Appendix V: Determination of Heavy Metals

Heavy metals refer to the heavy metals and their respective compounds arising from external contamination, and are absorbed and accumulated in CMM. Arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg) are those heavy metals with relatively high toxicity to human beings.

Method –

(1) **Analysis of heavy metals** – The analytical procedures must be validated and satisfy with all of the following criteria –

    (a)   the selected method is suitable for the analysis of the targeted heavy metals;

    (b)   the limits of detection and quantification are determined for each targeted heavy metal;

    (c)   the limit of quantification for each targeted heavy metal is set at 0.05 mg/kg;

    (d)   the recovery for each targeted heavy metal is between 75 and 125%;

    (e)   the repeatability of the method is less than 15% RSD; and

    (f)   a linear response is obtained from the analytical detector within the calibration range.

(2) **Reagents** – All reagents used should be of analytical grade or equivalent and free from any contaminant which may interfere with the analysis.

(3) **Apparatus** – Before using the laboratory wares which have been in contact with the samples, the standard and test solutions, clean them with dilute acids and then rinse them with distilled and de-ionized water.

(4) **Preparation of test sample** – Take a representative CMM sample and cut it into pieces, if necessary, before grinding. Powder the sample before the analysis. Whenever possible, the quantity of sample to be powdered should be of at least five times as much as those needed for the analysis.

(5) **Procedure** – The following procedures are applicable for the quantitative detection of As, Cd, Pb and Hg contents in CMM samples. It may have to modify the procedures for the analysis of some samples.

(a) **Microwave assisted acid digestion** – Weigh accurately 0.5 g of the sample in a PTFE microwave digestion vessel, add 7.5 mL of nitric acid. Allow the vessel to stand a while until the reaction ceases, then seal all vessels properly and place the completed vessel modules in the turntable of the microwave unit. Start the digestion programme, the selection of low-pressure or high-pressure microwave assisted acid digestion depends on the type of microwave digestion vessel available in the individual laboratory. Upon the completion of the programme, cool the mixture and vent the vessel manually. Transfer the digested sample solution to a 50-mL volumetric flask and make up to the mark with water, then transfer the solution to a centrifuge tube and centrifuge for 5 min. Pipette 10 mL of this solution into another 50-mL volumetric flask and make up to the mark with water. This is the test solution for subsequent instrumental analysis.

(b) **Quantitative analysis** – Quantify the heavy metals by using ICP-MS with indium (In) as an internal standard. Internal standards other than In can also be used provided that the method is properly validated.

Use an ICP-MS system that satisfies with all of the following criteria –

- a resolution better than or equal to 0.7 amu at 10% peak height;
- a mass range from at least 6 to 240 amu and a mass accuracy of ±0.05 amu; and
- a data system that allows correction for isobaric interferences and with an application of internal standard technique.

Prepare at least four standard solutions in dilute nitric acid (3%, v/v) containing all the targeted heavy metals at concentrations suitable for plotting calibration curves.

Note: The concentration of the internal standard in the test solution should be same as those in the standard solutions.

The suggested operation parameters are as follows –

Nebulizer Gas Flow	:	~ 0.9 L/min
Auxiliary Gas Flow	:	~ 1.2 L/min
Plasma Gas Flow	:	~ 15 L/min
Integration Time	:	1000 ms
ICP RF Power	:	1200 W
Detector	:	Dual mode
Scan Mode	:	Peak hopping

Set up and optimize the ICP-MS according to the manufacturer's recommended procedures. Calibrate the instrument with the mixed standard solution. Prior to data collection, flush the system with rinse blank until the signal level returns to the calibration blank level. Where appropriate, several isotopes of an element may be monitored with appropriate signal correction to counter-check the presence of spectral interferences. The isotopes recommended for monitoring the heavy metals are listed in Table 12. The calculation for As, Cd and Hg contents should be based on the signals of isotopes of 75 m/z, 114 m/z and 202 m/z, respectively. For Pb, the calculation should be based on the summation of the signal of the isotopes 206 m/z, 207 m/z, and 208 m/z.

Table 12 Recommended isotopes for monitoring the heavy metals

Heavy Metal	Isotope for Monitoring (m/z)
Arsenic	75
Cadmium	111, 114
Lead	206, 207, 208
Mercury	200, 202

Limits – The amount of heavy metals in CMM samples should comply with the limits listed in Table 13 below.

Table 13 The recommended limits of heavy metals in CMM samples

Heavy Metal	Limit (Not more than)
Arsenic	2.0 mg/kg
Cadmium	0.3 mg/kg
Lead	5.0 mg/kg
Mercury	0.2 mg/kg