Reference Manual Book 5: Laboratory Policies and Procedures

Part B: Test Method Section

Method C02.3.1 : Determination of Total Lead and Cadmium in Plastic Consumer Products by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

1 SCOPE

1.1 This method describes a general procedure for the determination of total lead (Pb) and cadmium (Cd) in plastic consumer products by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) as applicable under the *Children's Jewellery Regulations* (SOR/2018-82, Sections 2 and 3).

2 SAFETY

2.1 In general, all work done when preparing samples and working solutions should be conducted in a well ventilated space/area equipped with a fume hood.

2.2 Hazards

2.2.1 Concentrated nitric acid is a liquid that is corrosive to the skin and the respiratory tract if inhaled. Adequate precautions must be taken to avoid undue exposure. Wherever possible, all steps of the analytical process that make use of this compound must be conducted in a well-ventilated fume hood.

3 APPLICABLE DOCUMENTS

3.1 Log book LBC-69, MARS 6 #1

3.2 Log book LBC-70, MARS 6 #2

3.3 Log book LBC-82, Agilent 5100 ICP-OES

3.4 SOPC-12, Standard Operating Procedure for Balances

3.5 SOPC-82, Standard Operating Procedure for the Agilent 5100 ICP-OES using Cetac ASX-520 Series Auto sampler

4 DEFINITIONS

4.1 N/A

5 REAGENTS AND APPARATUS

5.1 Reagents

5.1.1 ERM-EC681m, Polyethylene (high level element content) Certified Reference Material (certified value for Pb: 69.7±2.5 mg/kg, Cd: 146±5 mg/kg), Institute for Reference Materials and Measurements (IRMM)

5.1.2 Milli-Q® Reference ultrapure water Type 1 (resistivity of 18.2 MΩ.cm at 25 °C)

5.1.3 Nitric acid, 67-70% (w/w) TraceMetal™ Grade, Fisher Scientific or equivalent.

5.1.4 PlasmaCAL 1.00 µg/mL Cd and 10.0 µg/mL Pb in 5% nitric acid Certified Multi Element Reference Standard for ICP-AES & -MS, SCP Science or equivalent. Certified value (see Certificate of Analysis).

5.1.5 PlasmaCAL 50 µg/mL Multi-Element Tuning Solution in 5% nitric acid for ICP-AES & -MS, SCP Science or equivalent. Certified value (see Certificate of Analysis).

5.1.6 PlasmaCAL 100 µg/mL Cd in 5% nitric acid Certified Standard for ICP-AES & -MS, SCP Science or equivalent. Certified value (see Certificate of Analysis).

5.1.7 PlasmaCAL 1000 µg/mL Pb in 5% nitric acid Certified Standard for ICP-AES & -MS, SCP Science or equivalent. Certified value (see Certificate of Analysis).

5.1.8 10% nitric acid solution for cleaning vessels.

5.1.9 Alconox™ detergent solution for cleaning

5.1.10 Aqua regia solution for cleaning

5.2 Labware

5.2.1 Disposable scintillation glass vials, 20 mL or equivalent

5.2.2 Filtration funnels

5.2.3 Scalpel or similar scraping device

5.2.4 Volumetric flasks: 250 mL, 1L and other volumes as required

5.2.5 Whatman # 40 filter paper

5.2.6 50 mL class A polypropylene DigiTUBEs

5.3 Equipment

5.3.1 CEM MARS 6 Microwave Accelerated Reaction System, MARSXpress Teflon® digestion vessels and accessories

5.3.2 Eppendorf Mechanical pipettes (as required): 10-100 µL, 100-1000 µL, 500-2500 µL, 1-10mL

5.3.3 Fortuna® Optifix® Bottle-top dispenser, 2-10 mL or equivalent.

5.4 Analytical Instruments

5.4.1 Agilent 5100 Inductively coupled plasma optical emission (ICP-OES) spectrometer equipped with Cetac ASX-500 series auto sampler

5.4.2 Analytical balance, 0.1 mg readability

6 EXPERIMENTAL PROCEDURE

6.1 Precaution

6.1.1 Store the certified reference material (ERM-EC681m) in an amber bottle at 18±5°C, as required by the certificate of analysis.

6.1.2 All lead and cadmium containing solutions must be properly stored and disposed of according to the applicable procedures.

6.1.3 Prior to being used, all glassware should be soaked overnight in a solution of aqua regia, and then rinsed with deionized water and air dried.

6.1.4 MARSXpress Teflon® digestion vessels should be sequentially soaked overnight in a solution of AlcanoxTM detergent, soaked overnight in a 10% nitric acid solution, rinsed with deionized water and air dried.

6.1.5 Should any residues remain inside the vessels after washing, run a cleaning digest with 10 mL of concentrated nitric acid (see LBC-69, LBC-70 for details), then soak the vessels overnight in a 10% nitric acid solution, rinse them with deionized water, and air dry them.

6.2 Preparation of Solutions

6.2.1 Prepare a 5% (v/v) nitric acid solution by adding 50 mL of concentrated nitric acid into a 1L volumetric flask. Make up to volume with Milli-Q water. This solution will be used to prepare working standards, as a rinse solution, and to dilute samples that are over the linear calibration range.

6.2.2 Prepare a 10µg/mL Pb intermediate solution by diluting an appropriate aliquot of the 1000 µg/mL certified Pb standard with the 5% nitric acid solution prepared in section 6.2.1.This will be used to prepare a sensitivity check solution (6.2.4).

6.2.3 Prepare a 10µg/mL Cd intermediate solution by diluting an appropriate aliquot of the 100 µg/mL certified Cd standard with the 5% nitric acid solution prepared in section 6.2.1. This will be used to prepare a sensitivity check solution (6.2.4).

6.2.4 Prepare a sensitivity check solution (0.1 µg/mL Pb and 0.05 µg/mL Cd) by diluting appropriate aliquots of the 10 µg/mL intermediate solutions for Pb and Cd with the 5% nitric acid solution prepared in section 6.2.1.

6.3 Preparation of Standards

6.3.1 Working standards

Prepare a series of at least six working standard solutions of: 0.1, 0.5, 2.0, 5.0, 10.0, 20.0 µg/mL Pb, and 0.1, 0.2, 0.5, 0.75, 1.0, and 1.8 µg/mL Cd in volumetric flasks, by making the appropriate diluting of the 1000 µg/mL Pb and 100 µg/mL Cd certified reference solution in 5 % (v/v) of conc. HNO_3 as prepared in section 6.2.1. Refer to the calibration standard preparation form for details.

6.4 Subsampling

6.4.1 With a clean scalpel blade, scrape or cut off small pieces of the clean and dry test article onto a clean surface. Collect the pieces in a scintillation vial and label with a sample and specimen number.

6.5 Sample Preparation

6.5.1 Transfer about 150 mg of the test article into a Teflon digestion vessel and weigh to the nearest 0.1 mg. Record the mass. Prepare the sample in triplicate.

6.5.2 Add 2.5 mL of concentrated nitric acid to the digestion vessels.

6.5.3 Plug, cap, and seal the vessels by tightening their caps with the rectangular cap tightener until a clicking sound is heard.

6.5.4 Insert the vessels in the composite sleeves of the MARS turntable rack according to the recommended distribution diagram in the MARS 6 logbooks (LBC-69, LBC-70) and place the rack into the microwave oven.

6.5.5 From the “ONE TOUCH” library menu on the MARS 6, select and run the “PVC” method from the list of preprogrammed methods.

6.5.6 The “PVC” method’s parameters are as follows:

Method: PVC.m6m Vessel Type: MARSXpress Control Style: Ramp to Temperature				Number of Vessels: 8-40 Volume per Vessel: 2.5 mL Sample weight: 0.1 g Acid: nitric, 65% (w/w)		
Stage	Power Wattage (W)	Maximum Power	Ramp Time (min)	Pressure Control (psi)	Maximum Temp.	Hold Time (min)
1	1030 to 1800	100%	20:00 to 25:00	Not applicable	210^{0}C	15:00

6.5.7 Following completion of the digestion program, allow the vessels to remain in the microwave oven until the temperature of the vessels is less than 40 °C. Carefully open the vessels and filter the digest solutions by gravity through Whatman filter paper #40 into 50 mL class A polypropylene DigiTubes. Rinse the digestion vessels, plugs and caps with Milli-Q water. Filter the rinsates, and make up the filtrate solutions to 50 mL with Milli-Q water.

6.6 Blank Preparation

6.6.1 Prepare a method blank solution by completing steps 6.5.1 to 6.5.7 while omitting the test sample.

6.7 Control Preparation

6.7.1 Complete steps 6.5.1 to 6.5.7 using the certified reference material (ERM-EC681m). Prepare the control in duplicate.

7 CALIBRATION

7.1 Analyse the 0.1, 0.5, 2.0, 5.0, 10.0, 20.0 µg/mL Pb; and the 0.1, 0.2, 0.5, 0.75, 1.0, and 1.8 µg/mL Cd standards prepared in section 6.3.1 on the ICP-OES using the analytical conditions specified in sections 8.1 and 8.2.

7.2 Prepare calibration curves of emission intensity versus concentration for all the emission lines described in section 8.2. Where possible, use linear regression. A correlation coefficient of at least 0.990 must be achieved.

8 DETERMINATION

8.1 Conduct the analysis on the Agilent 5100 ICP-OES with the following conditions (C02.3.1PbCd.ests):

Measurement Conditions		
Read time (s)	5	
Nebulizer flow rate (L/min)	0.7	
RF power (kW)	1.20	
Plasma flow (L/min)	12.0	
Aux flow (L/min)	1.0	
Stabilization time (s)	15	
Viewing mode	SVDV(dual view)	
Viewing Height (mm)	8	
Common Conditions		
Replicates	5	
Pump speed (rpm)	12	
Uptake delay (s)	30	Fast pump
Rinse time (s)	30	Fast pump

8.2 The following ICP-OES emission lines are analyzed:

Compound	Wavelength (nm)	Purpose
Cadmium	228.802	Quantification
	214.439	Interference check
	226.502	Interference check
Lead	220.353	Quantification
	217.000	Interference check
	283.305	Interference check

8.2.1 The concentration of Cd in the measured solutions is determined using the 228.802 nm emission line. The 214.439 nm and 226.502 nm emission lines are also monitored to ensure spectral interferences are not present.

8.2.2 The concentration of Pb in the measured solutions is determined using the 220.353 nm emission line. The 217.000 nm and 238.305 nm emission lines are also monitored to ensure spectral interferences are not present.

8.2.3 If spectral interferences are suspected or the readings between the three emission lines for lead or cadmium vary by more than 5%, perform an IntelliQuant analysis (see SOPC 82) and check the results for the presence of interfering elements.

8.2.4 If an interferent is determined to be present in sufficient concentration (> 1%), perform a FACT correction on the affected spectra (See SOPC82).

8.3 Determine the Cd and Pb concentration, in mg/kg, of the method blank solution prepared in section 6.6 before and after the analysis of a batch.

8.4 Verify the sensitivity of the instrument with the sensitivity check solution (0.1 µg/mL Pb, 0.05 µg/mL Cd) before and after the analysis of a batch. Record the results in an electronic control chart.

8.5 Verify the concentration of the certified reference solution containing 1 µg/mL Cd and 10 µg/mL Pb as a check standard before and after the analysis of a batch. Record the results in an electronic control chart.

8.6 Determine the Cd and Pb concentration, in mg/kg, of the of the ERM-EC-681m control samples prepared in section 6.7. Record the results in an electronic control chart.

8.7 Determine the Cd and Pb concentration, in mg/kg, of the test samples prepared in section 6.5. If necessary, dilute the sample solutions with 5% nitric acid by an appropriate factor such that the measurements taken fall within the calibration range.

9 CALCULATIONS AND REPORTING

9.1 Calculate the concentration, in mg/kg, of cadmium and lead in the test sample according to the following equations:

$$\text{Cadmium (Cd), mg/kg} = \frac{C_f \times V_f \times Df}{Wt}$$

$$\text{Lead (Pb), mg/kg} = \frac{C_f \times V_f \times Df}{Wt} + 5.19$$

Where:
C_f = Concentration of cadmium or lead measured by the instrument in the sample solution (mg/L),
V_f = Final volume of sample solution (mL),
Df= Dilution factor (if required),
Wt= Weight of test sample used (g)

9.2 Where the quantity of a sample available for testing is sufficient and where practical, the result of analysis will be reported as the average of a minimum of three replicate preparations having a precision which meets or exceeds the specifications defined in section 11.1.

9.3 Where applicable, the average (x.xx) of replicate determinations plus or minus Student's t (for a confidence level of 0.975) times the standard deviation (s) of replicate determinations (s for n > 2) divided by the square root of number of replicates will be calculated. Results of analysis are reported in the following format:

Sample no.	Specimen no.	Colour / Description	$[Pb]_{total}$ (mg/kg)	$[Cd]_{total}$ (mg/kg)
S20xx-0xxxx	A		$x.xx \pm \frac{t_{0.975[95\%]} \times s}{\sqrt{n}}$	$x.xx \pm \frac{t_{0.975[95\%]} \times s}{\sqrt{n}}$

Where:
$t_{0.975[95\%]}$ is the value for t obtained from Student's t values table
s = standard deviation for the sample
n = number of values in the data set

9.4 All test results below the method's limit of quantification as defined in section 12, shall be reported as less than this value.

10 QUALITY CONTROL PROCEDURE

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

10.1 If the calibration curve (section 7.2) has a correlation coefficient that is less than 0.990, recalibrate and/or repair the instrument to meet the prescribed operating conditions prior to proceeding with the analysis.

10.2 The normal and correct operation of the Agilent 5100 ICP-OES shall be verified according to the following guidelines:

10.2.1 Record the concentration of the sensitivity check solution containing 0.1 µg/mL Pb and 0.05 µg/mL Cd in the electronic control chart. If the instrument is found to be out of calibration or in a state of disrepair, it shall immediately be re-calibrated and/or repaired to meet the prescribed operating conditions prior to proceeding with the analysis.

10.2.2 Record the concentration of the certified solution containing 1 µg/mL Cd and 10 µg/mL Pb in the electronic control chart. If the instrument is found to be out of calibration or in a state of disrepair, it shall immediately be re-calibrated and/or repaired to meet the prescribed operating conditions prior to proceeding with the analysis.

10.3 If the method blank concentration is greater than the limit of quantitation of the method for Cd or Pb as defined in section 12, repeat the analysis.

10.4 Record the concentrations of the ERM-EC681m control samples in the electronic control chart. Verify that the measurements are within the control limits (±3s). If the control sample results are outside of the control limits, run the calibration standards a second time and re-calculate the results. If the control sample results are still outside of the control limits, the entire analytical procedure shall be repeated. Do not continue testing until the source of the problem is identified and resolved.

10.5 If the repeatability of the result of a given sample ($t_{0.975(95\%)} \times s/\sqrt{n}$) for a confidence interval of 95 % is equal or less than the repeatability limit of the method, the test result is considered within the limitations of the method.

10.5.1 If the repeatability of the result of a given sample does not meet the repeatability limit of the method (section 11.1) the analyst must consult with the section head before proceeding. It may be necessary to repeat the test method in triplicate, where the quantity of sample is sufficient and where practical. Unless an error in the original test is documented or a result is determined to be an outlier, all replicates should be used to determine the mean and the repeatability of the results for a given sample for a confidence interval of 95 %.

11 PRECISION AND BIAS

11.1 Repeatability

The repeatability of the method was determined by conducting 20 successive analyses on the ERM-EC681m certified reference material. The repeatability limit at 95% confidence level is calculated to be:

Repeatability limit for Pb = 7%

Repeatability limit for Cd = 8%

11.2 Bias

11.2.1 The method has a bias of -5.19 mg/kg for the determination of lead. A bias correction of +5.19 should be applied to calculation of test results as shown in the equations in section 9.1.

11.2.2 There is no bias correction for this method for the determination of cadmium.

12 LIMITS OF DETECTION AND QUANTIFICATION

12.1 The limit of detection (LOD) and limit of quantification (LOQ) of the method are presented in the following table:

Compound	Method LOD (mg/kg)	Method LOQ (mg/kg)
Cadmium	13	39
Lead	5	16

13 REFERENCES

13.1 Watson, C. *Revision of Method C02.3 "Determination of Total Lead in Polyvinyl Chloride Mini-Blinds by Closed Vessel Microwave Digestion"* ; Project # 2003-0756; Health Canada: Product Safety Laboratory, 2003.

13.2 Charette, M. *Determination of Total Lead in Polyvinyl Chloride Products by Closed Vessel Microwave Digestion*; Project # 2007-0999; Health Canada: Product Safety Laboratory, 2007.

13.3 Michaud, A. *Update of method C02.3 "Determination of Total Lead in Polyvinyl Chloride Products by Closed Vessel Microwave Digestion"*; Project # 2011-1308; Health Canada: Product Safety Laboratory, 2011.

13.4 Gudgeon, C. *Update of method C02.3 "Determination of Total Lead in Polyvinyl Chloride Products by Closed Vessel Microwave Digestion"*; Project # 2013-1485; Health Canada: Product Safety Laboratory, 2013.

13.5 ASTM E177-14, *Standard Practice for Use of the Terms Precision and Bias in ASTM Test Methods*, ASTM International, West Conshohocken, PA, 2014, www.astm.org.

13.6 Ali, Y. *Update of method C02.3 "Determination of Total Lead in Polyvinyl Chloride Products by Closed Vessel Microwave Digestion"*; Project # 2016-2216; Health Canada: Product Safety Laboratory, 2016.

13.7 PSL Reference Manual Book 5, Method C02.2, *Determination of Total Lead in Surface Coating Materials in Consumer Products by Flame Atomic Absorption Spectrometer*; Health Canada: Product Safety Laboratory, 2017.

13.8 Fafard, J.; Krushkova, S.; Ali, Y. *Method Development: C02.3.1 "Determination of Total Lead in Plastic Consumer Products by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)"*. Project # P2019-00048; Health Canada: Product Safety Laboratory, 2020.