and contains a subsection on the use of X-ray fluorescence spectromemtry (XRF) for determination of lead in such polymeric materials. The third section describes how to analyze the digested samples from the first two sections.

The method applies to most non-metal components other than paint, but is not recommended by CPSC staff for materials that when combined with the specified acid(s) result in an inappropriate combination of materials that would be inconsistent with safe laboratory practices. In such cases, the chemist should make a knowledge based decision on the proper modifications of the method to maintain laboratory safety while following the general approach described here.

The general approach is to grind any accessible component part of a sample to a powder; digest the powder completely in nitric acid or – for siliceous products – in a combination of hot, concentrated nitric and hydrofluoric acids; and analyze by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). Other analytical methods such as Inductively Coupled Plasma – Mass Spectrometry (ICP-MS), 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. Polymeric materials may also be analyzed using XRF following the standard test method of ASTM F 2617-08[1], with limitations as described below.

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*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] Standard Test Method for Identification of Chromium, Bromine, Cadmium, Mercury, and Lead in Polymeric Material Using Energy Dispersive X-ray Spectrometry

CPSC staff has concluded that the test methodologies provided in detail below are sufficient to determine lead content in most products. Knowledge based adjustments on a case by case basis may be necessary for products made from certain materials.

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 component parts such as a bead, crystal, 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) used by CPSC staff 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) – 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 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 purchased from a 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 should 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 a similar matrix as test samples with known lead levels. 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. Hydrofluoric Acid, Trace Metal Grade
3. Distilled Water
4. Microwave Digestion Apparatus
5. Cryogenic Mill
6. Liquid Nitrogen

7. CRMs such as ERM®-EC680k[2] and EC681k, low density polyethylene materials that contain lead and NIST SRM 89 and 1412, leaded glass.
8. 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 Lead in Ceramics, Glass and Crystal and other Siliceous Materials - Digestion

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 component type from a subsample is analyzed for total Pb content. CPSC staff uses a method based on EPA 3052[3] (http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3052.pdf) for determining lead content in ceramic or crystal materials. Certified reference materials, such as NIST SRM 89 and 1412, that closely match the material of the tested product should be used to verify accuracy of digestion and analysis methods. After digesting the sample according to this procedure, it should be tested by ICP, as described below in Section III.

1. Weigh out a 30-100 mg piece of crystal, glass or ceramic item into an appropriate microwave vessel equipped with a controlled pressure relief mechanism. Ceramic items generally weigh several grams or more, and consist of the base ceramic with a glaze and decoration fired on. The lead in ceramics is generally in the glaze or decoration. When analyzing ceramics or glass, the entire item including the glaze, decoration, and ceramic base material should be ground in a cryogenic mill and 30-100 mg of the ground ceramic/glass powder weighed in an appropriate microwave vessel. If used, the grinding apparatus must be thoroughly cleaned to prevent cross-contamination. Record actual weight to the nearest 0.1 mg.
2. At room temperature, add 3 ml of concentrated nitric acid and 1 ml of concentrated hydrofluoric acid to each vessel. Wait for completion of the initial reaction of the acid and the sample before sealing vessels. Seal vessels in accordance with the manufacturer's directions.
3. The microwave method should involve increasing the temperature of each sample to 180±5°C in approximately 5.5 minutes, and holding at 180±5°C for 9.5 minutes
4. Allow the samples to cool for a minimum of 5 minutes before removal from microwave. Vent the microwave vessels in fume hood before uncapping.
5. Add 30 ml of 4% (w/w) boric acid to each vessel to permit the complexation of fluoride to protect the ICP quartz plasma torch. Quantitatively transfer the sample to a 50 ml plastic volumetric flask or disposable volumetric digestion cup. Dilute to 50 ml with deionized water.

Caution: The analyst should wear protective gloves and face protection and must not at any time permit solution containing hydrofluoric acid to come in contact with skin or lungs. This document does not address all safety concerns, additional safety precautions are necessary for all steps, particularly when using hydrofluoric acid. This method is not to be used except by qualified, properly trained workers.

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[2] European Reference Material, produced and certified under Institute for Reference Material and Measurements (IRMM)

[3] Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices

II. Total Lead in Plastics, Polymers and other Non-Siliceous Materials

A. Acid Digestion

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 component type from a subsample is analyzed for total Pb content. CPSC staff uses a method based on methodology found in Canada Product Safety Bureau Method C-02.3[4] (http://www.hc-sc.gc.ca/cps-spc/prod-test-essai/_method-chem-chim/c-02_3-eng.php) for determining lead content in plastic materials such as polyethylene and polyvinyl chloride (PVC). EPA Method 3051A[5] (http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3051a.pdf) with modifications in sample weight, temperature, time, and acid volumes to match those given below is also acceptable. Certified reference materials that closely match the material of the tested product, such as ERM®-EC680k and EC681k (described above), should be used to verify accuracy of digestion and analysis methods. After digesting the sample according to this procedure, it should be tested by ICP, as described below in Section III.

1. Cut the test specimen into small pieces and cryogenically mill. Weigh out 150 mg of the milled plastic into an appropriate microwave vessel equipped with a controlled pressure relief mechanism. Ensure the milling apparatus is thoroughly clean between test specimens to avoid cross contamination. Record actual weight to the nearest 0.1 mg.
2. At room temperature, add 5 ml of concentrated nitric acid to each vessel. Wait for completion of the initial reaction of the acid and the sample before sealing vessels. Seal vessels in accordance with manufacturer's directions.
3. The microwave method should involve increasing temperature of each sample to 210±5°C in approximately 20 minutes, and holding at 210±5°C for 10 minutes.
4. Allow the samples to cool for a minimum of 5 minutes before removal from microwave. Vent the microwave vessels in a fume hood before uncapping.
5. Quantitatively transfer the sample to a 50 ml volumetric flask or disposable volumetric digestion cup. Dilute to 50 ml with deionized water

B. Identification and Quantification of Pb in Polymeric Materials using XRF

Alternately, Energy Dispersive XRF can be used with limitations to quantitatively determine the amount of Pb in polymeric materials by following ASTM F 2617-08. This standard is applicable only for homogeneous polymeric materials, and for XRF instruments meeting the requirements given in the ASTM method.

Components could be analyzed intact without any modification if they have suitable surface characteristics, geometry and homogeneity. Destructive sample preparation techniques may be required for certain components to create a uniform sample for testing. Excessive curvature, rough surface texture, or specimen thickness less than 2 millimeters

[4] Determination of Total Lead in Polyvinyl Chloride Products by Closed Vessel Microwave Digestion
[5] Microwave Assisted Acid Digestion of Sediments, Sludges, Soil, and Oils

requires proper sample preparation techniques such as compression molding as outlined in ASTM F 2617-08. Based on the inter-laboratory study of reference materials reported in this standard and the fact that actual consumer products to be tested are likely to be less homogeneous than the reference materials, CSPC staff has concluded that analysis using wet chemical procedures outlined in Sections II-A and III should be done on any samples with Pb results determined using XRF to be greater than 200mg/kg before certifying the item meets the Pb requirements of the Consumer Product Safety Improvement Act (CPSIA).

III. Total Pb in Acid Digests of Polymeric or Siliceous Materials - 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[6]. ICP-MS may also be employed with appropriate procedures, such as EPA 6020A[7]. Calculate total lead concentration in the component part from that of the diluted sample, accounting for all dilution. Report 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

    One other Pb line such as Pb 217.00 should be 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 should be performed a minimum of once a day when used for analysis, or each time the instrument is set up. Results for each standard should 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 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, 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

[6] 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

[7] Inductively Coupled Plasma-Mass Spectrometry

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 a similar material as the test specimen with a known amount of Pb. 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.
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:

1. Total Pb - % Pb (wt/wt) = 0.10cd/w
    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)

Examples:

Table 1: Total Pb Analysis

	(c)	(d)		(w)	
Item	Pb Concentration (µg/ml)	Dilution factor (ml)	Total Pb (µg)	Sample wt (mg)	% Pb
Crystal	20	1000	20,000	50	40