1 SCOPE

1.1 This method describes a general procedure for the determination of the quantity of lead and cadmium released from glazed ceramic and glassware products, as applicable to item 20.1 of Part II of Schedule I to the Hazardous Products Act (HPA).

1.2 This method has been prepared from HPA Regulations for procedural efficiency only. For legal purposes, the analyst should refer to the procedure described in the Hazardous Products (Glazed Ceramics and Glassware) Regulations.

1.3 Where a determination is specifically requested to be conducted on the lip and rim area of a glass or ceramicware having an exterior decoration within 20 mm of the rim, the procedure shall be conducted according to that described in ASTM Standard Test Method C927 (Attachment 1) with exceptions as noted in Section 6.3

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2 APPLICABLE DOCUMENTS

2.1 ASTM Standard Test Method C738 - 81 (reapproved, 1988).
2.2 ASTM Standard Test Method C927 - 80 (reapproved, 1993).
2.3 HPA, Hazardous Products (Glazed Ceramics and Glassware) Regulations (SOR 98-175).
2.4 International Standard ISO 6486/1-1981 (E).
2.5 SLSD, Project report 93-0381 (January, 1994).
2.6 SLSD, Project report 2001-0645 (April, 2002).
2.7 SOP Varian AA 220 FS AAS (Part B).

3 DEFINITIONS

3.1 *Cup and mug*: hollow-ware with a capacity of less than 1.1 L used for the consumption of liquids.
3.2 *Flatware*: a product having an internal depth not exceeding 25 mm, measured vertically from the lowest interior point to a horizontal plane passing though the point of overflow.
3.3 *Hollow-ware*: a product having an internal depth greater than 25 mm, measured vertically from the lowest interior point to a horizontal plane passing through the point of overflow.
3.4 *Large hollow-ware*: hollow-ware with a capacity of 1.1 L or more.
3.5 *Pitcher*: a hollow-ware vessel with a capacity of 1.1 L or more that is commonly used for storing and dispensing liquids but does not include a creamer, a coffeepot or teapot.
3.6 *Small hollow-ware*: hollow-ware with a capacity of less than 1.1 L.

4 REAGENTS AND APPARATUS

4.1 A ruler having an accuracy of ± 0.5 mm.
4.2 100 mL nalgene beaker (or suitable container).
4.3 Whatman #40 filter paper.
4.4 Acetic acid (CH_3COOH) solution, 4% (volume/volume): Prepare a solution of 4 mL glacial acetic acid per 100 mL in distilled water (4+96 by volume) sufficient to fill all the samples, and to prepare a set of standards and a standards blank.
4.5 Atomic Absorption Spectrophotometer (AAS), or other analytical instrument capable of detecting: (I) lead at 0.1 mg/L or less, and (ii) cadmium at 0.02 mg/L or less.
4.6 Cadmium (Cd) certified reference solution of known concentration, *e.g.* 1000 mg/L.
4.7 Lead (Pb) certified reference solution of known concentration, *e.g.* 1000 mg/L.
4.8 Dilute non-acidic detergent solution: Prepare a solution of 2 - 3 mL of a suitable non-acidic dishwashing detergent *(Note 1)* per litre of lukewarm tap water.
4.9 Suitably-sized (1.25 to 2 times the rim diameter), chemically inert, laboratory containers in which to invert drinking vessels (Lip and Rim Test only).
4.10 Inert, opaque covers for samples, or above containers.
4.11 Sampling bottles, plastic, clean and non-contaminating (or acid washed: Allow to soak overnight in a solution of 0.75M HCl + 0.25M HNO_3 , rinse with distilled water, and air dry.)

5 SAMPLING

5.1 A sample of six identical specimens of the product are required for the Food Contact Surface test. A separate sample of six identical specimens of the product are required for the Lip and Rim test.

6 EXPERIMENTAL PROCEDURE

6.1 Identification and Warning Labelling for Decorative Products

6.1.1 Note if the product has a design feature such as a hole, mounting hook or any other feature that distinguishes the product as decorative.
6.1.2 Note the exact content of the warning label on the product (including English and/or French text and whether the lettering is in all capital letters) of any warning labelling on the product. Measure and record the height of the capital letters of the text in millimetres.
6.1.3 Note if the warning label is easily removed by use of one's fingernail to determine permanency of the warning label.

Note 1: *Sunlight® Dishwashing Liquid, a trademark product of Lever, Toronto, Ont. M4M 1B6, has been found suitable for this application.*

6.2 Food Contact Surface

6.2.1 Carefully handwash the sample, avoiding scratching the test surface, with a dilute non-abrasive non-acidic detergent solution. Rinse with tap water, followed with distilled water, and allow to air dry.

6.2.2 Measure and record the internal depth of any plate or bowl vertically from the lowest interior point to a horizontal plane passing through the point of overflow.

6.2.3 Fill the sample article to within 5 mm of overflowing (distance measured along the surface of the sample from the rim, not vertically) with a 4% (v/v) acetic acid (CH_3COOH) solution at 22 ± 2°C. Measure and record the volume of acetic acid solution required.

6.2.4 Cover with an inert, opaque cover, to prevent evaporation of the solution. Let stand in total darkness *(Note 2)* for a period of 24 hours ± 10 minutes at room temperature (22°C ± 2°C).

6.2.5 After the 24 hour extraction period, thoroughly mix the extraction solution to ensure homogeneity taking care not to abrade the surface of the test sample.

6.2.6 Transfer an aliquot of the solution into a sampling bottle. The solution must be analyzed within 8 hours.

6.3 Lip and Rim

The following method, essentially from the Canada Gazette Part II, Vol. 132, No. 7, April 1, 1998, which is based on ASTM standard C927-80 (1993) **differs** from ASTM in the following way:

The **distance** measured along the inside surface of the vessel from the rim, to establish the internal volume, is **5 mm** (not 7 mm).

6.3.1 Carefully handwash the drinking vessel, avoiding scratching the surface, with a dilute non-abrasive, non-acidic detergent solution, rinse with tap water *(Note 3)*, then rinse with distilled water, and air dry.

6.3.2 Measure the internal volume of the drinking vessel in millilitres by filling with water to within 5 mm of the level of overflowing *(Note 4)*, record the internal volume (V_2), and discard the water; if distilled water was not used, rinse with distilled water and air dry.

6.3.3 Invert the drinking vessel in an appropriate laboratory container whose diameter is a minimum of 1.25 times and a maximum of 2 times the external diameter of the test specimen as measured at the rim.

Note 2: *Alternatively, if an opaque cover is not available, cover the product with suitable opaque material to prevent exposure to light. The amount of cadmium released in solution has been found dependent on the presence of light during the leaching process. However, this provision may be omitted if only leachable lead is being determined.*

Note 3: *It may be convenient to measure the volume at this stage as described in the next step, using tap water, before rinsing with distilled water.*

Note 4: *The 5mm distance shall be measured along the surface of the item tested, from the rim, not in the vertical direction.*

6.3.4 Add to the laboratory container the volume of an extraction solution of 4% (volume/volume) of acetic acid in water that just covers the drinking vessel up to 20 mm from the rim, and record the volume of extraction solution used (V_1).

6.3.5 Cover the laboratory container with an inert opaque cover *(Note 2)* and allow to stand for 24 hours ± 10 minutes at 22°C ± 2°C.

6.3.6 Remove the drinking vessel and stir the extraction solution to ensure homogeneity.

6.3.7 Take an aliquot of the extraction solution and place it in a sampling bottle. The solution must be analyzed within 8 hours.

7 DETERMINATION

7.1 Prepare a series of at least three lead and cadmium working standard solutions, of appropriate concentrations, by diluting as required, the Pb and Cd certified reference solutions (*e.g.* 1 000 mg/L) in the same batch of 4% (v/v) acetic acid (CH_3COOH) that was used for the extraction. Prepare a standard blank with the same batch of 4% (v/v) acetic acid.

7.2 Use an analytical technique that is capable of detecting
(I) lead at 0.1 mg/L or less, and
(ii) cadmium at 0.02 mg/L or less.

Measure the absorbance of the standards and sample leaching solution, as prepared in par. 6.2 or 6.3 using the Atomic Absorption Spectrophotometer operated in either flame or graphite furnace mode at a wavelength of 217.0 nm or 283.3 nm for lead, and at 228.8 nm for cadmium according to the instrument manufacturer's instructions *(Note 5)*. Prepare a calibration curve of absorbance versus concentration for each element, using the lead and cadmium working standard solutions in the appropriate range, and determine the concentration of lead and cadmium in the test sample solution. Determine the lead and cadmium content of the blank solution and if present, subtract from the lead and cadmium content of the sample. If necessary, dilute the sample leaching solution with 4% (v/v) acetic acid (CH_3COOH) by an appropriate factor to ensure that the measurements are taken within the instrument's linear dynamic range.

7.3 Refer to SOP of instruments, in Part B, for proper operation and maintenance of instruments.

8 REPORTING

8.1 Report the presence of any design feature that distinguishes the product as decorative.

Note 5: *Other instrumental measurement techniques such as ICP-MS or ICP-AES have been found suitable for this determination.*

8.2 Report the presence of a warning label, the exact content in English and French, the height of the capital letters and whether the label could be easily removed.

8.3 Include a picture of the product in the report. Include additional pictures as necessary to show any warning labels, holes, mounting hooks or any other feature that distinguish the product as decorative.

8.4 Where lead and/or cadmium are not detected, the results of analysis shall be reported as less than the detection limit of the measurement technique used, or that which is defined in Section 11.

8.5 Food Contact Surface

8.5.1 Report the quantity of metallic lead and cadmium measured directly in the sample leaching solution expressed in milligrams per litre for each article tested.

8.5.2 Where applicable, the results of analysis shall be reported according to the following format:

Sample no.	*Specimen no.*	*Product category*†	*Volume (mL)*	$[Pb]_{leachable}$ *(mg/L)*††	$[Cd]_{leachable}$ *(mg/L)*
999990	*1*	*small hollow-ware*	*450*	*xx.x*	*x.xx*
999990	*2...*	*small hollow-ware...*	*460...*	*xx.x*	*x.xx*
999990	*6*	*small hollow-ware*	*455*	*xx.x*	*x.xx*

† *Product Category ="cup and mug", "flatware", "small hollow-ware", "large hollow-ware" or "pitcher" as defined in Section 3.*

†† *1 ppm = 1 mg/L*

8.6 **Lip and Rim**

8.6.1 Report the results as the quantity of the lead and cadmium in milligrams per litre of the extraction solution relative to the internal volume of the drinking vessel as follows:

$$A = \frac{C \times V_1}{V_2}$$

where

C is the concentration of lead or cadmium in mg/L in the extraction solution,

V_1 is the volume in millilitres of the extraction solution used, and

V_2 is the internal volume in millilitres of the drinking vessel.

Sample No.	*Specimen No.*	*Leaching sol'n vol. V_1 (mL)*	*Internal vol. V_2 (mL)*	*[Cd] in Leachate C_{Cd} (mg/L)*	*[Cd] rel. to Int. Vol. A_{Cd} (mg/L)*	*[Pb] in Leachate C_{Pb} (mg/L)*	*[Pb] rel. to Int. Vol. A_{Pb} (mg/L)*
999991	*1*	*193*	*164*	*c.cc*	*a.aa*	*cc.c*	*aa.a*
999991	*2...*	*211*	*164*	*...*	*...*	*...*	*...*
999991	*6*	*196*	*168*	*c.cc*	*a.aa*	*cc.c*	*aa.a*

9 QUALITY CONTROL PROCEDURE

9.1 In order to ensure the proper operation of the available instrumentation and that the precision and accuracy of the analytical measurements meet the specifications of the method, the following quality control procedures shall be conducted concurrently with the analysis of the test sample.

9.2 The normal and correct operation of the AAS shall be verified according to the following guidelines:

9.2.1 *For flame AAS:* Measure the absorbance of a 10 mg/L Pb and a 1.0 mg/L Cd working standard solutions.

9.2.2 Record the absorbance of the working standard solutions in the analytical instrument's QC logbook, and verify that the measurements are within the tolerance limits of the expected values. If these control measurements fall within acceptable limits, a note shall be entered in the test sample file to the effect that the instrument calibration was found to be "within control". Should the instrument be found in a state of disrepair or out of calibration, the AAS shall immediately be repaired and/or recalibrated to meet the prescribed operating conditions prior to proceeding with the analysis.

9.3 The normal and correct operation of the test method shall be verified according to the following guidelines:

9.3.1 Accurately weigh 50 mg of a reference material such as the Fusion Ceramics, Inc., FZ-6 lead glaze frit in a suitable plastic container. Add 50 mL of the 4% (v/v) acetic acid (CH_3COOH) leaching solution, cover and let stand for 24 hours under identical experimental conditions to that of the test sample. Filter the solution into a suitable sampling bottle and determine the concentration of lead in the filtrate. Record the test result in the analytical instrument's QC logbook, and verify that the result is within the tolerance limits of the expected value. If

this control sample result falls within acceptable limits, a note shall be entered in the test sample file to the effect that the test method was found to be "within control". Should the test result of the control sample be found to fall outside the specifications of the method, the entire analytical procedure shall be repeated, providing a fresh test sample is available *(Note 6)*.

10 PRECISION AND BIAS

10.1 *Repeatability.* The deviation between replicate test results, as obtained on the Frit FZ-6 lead glaze frit, by the same analyst with the same apparatus under constant operating conditions on identical test material, should, in the normal and correct operation of the test method, meet or exceed a 13.3% repeatability limit at a 95% probability level for a nominal test value of 2.98 mg/L leachable Pb.

10.2 *Reproducibility*: This section of the test method is under development and will be added in a revised issue when completed.

10.3 *Bias*: This section of the test method is under development and will be added in a revised issue when completed.

11 LIMIT OF DETECTION

11.1 The limit of detection of this method, as determined by flame AAS at 283.3 nm for lead and 228.8 nm for cadmium, has been determined to be 0.03 mg/L and 0.02 mg/L respectively.

12 LIMIT OF QUANTITATION

12.1 The limit of quantitation of the method, as determined by flame AAS at 283.3 nm for lead and 228.8 nm for cadmium, has been determined to be 0.1 mg/L and 0.07 mg/L respectively.

Note 6: *In view of the destructive nature of this determination on the sample's test surface, once an analysis has been conducted the same sample article cannot be retested. A repeat analysis may therefore be conducted only on a fresh test article.*

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