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1 **Scope**

- 1.1 This method describes a general procedure for the determination of leachable **arsenic, selenium, cadmium, antimony, and barium** in decorative or protective coatings applicable to item 9(c) of Part I, Schedule I of the Hazardous Products Act (**SOR 2005-344**).

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 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).
- 2.5 C. Watson, "Update of Method C-03, Determination of Leachable Cadmium (Cd), Barium (Ba), Antimony (Sb), Selenium (Se) and Arsenic (As) in Applied Coatings." Product Safety Laboratory, Project Report No. 2004-0801. (Nov. 2004)
- 2.6 **A. Babcock, "Update of Method C-03, Determination of Leachable Arsenic (As), Selenium (Se), Cadmium (Cd), Antimony (Sb), and Barium (Ba) in Applied Coatings." Product Safety Laboratory, Project Report No. 2005-0881. (Oct. 2007)**

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3 **Reagents and Apparatus** (Note 1)

- 3.1 ICP-MS Agilent 7500a equipped with an internal standards addition Tee
- 3.2 Arsenic, Selenium, Cadmium, Antimony and Barium standards, 1000 ppm, or As, Se, Cd, Sb, Ba (+ others) multi-element standard 10.0 ppm $\pm$ 0.5%, SCP Science or equivalent, traceable to NIST, for calibration
- 3.3 10.0 ppb As, Se, Cd, Sb, Ba calibration control standard
- 3.4 Gallium, Indium and Bismuth standards, 1000 ppm (nominal), SCP Science or equivalent, traceable to NIST, for internal standards
- 3.5 Ultra-pure (18.2 M Ω) water, free of As, Se, Cd, Sb, Ba
- 3.6 Hydrochloric acid, concentrated (~ 37% w/w), Trace Metal Grade, Fisher Scientific
- 3.7 Nitric acid, concentrated (~ 69% w/w), Trace Metal Grade, Fisher Scientific
- 3.8 Scalpel or other suitable scraping tool.
- 3.9 Tetrahydrofuran (THF) HPLC Grade, Caledon Laboratories, Ltd.
- 3.10 Electric grinder
- 3.11 Mortar and pestle
- 3.12 Air convection oven
- 3.13 Desiccator
- 3.14 Sieves, 250 and 500 μ m mesh
- 3.15 Sample bottles for sieved paint
- 3.16 Analytical Balance, with a precision of 0.1mg
- 3.17 Weighing vessels
- 3.18 Glass beakers, 50 mL
- 3.19 Oscillating hot plate or magnetic stirrer
- 3.20 Filter paper, Whatman no. 40
- 3.21 Funnels to fit 50 mL flasks or tubes
- 3.22 Volumetric flasks, 50 mL, 2 L
- 3.23 Sample tubes, screw cap, 50 mL certified volume
- 3.24 Pipettes adjustable 10 - 100 μ L, 100 - 1000 μ L, 0.500 - 2.50 mL, 1.00 - 10.00 mL
- 3.25 NIST SRM 1633b, Coal Fly Ash, used as a control

Note 1: Equivalent materials and apparatus may be used.

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4 Experimental Procedure

- 4.1 Scrape off the applied coating from the test sample with a scalpel, or other suitable **scraping** tool, being careful not to remove any of the underlying substrate material. Alternatively, the coating can be removed with tetrahydrofuran (THF) or a suitable solvent (*Note 2*), and collected **ed** 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°C ± 3°C**. **This may take several hours**. 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 **through** the 500 µm **sieve** is then **sieved** through a 250 µm **sieve**. The portion of the ground coating that passes the 500 µm and **does** not pass the 250 µm is used for the **leaching** test. Place the **sieved** portion in a weighing vessel and dry to constant weight (to the nearest 1 mg) in an air convection oven at **60°C ± 3°C**. **This may take about an** hour. Remove the vessel from the oven and cool in a desiccator.
- 4.3 Prepare the 5% (v/v) HCl leaching solution by diluting 50 mL of concentrated (approx. 37% w/w) hydrochloric acid to 1000mL with ultra-pure water.
- 4.4 Transfer about 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 minutes** at **20°C ± 3°C** with the use of an oscillating hotplate or a magnetic stirrer. **At the end of the 10 ± 1 minutes, immediately** filter the solution, **through** a Whatman no. 40 filter paper in a funnel, into a 50 mL volumetric flask **or certified 50 mL sample tube**, wash with a few mL of **ultra-pure** water, add 1 mL of concentrated nitric acid, and make up to volume with **ultra-pure** water. At least **three** replicate analyses should be performed **on each coating sample**.
- 4.5 Prepare a blank solution by adding 20 mL of the **5%** (v/v) HCl leaching solution to a 100 mL beaker and immediately start stirring for **10 ± 1 min.** at **20°C ± 3°C** with the use of an oscillating hotplate or a magnetic stirrer. **At the end of the 10 ± 1 min. immediately** filter the solution, **through** a **Whatman no. 40** filter paper

Note 2: Acetone or dichloromethane may be used to facilitate the removal of the applied coating, solvents like tetrahydrofuran should not be used if the test article's substrate material is a plastic.

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and a funnel, into a 50 mL volumetric flask or certified 50 mL sample tube, wash with a few mL of ultra-pure water, add 1 mL of concentrated nitric acid, and make up to volume with ultra-pure water.

- 4.6 Prepare a 2.0% (v/v) nitric acid diluting solution by diluting 20 mL of concentrated (approx. 69% w/w) nitric acid to 1000mL with ultra-pure water.
- 4.7 Dilute the worked-up leachate ten times using 2% (v/v) nitric acid (the 50 mL leachate from section 4.4).

5 Calibration

- 5.1 Prepare an acid solution consisting of 0.2% (v/v) hydrochloric acid and 2.0% (v/v) nitric acid in a 2 L volumetric flask. Use 4 mL of conc. HCl and 40 mL of conc. HNO₃ and make up to 2 L volume with ultra-pure water. This solution will be used as a blank solution, to prepare calibration standard solutions, and to dilute samples that are over the linear dynamic range of the instrument.
- 5.2 Prepare a series of at least three working calibration 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. These standards should be in the following range: 0 ppb to 100 or 200 ppb diluted from a 10 ppm solution of the five elements. Make up all calibration standards in 0.2% (v/v) hydrochloric acid and 2.0% (v/v) nitric acid.
- 5.3 Prepare about 100 - 250 mL of a 100 ppb solution of the internal standards Ga, In, Ba in 5% nitric acid. This solution is pumped into the internal standard addition Tee (on the back of the peristaltic pump) where it mixes with the sample before going to the spray chamber of the ICP-MS.
- 5.4 Prepare separately from the standards a 10 ppb multi-element calibration control solution, or buy it ready-made with a NIST traceable certificate of analysis.
- 5.5 Analyse the calibration standards using a minimum of five replicate readings in the ICP-MS method. Use the same ICP-MS method that will be used for the blanks, controls, and samples. Obtain a calibration curve of ion counts per second vs. concentration and check it for suitability (e.g. outliers & linearity / curve fitting) for each element before proceeding with the analysis of the samples.

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6 Determination

- 6.1 Analyse the method blank before and after each batch of samples.
- 6.2 Check the calibration by analysing the 10 ppb multi-element calibration control solution. If the calibration is not in control, it may be necessary to re-make the control solution and / or the calibration standards.
- 6.3 Analyse the control sample (NIST 1633b - coal fly ash) for all five elements. Record the results in the logbook method control chart (Use CCPro software).
- 6.4 Analyse the sample solutions using a minimum of five replicate readings in the ICP-MS method. The use of nine or more replicate readings gives better statistics, but results in slightly longer analysis times. If necessary, dilute the sample with 0.2% HCl and 2.0% HNO₃ (as prepared in § 5.1) to keep the results within the range of the calibration.

7 Calculations and Reporting

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

$$\text{Leachable elements \% (w/w)} = \frac{Ci \times 50 \times 10 \times Df}{m \times 10,000,000}$$

where:

- Ci** = Concentration of element in the leaching solution (ppb) from the instrument § 6.4
- 50** = Volume of worked-up leachate (filtered, rinsed, acidified) § 4.5
- 10** = Dilution of leachate § 4.7
- Df** = Further Dilution factor (if required to stay within calibration) § 6.4
- m** = mass (g) of test sample used § 4.4
- 10,000,000** = ppb / percent

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

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- 7.3 Where applicable, the **average ($\bar{x} \times 10^{+e}$)** and the **sample** standard deviation (**$s \times 10^{+e}$**) of replicate determinations (s for n > 2) shall be calculated (Note 3), and the result of analysis reported in the following format:

Sample No.	Specimen No.	Colour / Description	[As] Leachable % (w/w)	[Se] Leachable % (w/w)	[Cd] Leachable % (w/w)	[Sb] Leachable % (w/w)	[Ba] Leachable % (w/w)
S-1001234	1A	red paint	$(\bar{x}.x \pm 2s.s) \times 10^{+e}$	$(\bar{x}.x \pm 2s.s) \times 10^{+e}$	$(\bar{x}.x \pm 2s.s) \times 10^{+e}$	$(\bar{x}.x \pm 2s.s) \times 10^{+e}$	$(\bar{x}.x \pm 2s.s) \times 10^{+e}$
S-1001234	2A	blue paint	$(\bar{x}.x \pm 2s.s) \times 10^{+e}$	$(\bar{x}.x \pm 2s.s) \times 10^{+e}$	$(\bar{x}.x \pm 2s.s) \times 10^{+e}$	$(\bar{x}.x \pm 2s.s) \times 10^{+e}$	$(\bar{x}.x \pm 2s.s) \times 10^{+e}$

8 Quality Control Procedure

- 8.1 To ensure the proper operation of the **instrument** and that the precision 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.
- 8.2 The normal and correct operation of the ICP-MS shall be verified according to the following guidelines:
- 8.2.1 Run the ICP-MS **Tune program** and verify that the **values (ion counts per second)** for the tuning solution elements (typically Li Y TI) are within acceptable limits of the historical values. A slow decline in the numbers is to be expected as the detector wears out over a period of about two years. Record the tuning element values in the ICP-MS logbook and include a copy of the tune program printout in the sample or report file. If the tuning values are too low, re-tune the instrument to get acceptable values. Minimum acceptable values are Li 6400, Y 16000, TI 9600 .

Note 3: The standard deviation (s) of the test results may be calculated according to the following equation, where x_i is the result of an individual determination, $\bar{x}$ is the average of the replicate determinations, and n is the total number of replicates.

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{(n-1)}}$$

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

8.3.1 Conduct **an** analysis of **the leachate of** NIST SRM 1633b, coal fly ash, **tested** under identical experimental conditions **(except for grinding and sieving)** to **those** of the **coating** sample. Record the **analytical test results** for **all of** the elements in the **ICP-MS** QC logbook. Verify that the **results are** within acceptable limits **on** the control chart, **and if so, enter a note** in the sample **folder(s)** to the effect that the test method was found to be "within control". **If** the test **results** of the control sample fall outside the specifications of the method, the entire analytical procedure shall be repeated.

9 Precision and Bias

9.1 Repeatability (r): The deviation between replicate test results, as obtained from analysis of NIST 1633b (coal fly ash) by the same analyst using the same instrument under constant operating conditions, in the normal and correct operation of the test method, should not differ by more than the following repeatability limit at a 95% probability level ($1.960 \times \sqrt{2} \times CV\% = 2.772 \times CV\%$).
As: 11% Se: 100% Cd: n/a Sb: n/a Ba: 50%

9.2 **Bias:** The bias cannot be established due to the absence of an accepted "leachable" reference value in paint.

10 Limit of Detection

10.1 The limit of detection (LOD) of this method, as determined by ICP-MS has been calculated **(Note 4)** to be:

Arsenic: 0.00018% (w/w)
Selenium: 0.00015% (w/w)
Cadmium: 0.00019% (w/w)
Antimony: 0.00043% (w/w)
Barium: 0.00041% (w/w)

Note 4: ASTM test method D4210.

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11 Limit of Quantitation

- 10.1 The limit of quantitation (LOQ) of this method, as determined by ICP-MS has been calculated (Note 5) to be :

Arsenic: 0.00055% (w/w)
Selenium: 0.00047% (w/w)
Cadmium: 0.00059% (w/w)
Antimony: 0.0013% (w/w)
Barium: 0.0012% (w/w)

..... End

Note 5: ASTM test method D4210

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