# HS 1003 Heavy Metals Test

## 1. Purpose

This test method is used to analyse the heavy metal content in an aliquot portion of stabilised hot acetic acid extract by Atomic Absorption Spectroscopy (AAS).

*Note: Other analytical instrument such as Inductively Coupled Plasma (ICP) and Inductively Coupled Plasma Mass Spectrometry (ICPMS) can also be used, provided that they are capable to measure down to the required detection limit.*

## 2. Apparatus

2.1 Volumetric flasks, 1000mL and 250 mL.

2.2 Analytical balance, accuracy 0.1 mg.

2.3 Micropipettes from 5.0 μL to 20.0 μL with plastic tips (high density polyethylene/polypropylene).

2.4 Pipettes from 100 μL to 10 mL, glass or plastic, (high density polyethylene/polypropylene).

2.5 500 mL conical flask, wide neck with ground glass stopper with tap.

2.6 Filtration equipment, fritted-glass filter porosity 4 (nom. Size 90) with filter flask of 500 mL (see ISO 6556).

2.7 Graduated measuring cylinder, 250 mL.

2.8 Protective gloves.

2.9 Thermostatically controlled oven, suitable to control temperature in the range of 70 °C ± 2 °C.

2.10 Atomic absorption spectrometer with an appropriate detection system and sensitivity.

## 3. Reagents

All reagents and water used should be suitable for trace element analysis.

Store the solutions in High Density Polyethylene/Polypropylene bottles.

3.1 Acetylene, standard commercial grade.

3.2 Metal-free water

Prepare metal-free water by deionising tap water and/or by using the following processes: single distillation, redistillation or sub-boiling.

3.3 Nitric acid ($HNO_3$), concentrated and 1 + 1.

3.4 Concentrated sulphuric acid $H_2SO_4$.

3.5 Cadmium – stock solution (100 ppm)

*Warning: Cadmium is toxic.*

Dissolve 0.100 g of cadmium metal in 4 mL concentrated nitric acid. Add 8.0 mL

concentrated nitric acid and dilute to 1000 mL with water (1.00 mL = 100 μg Cd).

3.6 Lead – stock solution (100 ppm)

Dissolve 0.1598 g of lead nitrate ($Pb(NO_3)_2$) in the minimum volume of 1+1 nitric acid. Add 10 mL concentrated nitric acid and dilute to 1000 mL with water (1.00 mL = 100 μg Pb).

3.7 Chromium – stock solution (100 ppm)

Dissolve 0.1923 g of chromium (VI) oxide ($CrO_3$) in water. When solution is complete, acidify with 10 mL concentrated nitric acid and dilute to 1000 mL with water (1.00 mL = 100 μg Cr).

3.8 Mercury – stock solution (1000 ppm)

*Warning: Mercury is toxic.*

Dissolve 0.1354 g of mercuric chloride in 70 mL of metal-free water. Add 1.0 mL of concentrated nitric acid and dilute to 100 mL with water (1.00 mL = 1.00 mg Hg).

*Note: All stock standard solutions are commercially available.*

3.9 Hydrogen peroxide $H_2O_2$, 30 %.

3.10 Stannous ion ($Sn^{2+}$) solution

Use either stannous chloride, or stannous sulphate to prepare this solution containing about 7.0 g $Sn^{2+}$/100 mL.

- Dissolve 10 g $SnCl_2$ in water containing 20 mL conc. HCl and dilute to 100 mL.
- Dissolve 11 g $SnSO_4$ in water containing 7 mL conc. $H_2SO_4$ and dilute to 100 mL.

*Note: Both solutions decompose with aging. If a suspension forms, stir reagent continuously during use.*

3.11 Acetic acid 5 % (w/v) in aqueous solution.

## 4. Preparation of samples

### 4.1 General

The sample taken for testing should be in its ready-for-use state. Obtain a sample that meets the requirements of the sampling programme and handle it in such a manner to avoid contamination prior to testing. The sample should be put into a container or bags instantly after collect. To avoid contamination, certain precautions are necessary which are common to all sampling procedures:

- Scrupulous care should be taken to avoid accidental contamination of the sample during collection and subsequent handling.
- The sample should be collected in a sufficient amount and tested as soon as possible after collection.

### 4.2 Preparation of hot acetic acid extract for articles in container form

4.2.1 Measure a sufficient volume of 5 % acetic acid by measuring cylinder and preheat in the oven at 70 °C ± 2 °C. Fill the test specimen with acetic acid to a level within 0.5 cm of the top of the test specimen. Record the volume of acetic acid that has been used.

4.2.2 Cover the test specimen with an inert material to prevent evaporation, e.g. glass. This part of the operation should be carried out in the minimum time to prevent evaporation of acetic acid. The bottom of test specimen should be wrapped by aluminum foil to prevent leakage of solution. Leave this preparation for 2 hours in a thermostatically controlled oven maintained at 70 °C ± 2 °C.

4.2.3 Decant the solution and wash test specimen twice with acetic acid. If it contains precipitate, filter the solution and washings. Filter paper should be pre-washed with distilled water to remove artifacts. The total volume of acetic acid for washing should not exceed 5% of the volume used for filling up the container.

4.2.4 Stabilise the acetic acid extract by the addition of concentrated nitric acid in the ratio of 3.5 mL per 100 mL of sample. Mix the aqueous extract well and take an aliquot portion for investigation.

### 4.3 Preparation of hot acetic acid extract for articles in bag form

4.3.1 Tear or cut sample as taken into pieces approximately 1 $cm^2$ to 2 $cm^2$. Wear protective gloves to prevent contamination.

4.3.2 Weigh 10 ± 0.1 g of the test pieces to accuracy of 0.01 g, put them into the conical flask, add 200 mL of 5 % acetic acid and stopper the flask. Leave this preparation to stand for 2 hours in a water bath of 70 °C ± 2 °C, shake occasionally.

4.3.3 Decant the solution and wash test pieces in the flask twice with a fresh portion of 5 % acetic acid of 70 °C ± 2 °C. If it contains precipitate, filter the hot preparation. Transfer the extract and washings or the filtrate to a marked 250 mL volumetric flask, cool to 23 °C ± 2 °C. Stabilise the extract by addition of concentrated nitric acid in the ratio of 3.5 mL per 100 mL of sample. Fill up to the mark with water. Use the content of the flask for further investigation.

*Note: If necessary, it can scale up the solution but not more than twice of its original volume.*

## 5. Operating Procedures

### 5.1 General

Detailed instructions depend on the type of the equipment used. Follow the instructions of the manufacturer of the equipment. Correct the background absorption by using a suitable system.

**5.2 Determination of Cadmium, Lead, Chromium and Mercury content in hot acetic acid extract**

5.2.1 Suggested spectrometer settings and sensitivity

The suggest AA spectrometer settings are as follows:

- Cadmium 228.8 nm
- Lead 217.0 nm or
  283.3 nm (preferred)
- Chromium 357.9 nm
- Mercury 253.7 nm

And the method detection limit of the equipment for metal analysis should be:

- Cadmium 0.5 μg/L
- Lead 2 μg/L
- Chromium 1 μg/L
- Mercury 0.5 μg/L

*Note : 1 μg/L = 1 ppb*

5.2.2 Preparation of reference solutions

- Prepare a series of standard metal solution in the optimum concentration range, the reference solutions should prepared daily by diluting the single stock element solutions with water containing 1.5 mL concentrated nitric acid/litre. The concentration to be selected will depend on the instrument used and the expected concentrations in the extract. Prepare a calibration blank using all the reagents except for the metal stock solutions.
- Select at least three concentrations of each standard metal solution to bracket the expected metal concentration of sample. Aspirate the system with the blank solution and standard solution alternatively and run the next standard in the same manner.
- Prepare a calibration curve by plotting the absorbance of standards versus their concentrations.

5.2.3 Determination of the metal content

- Follow the instructions given by the manufacturer of the spectrometer in order to reduce interference and background noise. The details of the measurement depend on the type of the spectrometer. Follow the instructions and record the peaks for each element.
- Three parallel extractions should be carried out. From each extract, at least two parallel determinations should be carried out. Determine the concentration of each element by means of the calibration graph or

alternatively, by use of the method of standard addition.

- Aspirate the sample prepared in Section 4.2.4 and 4.3.3 and calculate the concentration of each element from the measured absorbance.
- Submit the 5 % acetic acid used for the extraction to the test procedure to provide a blank value to be deducted from the extract value.
- When using atomic absorption spectrometer to determine chromium, mix 1 mL of 30 % hydrogen peroxide with each 100 mL of standard solution or sample before aspirating. Alternatively use proportionally smaller volumes. The calibration curve for chromium should be based on an original standard concentration before addition of hydrogen peroxide.
- When using atomic absorption spectrometer to determine mercury, stabilise the extract by addition of potassium dichromate solution to a content of approximately 10 mg of potassium dichromate per 100 mL of extract.

  *Note: Organic mercury compounds will not respond to the flameless technique unless they are decomposed into mercury (II) ions. Potassium dichromate oxidises these compounds.*

  *Add 4 ml of hydroxyl ammonium chloride solution per 100 ml of extract to inactivate the surplus of potassium dichromate.*
- Follow the instructions given by the manufacturer of the spectrometer in order to reduce the mercury (II) ions to mercury. The reducing agent to be used is either tin(II) chloride or sodium tetra hydroborate and the appropriate amount is specified in the instructions.

## 6. Expression of results

Calculate the results with a computer or graphically. Correct, where appropriate, for background absorption. Take the blank value into consideration in the evaluation.

Express the results in mg/L or μg/L of the extract.

*Note: Trace element determinations are sensitive to a number of sources of error. It is therefore recommended to check the performance of the system by running standard reference materials.*

Special attention should be paid to factors such as high blank levels caused by impure reagents of modifiers, contamination during handling of the solutions, adsorption on the walls of vessels, inadequate background correction or unmatched acid concentrations of sample and calibration solutions.

The detection limit should be established by measuring a sufficient number of blanks to allow calculation of the standard deviation of the blank. The detection limit is determined as three times this standard deviation.

## 7. References

1. BS EN 647:1994, Paper and board intended to come into contact with foodstuffs: Preparation of a hot water extract, British Standards Institution, London.
2. DDENV 12497:1998, Paper and board – Paper and board intended to come into contact with foodstuffs – Determination of mercury in an aqueous extract, CEN, European Committee for Standardization, Brussels.
3. DDENV 12498:1998, Paper and board – Paper and board intended to come into contact with foodstuffs – Determination of cadmium, lead and chromium in an aqueous extract, CEN, European Committee for Standardization, Brussels.
4. APHA 3111B, Direct Air-Acetylene Flame Method, Standard Methods for the Examination of Water and Wastewater, 20th Edition, APHA, AWWA, WEF.
5. APHA 3112B, Cold-Vapor Atomic Absorption Spectrometric Method, Standard Methods for the Examination of Water and Wastewater, 20th Edition, APHA, AWWA, WEF.