



United States
Consumer Product Safety Commission
Directorate for Laboratory Sciences
Division of Chemistry
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Test Method: CPSC-CH-E1004-11
Standard Operating Procedure for Determining Cadmium (Cd) Extractability
from Children's Metal Jewelry
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1. Scope

This document provides detailed information on two test methodologies that will be used by the U.S. Consumer Product Safety Commission's (CPSC) testing laboratory (LSC) in the analysis of metal items, such as children's metal jewelry, for extractable cadmium. Utilizing different sample preparation techniques, both methods will determine whether a children's jewelry item contains extractable cadmium content. This information then can be used in the development of a risk assessment to support findings under the Federal Hazardous Substances Act (FHSA).

This document is provided to inform interested parties of the methods utilized by LSC for assessing potential human exposure. The methods are not required to be followed by other laboratories performing such analyses; however, other laboratories should consider using these procedures to ensure that they obtain analytical results consistent with CPSC staff's for purposes of enforcement by CPSC's Office of Compliance.

2. Summary of Test Methods

Test Procedure – The intact jewelry item is suspended in 0.07 N hydrochloric acid, the volume of which will be equal in milliliters to 50 times the jewelry item's mass in grams. The flask containing the jewelry item and acid is placed in a shaker bath at 37°C for a period of 24 hours. An aliquot of the acid then is analyzed for cadmium content via inductively

coupled plasma optical emission spectrometer (ICP-OES), or by inductively coupled plasma mass spectrometer (ICP-MS).

Alternate Test Procedure – An accurately weighed aliquot of approximately 0.15g of the representative and homogenous powder, resulting from grinding the jewelry item, is passed through a metal sieve of aperture 0.5 mm. The fine, homogenous powder is submerged in 0.07 N hydrochloric acid, the volume of which will be equal in milliliters to 50 times the fine powder's mass in grams. The flask containing the powder and acid is placed in a shaker bath at 37°C for a period of two hours. A filtered aliquot of the acid then is analyzed for cadmium content via ICP-OES or ICP-MS. Finally, the cadmium extraction calculation is adjusted to approximate the results of the gentler 24-hour intact jewelry item procedure.

3. Apparatus

- 125 ml Erlenmeyer flasks;
- Cadmium-free wire, twine, or similar string;
- Temperature-controlled shaker bath, lateral travel distance approximately one inch or greater;
- Analytical balance;
- Metal sieve, aperture 0.5 mm;
- Dremel[®] tool (or similar device capable of grinding metal);
- Filter, 0.45µm; and
- Disposable Digestion Vessel with Screw Cap, 68 ml or similar.

4. Reagents

- Distilled water; and
- Hydrochloric acid, trace metal grade, or better.

5. Test Method

This acid extraction procedure simulates exposure to metal that is ingested and undergoes digestion in the alimentary tract. The analysis is to be performed on an intact item or component (i.e., a pendant that can be removed undamaged from a necklace chain).

5.1 Accurately weigh the jewelry item or undamaged component of interest in grams on an analytical balance.

5.2 Calculate the volume of 0.07N HCl acid necessary accordingly:

$$\text{Acid Volume (ml)} = \text{Jewelry Mass (g)} \times 50$$

5.3 Using cadmium-free wire, twine, or similar string, suspend the children's metal jewelry item or undamaged component of interest in a 125 ml Erlenmeyer flask, such that the item does not touch the bottom or edges of the flask, yet would be submerged by the calculated acid volume.

5.3.1 For items too large or too small for this approach, use the appropriate Erlenmeyer flask such that the calculated volume of acid (Sec 5.2) at least will submerge the suspended sample, yet the flask shall not be more than 75 percent filled.

5.4 Add the exact volume of acid calculated in 5.2 to the flask prepared in 5.3; the jewelry item should be submerged fully in the acid and capable of a pendulum motion; securely cover the flask with stopper, parafilm, or equivalent.

5.5 Place the flask in a temperature-controlled shaker bath with lateral travel approximately one inch or greater, set to 37°C and 60 rpm, and record the start time.

5.6 After 24 hours, decant an aliquot of acid solution from the flask and save for analysis.

6. Analysis

6.1 The saved aliquot representing 24 hours of cadmium extraction is analyzed for cadmium content, using an inductively coupled plasma optical emission spectrometer (ICP-OES).

6.2 The analytical procedure for ICP generally should follow ASTM E1613 "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," substituting cadmium for lead. Cadmium wavelengths common to CPSC staff include 214.439 and 228.802. Alternately, ICP-MS can be used with appropriate conditions for the matrix and analyte.

6.3 Ensure the ICP is wavelength-calibrated monthly and maintained as per manufacturer's specifications. Results for each calibration standard shall be within five percent of the true value. If the results do not fall into this range, recalibration is necessary.

6.4 At least five cadmium (Cd) standards shall be used to generate a standard curve, but also include a reagent blank, and quality control standard (QCS) to the ICP run. The QCS is typically a stock solution purchased from a standards manufacturer and utilized as an instrument check. The QCS must agree with the true value ± 15 percent.

7. Calculations

7.1 The results are calculated and reported as follows:

$$7.1.1 \quad \mu\text{g Cd extracted} = C \times V$$

Where C = $\mu\text{g/ml}$ Cd in the aliquot as determined by ICP-OES

V = volume of acid used for the extraction

7.1.2 This calculation results in the total mass of cadmium extracted from a sample, per item. This calculation intentionally does NOT divide the extracted cadmium content by the overall jewelry item mass. The mass of the jewelry item or component of interest was utilized in determining the volume of acid to use.

7.2 Example: A jewelry item was screened previously and a component of the jewelry item was identified for extraction testing. The component was removed from the jewelry item without being damaged, and the mass of the component was determined to be 2.0000 grams.

$$7.2.1 \quad \text{Acid Volume (ml)} = \text{Jewelry Mass (g)} \times 50$$

$$\text{Acid Volume (ml)} = 2.0000 \text{ g} \times 50$$

Therefore, the volume of acid necessary for the extraction is 100 ml.

7.2.2 After the 24-hour extraction, an aliquot of the acid is analyzed properly by ICP-OES, and the concentration of cadmium in the aliquot was determined to be 2.000 $\mu\text{g Cd/ml}$ acid. Therefore, the cadmium extracted is determined:

$$7.2.3 \quad \mu\text{g Cd extracted} = C \times V$$

$$\mu\text{g Cd extracted} = 2.000 \mu\text{g Cd/ml acid} \times 100 \text{ ml acid}$$

$$\mu\text{g Cd extracted} = 200 \mu\text{g Cd}$$

7.2.4 We recognize that certain laboratories are accustomed to reporting extractable amounts of metal as a ratio to the weight of the original sample. In the example above, the 200 $\mu\text{g Cd}$ extracted came from 2.0000 g of jewelry, which could be reported as 100 $\mu\text{g Cd/g}$ jewelry, but for later comparison to CPSC staff guidance for risk levels for Cd due to ingestion, it is imperative that the result be given per jewelry item (200 μg in the above example) instead of per gram (100 $\mu\text{g Cd/g}$ jewelry in the above example), in order to match the risk assessment methodology, which assumes ingestion of the entire component part.

8. Alternate Test Procedure

This acid extraction procedure simulates exposure to metal that is ingested and then digested in the alimentary tract. The analysis is to be performed on a powdered item or component.

8.1 Record the mass of the jewelry item or component of interest to be analyzed.

8.2 Grind the jewelry item or component of interest into a fine powder using a mill or a rotary grinder, such as a Dremel[®] tool with an appropriate bit (a representative portion, such as bisecting the item, may be acceptable if the area ground accurately represents the entire item or component of interest), and pass the grindings through a metal sieve of aperture 0.5 mm.

8.3 Accurately weigh approximately 0.15 grams (± 0.01 grams) of sieved powder on an analytical balance.

8.4 Calculate the volume of 0.07N HCl acid necessary accordingly:

$$\text{Acid Volume (ml)} = \text{Powder Mass (g)} \times 50$$

8.4.1 This acid volume will be 7.5 ml if the mass is exactly 0.15 grams, but in practice may be $7.5 \text{ ml} \pm 0.5 \text{ ml}$ for the mass range of 0.14–0.16 grams. Follow the required volume to the nearest 0.1 ml for the exact mass used.

8.5 Add the exact volume of acid calculated in 8.4 to an appropriately sized flask containing the weighed powder; the powder should be fully submerged in the acid and remain submerged even with the movement of a shaker bath; securely cover the flask with stopper, parafilm, or equivalent.

8.5.1 CPSC staff commonly uses a disposable “Digestion Vessel with Screw Cap” catalog number SC475 from Environmental Express. The inner diameter of these vessels at the bottom is roughly one inch.

8.6 Place the flask in a temperature-controlled shaker bath with lateral travel approximately one inch or greater, set to 37°C and 60 rpm, and record the start time.

8.7 After two hours, decant an aliquot of acid solution from the flask, using a 0.45 μm filter to remove solids, and save the filtrate for analysis.

9. Analysis (for Alternate Test Procedure)

- 9.1 The saved aliquot, representing two hours of cadmium extraction from a ground portion of the sample, is analyzed for cadmium content using an inductively coupled plasma optical emission spectrometer (ICP-OES).
- 9.2 The analytical procedure for ICP should follow generally ASTM E1613 “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,” substituting cadmium for lead. Cadmium wavelengths common to CPSC staff include 214.439 and 228.802. Alternately, ICP-MS can be used with appropriate conditions for the matrix and analyte.
- 9.3 Ensure the ICP is calibrated monthly and maintained as per manufacturer’s specifications. Results for each calibration standard shall be within five percent of the true value. If the results do not fall into this range, recalibration is necessary.
- 9.4 At least five cadmium standards shall be used to generate a standard curve, but also include a reagent blank, and quality control standard (QCS) to the ICP run. QCS must agree with the true value ± 15 percent.

10. Calculations (for Alternate Test Procedure)

- 10.1 The results are calculated and reported as follows:

10.1.1 $\mu\text{g Cd extracted} = C \times V$

Where $C = \mu\text{g/ml Cd in the aliquot as determined by ICP-OES}$
 $V = \text{volume of acid used for the extraction}$

10.1.2 $\text{Accelerated } \mu\text{g Cd extracted} = (E \div M) \times W$

Where $E = \mu\text{g Cd extracted as calculated in 10.1.1}$
 $M = \text{mass of powder used (typically } 0.15 \pm 0.01 \text{ grams)}$
 $W = \text{mass of the entire jewelry item or component of interest before grinding or milling}$

10.1.3 $\text{Adjusted (to 24 hours) } \mu\text{g Cd extracted} = A \div 10$

Where $A = \text{accelerated } \mu\text{g Cd extracted as calculated in 10.1.2}$
 $10 = \text{adjustment factor, as the alternate test procedure (powdered metal) has been determined to yield at least 10 times the extractable cadmium than the test procedure (intact metal) due to the high surface area of the powder. See Appendix A.}$

10.1.4 This calculation results in the (adjusted) mass of cadmium predicted to be extracted from a sample in a 24-hour extraction. This calculation intentionally does NOT divide the extracted cadmium content by the overall jewelry item mass. The mass of the jewelry item or component of interest was utilized in determining the volume of acid to use.

10.2 Example: A jewelry item was screened previously and a component of the jewelry item was identified for extraction testing. The component was removed from the jewelry item without being damaged, and the mass of the component was determined to be 2.0000 grams. The component was ground to a powder and analyzed according to section 8 Alternate Test Procedure.

$$\begin{aligned} 10.2.1 \quad \text{Acid Volume (ml)} &= \text{Jewelry Mass (g)} \times 50 \\ \text{Acid Volume (ml)} &= 0.1500 \text{ g} \times 50 \end{aligned}$$

Therefore, the volume of acid necessary for the extraction is 7.5 ml.

10.2.2 After the two-hour extraction, a filtered aliquot of the acid is analyzed properly by ICP-OES, and the concentration of cadmium in the aliquot was determined to be 20.000 µg Cd/ml acid. Therefore, the cadmium extracted is determined:

$$\begin{aligned} 10.2.3 \quad \mu\text{g Cd extracted} &= C \times V \\ \mu\text{g Cd extracted} &= 20.000 \mu\text{g Cd/ml acid} \times 7.5 \text{ ml acid} \\ \mu\text{g Cd extracted} &= 150.0 \mu\text{g Cd} \end{aligned}$$

$$\begin{aligned} 10.2.4 \quad \text{Accelerated } \mu\text{g Cd extracted} &= (E \div M) \times W \\ \text{Accelerated } \mu\text{g Cd extracted} &= (150.0 \mu\text{g Cd} \div 0.1500 \text{ g}) \times 2.0000 \text{ g} \\ \text{Accelerated } \mu\text{g Cd extracted} &= 2000 \mu\text{g Cd} \end{aligned}$$

$$\begin{aligned} 10.2.5 \quad \text{Adjusted } \mu\text{g Cd extracted} &= P \div 10 \\ \text{Adjusted } \mu\text{g Cd extracted} &= 2000 \mu\text{g Cd} \div 10 \\ \text{Adjusted } \mu\text{g Cd extracted} &= 200 \mu\text{g Cd (predicted for 24 hours extraction)} \end{aligned}$$

10.2.6 We recognize that certain laboratories are accustomed to reporting extractable amounts of metal as a ratio to the weight of the original sample. In the example above, the 200 µg Cd extracted (adjusted) came from 2.0000 g of jewelry, which could be reported as 100 µg Cd/g jewelry, but for later comparison to CPSC staff guidance for risk levels for Cd due to ingestion, it is imperative that the result be given per jewelry item (200 µg in the above example) instead of per gram (100 µg Cd/g jewelry in the above example), in order to match the risk assessment methodology, which assumes ingestion of the entire component part.

11. Appendix A

Table 1: Actual Metal Item Extractions

Sample	%CoA	Intact Metal Extraction (µg Cd) (1 g item)	Powdered Metal “Extracted” (µg Cd) (0.15 g powder)	Powdered Metal “Accelerated” (µg Cd) (assumes 1 g item)	Powdered Metal “Adjusted” (µg Cd) (adjusted to compare with intact item extraction)
Metal A	<0.01	N/D	2	13.3	1.33
Metal B	14.42	227	267	1780	178.0
Metal C	19.042	2.5	4.66	31.1	3.11
Metal D	24.01	78	351	2340	234.0
Metal E	32.398	2884	3029	20193	2019.3

11.1 All metal samples in Appendix A have a certificate of analysis (CoA) for cadmium content. All metal samples in Table 1 are different alloys.

11.2 Intact metal extractions were performed with a sample mass of 1.0 grams.

11.3 Powdered metal extractions were performed with a sample mass of 0.15 grams.

11.4 Accelerated metal calculations assume an original sample mass of 1.0 grams.

11.5 Final cadmium extraction on intact metal and powdered metal do not yield the same results; however, this method is used as a guide in hazard identification and not an exact measure of actual cadmium that would be extracted into a human body as a result of ingestion.