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CONSUMER PRODUCT SAFETY COMMISSION
DIRECTORATE FOR LABORATORY SCIENCES
DIVISION OF CHEMISTRY
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Test Method: CPSC-CH-E1002-08.3
Standard Operating Procedure for Determining Total Lead (Pb) in Nonmetal Children's Products, Revision November 15, 2012*

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 nonmetal 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, and it contains a subsection on the use of X-ray fluorescence spectrometry (XRF) for determination of lead in such 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 it contains a subsection on the use of X-ray fluorescence spectrometry (XRF) for determination of lead in such polymeric materials. The third section describes how to analyze the digested samples from the first two sections. This revision recognizes use of X-ray fluorescent spectroscopy measurement techniques in additional materials with certain limitations and acceptable ranges and replaces the previously issued Test Method CPSC-CH-E1002-08.2.

The method applies to most nonmetal components other than paint, but it is not recommended by CPSC staff for materials, which when combined with the specified acid(s), results 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 or cut any accessible component part of a sample into small pieces or a powder; digest an aliquot 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. Nonmetal materials

* This is a revision of Test Method CPSC-CH-E1002-08.1. This document was prepared by CPSC staff, has not been reviewed or approved by, and may not necessarily reflect the views of, the Commission.

may also be analyzed, using XRF, following the standard test method of ASTM F2617-08[1] or ASTM F2853-10e1,[2] with limitations described below. 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.

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–An individual subunit within the total sample. An item, such as a bracelet, may be broken into component parts, such as a bead, crystal, 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.
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 percent confidence level for 7 replicates), S= standard deviation.
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–1,000 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 percent nitric acid matrix are used. A minimum of 4 calibration standards are used. Calibration standards should be prepared on a biweekly basis at 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 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

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

[2] 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.

those listed in the Equipment and Supplies section below. Appropriate CRMs from other sources are also acceptable.

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[3] and EC681k, low-density polyethylene materials that contain lead and NIST SRM 89 and 610, 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

A. Acid Digestion

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 component type from a subsample is analyzed for total Pb content. CPSC staff uses a method based on EPA 3052[4] (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 610, which 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 cleaned thoroughly 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] European Reference Material, produced and certified under Institute for Reference Material and Measurements (IRMM).
[4] Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices.

3. The microwave method should involve increasing the temperature of each sample to at least 180°C in approximately 5.5 minutes, and holding at 180°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 percent (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.

B. Identification and Quantification of Pb in Siliceous 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 with limitations to determine quantitatively the amount of Pb in siliceous materials by following ASTM F 2853-10e1. This standard is applicable only for homogeneous siliceous 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 glazed ceramics.
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 small enough that distinct different measurements could not be made. If the relative standard deviation on 3 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 that the items meet CPSIA requirements for lead. If each of the three 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.[5]

[5] 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

4. For "inconclusive" results, additional testing is necessary in order to make a determination, such as by digestion and ICP analysis, per sections IA and III.

C. Identification and Quantification of Pb in Siliceous 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 siliceous materials, with limitations. The following limitations, in addition to those outlined in Section I-B for HDXRF, apply:

1. Follow sampling, testing, calibration, quality control guidelines described in section 6 of International Electrotechnical Commission (IEC) Method 62321 ED 1.0 B.
2. A set of at least four glass calibration standards should be used to validate that the instrument is suitable for testing for Pb in siliceous materials. 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 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 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 given uncertainty of the reference materials.
4. The limit of detection (LOD) for lead in glass 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 sensitivity to obtain sufficient LOD for certifying to lead requirements.

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 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 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[6] (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

material subject to the CPSIA limit of 100 ppm as 68 ppm is more than 30 percent below the applicable limit of 100 ppm.

[6] Determination of Total Lead in Polyvinyl Chloride Products by Closed Vessel Microwave Digestion.

materials, such as polyethylene and polyvinyl chloride (PVC). EPA Method 3051A[7] (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 the 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. Hard to digest plastics may need to be cryomilled to get finer powder. Weigh out 150 mg of the milled or cut plastic into an appropriate microwave vessel equipped with a controlled-pressure relief mechanism. Ensure that 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 at least 200°C in approximately 20 minutes, and holding 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 and Other Nonmetal Materials Using XRF

Alternately, Energy Dispersive XRF can be used with limitations to determine quantitatively the amount of Pb in polymeric materials by following ASTM F 2617-08 or ASTM F2853-10e1. These standards are applicable only for homogeneous polymeric materials and for XRF instruments meeting the requirements given in the ASTM methods.

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, may require sample preparation techniques, such as compression molding, as outlined in ASTM F 2617-08. Based on the interlaboratory 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 70 percent of the Pb requirements of the Consumer Product Safety Improvement Act (CPSIA) before certifying compliance.

Other homogeneous nonmetal materials such as wood and fabric can be analyzed by XRF following ASTM F2853-10e1 subject to the same limitations given in Section I-B above

[7] Microwave Assisted Acid Digestion of Sediments, Sludges, Soil, and Oils.

or using other types of XRF spectrometers that do not meet the requirements of ASTM F2853-10e1 subject to the same limitations given in Section I-C above.

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.[8] ICP-MS may also be employed with appropriate procedures, such as EPA 6020A.[9] 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.
    b. 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 three 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 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, 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 a similar material as the test specimen with a known amount of Pb. Analyte recoveries should be within ±20 percent of expected values. If

[8] 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.
[9] Inductively Coupled Plasma-Mass Spectrometry.

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 ppm)
    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	ppm Pb	Dilution factor	Total Pb (µg)	Sample wt (mg)	% Pb
Crystal	20	1,000	20,000	50	40

Summary of changes in Revision CPSC-CH-E1002-08.1

1. Page 1, revised test method # and date.
2. Page 1, last paragraph first sentence, allowed for polymeric materials to be cut into small pieces.
3. Page 2, removed IDL and MDL CPSC lab values; not relevant to method and new instruments will have different values.
4. Page 2, definition 10, last sentence revised to include other sources for CRMs.
5. Page 3, removed reference to NIST SRM 1412 and added 610. 1412 no longer available.
6. Page 3, step 3, changed temperature requirements from "180±5°C" to "at least 180°C"
7. Page 4, step 1, removed requirement for cryomilling.
8. Page 4, step 3, changed temperature requirements from "210±5°C" to "at least 200°C."
9. Page 5, first paragraph, changed ">200mg/kg" to "greater than 70% of CPSIA Pb limit" to generalize for future changes to limit.

Summary of Changes in Revision CPSC-CH-E-1002-8.2

1. Page 1, revised test method # and date, added statement that SOP contains a subsection on the use of X-ray fluorescence spectrometry (XRF) for determination of lead in such siliceous materials.
2. Page 2, change to biweekly from weekly minimum time between calibration standard preparation.
3. Page 7, **Analysis** step 5, added statement that calibration blank should be < 5 times MDL.
4. Page 7, **Analysis** step 6, removed "immediately" after QCS and added" and before any sample" after calibration.
5. Page 7, **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 difficulty in LRB meeting 3 times MDL.
6. Page 4, added subsections B and C to section I that outline XRF testing procedures for determining Pb in glass or siliceous materials.

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

1. Page 4, 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 percent RSD, and made allowance for component parts which are too small for multiple distinct measurements.