1 SCOPE

1.1 This method describes a general procedure for the determination of leachable cadmium, barium, antimony, selenium and arsenic in decorative or protective coatings applicable to item 9(c) of Part I, Schedule I of the Hazardous Products Act.

2 APPLICABLE DOCUMENTS

2.1 Standard Practice for Use of the Terms Precision and Bias in ASTM Test Methods. Volume 14.02, ASTM E177-90a (1996), pp.79-90.

2.2 Standard Practice for Intra laboratory quality Control Procedures and a Discussion on Reporting Low-Level Data. Volume 11.01, ASTM D4210-89, pp.412-419, 1998.

2.3 John Keenan Taylor, Quality Assurance of Chemical Measurements. Lewis Publishers, INC. 328 pages, 1987.

2.4 Standard Operating Procedure (SOP) for the Elan 5000 ICP-MS. Part B, Book 5, SOP-04.

2.5 National Standard of Canada - Methods of test for toxic trace elements in protective coatings. CGSB Standard Test Method 1-GP-500.2, 1-GP-500.3, 1-GP-500.4, 1-GP-500.5, 1-GP-500.7. Specifications Board. (December, 1973). CGSB Standard Test Method 1-GP-500.2 (December, 1973).

2.6 B. Marchand, “Determination of leachable cadmium, barium, antimony, selenium and arsenic in decorative or protective coatings”. Product Safety Laboratory, Project Report No. 2000-0596, 2001.

3 REAGENTS AND APPARATUS

3.1 ICP-MS Elan 5000, Perkin-Elmer.
3.2 Cadmium, barium, antimony, selenium and arsenic Standards, 1000 ppm, SCP Science.
3.3 Hydrochloric acid, Fisher Scientific, Reagent A.C.S.
3.4 Air convection oven.
3.5 Mortar and pestle.
3.6 Desiccator.
3.7 Nitric Acid, Trace Metal Grade, Fisher Scientific.
3.8 Filter paper, Whatman no. 40.
3.9 Centrifuge tubes, disposable, 50 and 15 mL, Fisher Scientific.
3.10 Glass beakers, 50 mL and glass funnels.
3.11 Sieves, 250 and 500 µm mesh.
3.12 Rainin Electronic pipette, 10 mL.

3.13 Analytical Balance, with a precision of 0.1mg. Mettler AG204.
3.14 Oscillating hot plate or magnetic stirrer.
3.15 Scalpel or other suitable tool.
3.16 Electric grinder.
3.17 Weighing vessel (Aluminium) Fisherbrand, Cat. No. 08-732
3.18 Tetrahydrofurran(THF) HPLC Grade, Caledon Laboratories, Ltd.
3.19 Barium carbonate, Certified A.C.S., Fisher Scientific.
3.20 Antimony trioxide, Certified A.C.S., Fisher Scientific.
3.21 Cadmium chloride, Certified A.C.S., Fisher Scientific.
3.22 Arsenic (III) oxide, Reagent A.C.S., primary standard, Acros Organics.
3.23 Selenium dioxide, BDH Laboratory.
3.24 NIST SRM 1633b, Coal Fly Ash used as a control.

4 EXPERIMENTAL PROCEDURE

4.1 Scrape off the applied coating from the test sample with a scalpel, or other suitable blade tool, being careful not to remove any of the underlying substrate material. Alternatively, the coating can be removed with the tetrahydrofurran (THF) or a suitable solvent *(Note 1)*, and collect into an appropriate vessel. Evaporate the solvent from the removed coating and dry to constant weight (to the nearest 1 mg) in an air convection oven at 60^{O}C for about 1 hour. Remove the vessel from the oven and cool in a desiccator.

4.2 Transfer the removed coating to a mortar and grind the sample with a pestle. An electric grinder may be used when the sample is too difficult to grind with a pestle and a mortar. Sieve the ground coating with a 500 µm sieve. The sample passing the 500 µm is then sieve through a 250 µm. The portion of the ground coating that passes the 500 µm and do not pass the 250 µm is used for the test. Place the portion in a weighing vessel and dry to constant weight (to the nearest 1 mg) in an air convection oven at 60^{O}C for 1 hour. Remove the vessel from the oven and cool in a desiccator.

4.3 Accurately transfer 100 mg of the dried coating into a tared 100 mL beaker and weigh to the nearest 0.1 mg. Add 20 mL of the 5% (v/v) HCl leaching solution and immediately start stirring for 10 ±1 min at 20 ± 2°C with the use of an oscillating hotplate or a magnetic stirrer. Filter the solution, with a filter paper Whatman no.40 and a glass funnel, into a 50 mL centrifuge tube, wash with a few mL of deionized water, add 1 mL of concentrated nitric acid, and make up to volume with deionized water.

Note 1: Acetone or dichloromethane may be used to facilitate the removal of the applied coating. These solvents like the tetrahydrofurran , however, should not be used if the test article's substrate material is a plastic.

4.4 Prepare a 10-fold dilution from the 50 mL centrifuge tube into the 15 mL centrifuge tube using 2% (v/v) nitric acid.

5 DETERMINATION

5.1 Prepare a blank solution consisting of 0.2% (v/v) hydrochloric acid and 2% (v/v) nitric acid into a 50 mL centrifuge tube. Make up to volume with deionized water.

5.2 Prepare a minimum of three working standards in the linear range of the detector of the instrument to obtain a linear calibration curve with a correlation coefficient of at least 0.99. The working standards used to built the calibration curves were as follows: 10 ppb, 20 ppb, 50 ppb and 100 ppb from a 5 ppm mix stock solution of the five elements in 0.2% (v/v) hydrochloric acid and 2% (v/v) nitric acid.

5.3 The standards and the control (Nist SRM 1633b, coal fly ash) should be analysed using five replicates. For the samples, two or three different aliquots (if possible) should also be analysed using five replicates.

5.4 Analysis conditions:

Instrument: Elan 5000 ICP-MS, Perkin-Elmer
Autosampler: AS-90
Flow Rates (L/min): Plasma:15.00, Auxiliary: 0.800, Nebulizer: 0.951
Gas: Liquid Argon
Plasma power: 1000 W
Replicate time (ms): 1500
Dwell time (ms): 300
Scanning mode: peak hop
Sweeps/reading: 5
Number of replicates: 5
Mass used: (Cd:114) (Ba:138) (Sb:123), (Se:82), (As:75)

6 CALCULATION AND REPORTING

6.1 Calculate the percentage by weight of leachable elements in the dry coating test sample according to the following equation:

$$\text{Leachable elements \% (w/w)} = \frac{0.05 \times C \times Df}{Wt}$$

where:

C = Concentration of the elements measured in the sample leaching solution (mg/L)
Df = Dilution factor (if required)
Wt = Weight of test sample used (g).
0.05 = 50 mL x 10 (dilution) ÷ 10,000

6.2 Where the quantity of sample for testing is sufficient and where practical, the result of analysis shall be reported as the average of a minimum of two independent replicate determinations having a precision which should not differ more than the specifications defined in section 8.

6.3 Where applicable, the deviation from the mean of the duplicate determinations or the standard deviation of replicate determinations (s for n > 2) shall be calculated *(Note 2)* and the result of analysis reported in the following format:

Sample No.	Specimen No.	Colour/ Description	[Cd] Leachable % (w/w)	[Ba] Leachable % (w/w)	[Sb] Leachable % (w/w)	[Se] Leachable % (w/w)	[As] Leachable % (w/w)
1	0.04167		x.xx ± 2s	x.xx ± 2s	x.xx ± 2s	x.xx ± 2s	x.xx ± 2s

7 QUALITY CONTROL PROCEDURE

7.1 In order to ensure the proper operation of the instrumentation and that the precision and bias 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.

7.2 The normal and correct operation of the ICP-MS shall be verified according to the following guidelines:

Note 2: The standard deviation (s) of the test results may be calculated according to the following equation, where: x_i is the result of each individual determination, $\bar{x}$ is the average of the replicate determinations and n is thetotal number of replicates. $\left[s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}} \right]$

7.2.1 Run the standard operating procedures for ICP-MS (SOP-04) and verify that the measurements are within the tolerance limits of the expected values. If the 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 specifications, the ICP-MS shall immediately be repaired and/or recalibrated to meet the prescribed operating conditions prior to proceeding with the analysis.

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

7.3.1 Conduct the analysis of a NIST SRM 1633b, coal fly ash analysed under identical experimental conditions to that of the test sample. Record the test result for the elements in the analytical instrument's QC logbook, and verify that the result is within acceptable limits of the control chart, 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.

8 PRECISION AND BIAS

8.1 *Repeatability*: The closeness of agreement between test results, as obtained by the same analyst with the same instrument under constant operating conditions on identical test material, should, in the normal and correct operation of the test method, not differ more than 16.0 %, 26.0 %, 19.2%, 16.0% and 29.8% repeatability limit at a 95% probability level (n=10) for a test value of 1.19% (w/w)arsenic, 0.31% (w/w)selenium, 0.28% (w/w)cadmium, 0.92% (w/w)antimony, and 0.60% (w/w)barium in a spike solution in “Armor Coat, Multi-Purpose Enamel Hunter Green” (#48-8708-8) paint.

95% repeatability limit = $1.960\sqrt{2}$ CV% = 2.8 CV% *(Note 3)*

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

8.3 *Bias*: The bias cannot be established due to the absence of an accepted “leachable” reference value in paint. However, the NIST SRM 1633b, coal fly ash, was used to verify the leachable value obtained for arsenic, selenium, barium, cadmium and antimony (n=5) compared to the known reference values. The following table shows the results.

Note 3: $CV\%_r$= Repeatability coefficient of variation in percent (within a laboratory)- ASTM E177-90a.

Elements in Nist SRM1633b	Leachable Concentration (ppm)	Reference Concentration (ppm)
As	88.5 ± 2.3	136.2 ± 2.6
Se	5.96 ± 0.68	10.26 ± 0.17
Ba	69.3 ± 2.1	709 ± 27
Cd	n.d.	0.784 ± 0.006
Sb	n.d.	6*

n.d. = Not detected
* = Non-certified value

9 LIMIT OF DETECTION

9.1 The limit of detection (LOD) of this method, as determined by the ICP-MS has been calculated to be:
0.0004% (w/w) for cadmium
0.0003% (w/w) for barium
0.0006% (w/w) for antimony
0.0010% (w/w) for selenium
0.0026% (w/w) for arsenic
using a 0.019% (w/w) of each of the elements (aqueous stock solutions) spiked in "Armor Coat, Multi-Purpose Enamel Hunter Green" (#48-8708-8) paint. *(Note 4)*

LOD=2 x 1.645 x s = 3.29 x s

S= standard deviation obtained from replicate analyses (n=9).

Note 4: ASTM test method D4210.

10 LIMIT OF QUANTIFICATION

10.1 The limit of quantification (LOQ) of this method, as determined by the ICP-MS has been calculated to be:
0.001% (w/w) for cadmium
0.001% (w/w) for barium
0.002% (w/w) for antimony
0.003% (w/w) for selenium
0.008% (w/w) for arsenic
using a 0.019% (w/w) of each of the elements spiked in "Armor Coat, Multi-Purpose Enamel Hunter Green" (#48-8708-8) paint. (*Note 4*)

Results below the limit of quantification are reported less than the LOQ.

LOQ=10 x s = 10 x s

S= standard deviation obtained from replicate analyses (n=9).

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