British American Tobacco Group Research & Development

Method - Determination of metals in mainstream cigarette smoke.

1 SCOPE OF APPLICATION

The method is applicable to quantitative determination of the yields of chromium, nickel, arsenic, selenium, cadmium, mercury and lead in whole mainstream cigarette smoke, using inductively coupled plasma mass spectrometry.

2 NORMATIVE REFERENCES

ISO 3308:2000 – Routine analytical cigarette smoking machine – definitions and standard conditions

ISO 3402:1999 – Tobacco and tobacco products – atmospheres for conditioning and testing

ISO 4387:2000 – Cigarettes - Determination of total and nicotine-free dry particulate matter using a routine analytical smoking machine

ISO 8243:2006 – Cigarettes - Sampling

3 PRINCIPLE

Ten conditioned cigarettes are smoked per port for each cigarette sample tested using a modified linear 20 port Borgwaldt smoking machine to accommodate impinger trapping systems. The mainstream smoke is passed through a dry-ice cooled impinger containing glass packing beads and quartz wool. After smoking the impinger is extracted with 5% nitric acid and filtered through quartz wool. An aliquot of the resulting solution is submitted for analysis by inductively coupled plasma mass spectrometry (ICP/MS).

4 HEALTH & SAFETY

Read and understand the Material Safety Data Sheets for the chemicals used in this method. Read and understand the method risk assessment. Ensure that you understand the hazards and follow control measures relevant to the operation of this method. All preparation of standards and extraction of samples must be performed in a fume cupboard.

5 REAGENTS AND MATERIALS

All reagents are Analytical Grade or equivalent unless otherwise stated.

Nitric acid (trace metal analysis grade)

Deionised water (18.2MΩ.cm)

Chromium (1000ppm ICP/MS grade)

Nickel (1000ppm ICP/MS grade)

Arsenic (1000ppm ICP/MS grade)

Selenium (1000ppm ICP/MS grade)

Cadmium (1000ppm ICP/MS grade)

Mercury (1000ppm ICP/MS grade)

Lead (1000ppm ICP/MS grade)

Agilent 1ppb Tuning Solution for ICP/MS

Indium (1000ppm ICP/MS grade)

Lutetium (1000ppm ICP/MS grade)

Yttrium (10000ppm ICP/MS grade)

Dry ice

6 APPARATUS

Agilent 7500ce ICP/MS

Borgwaldt-KC LM20 linear 20 port smoke engine. – adapted for use with liquid traps

Smoke collection system for each port: A suitable trapping system has been constructed from modified Quickfit® tubes and Dreschel heads.

Soap bubble manometer to measure puff volume

50mL polypropylene centrifuge tubes

100mL plastic volumetric flasks with stoppers

Polystyrene boxes

Polystyrene ICP/MS autosampler test tubes

A range of variable auto pipettes capable of dispensing from 25µL to 1000µL

7 PRELIMINARY SAMPLE PREPARATION

Cigarettes should be conditioned according to normal procedures (ISO 3402:1999). Unless specifically requested, cigarettes are not subjected to any selection criteria other than the rejection of any obviously defective or damaged cigarettes. Butt marking is as specified in ISO 4387:2000 unless otherwise requested.

8 ANALYTICAL PROCEDURE –SOLUTION PREPARATION

8.1 Extracting Solutions

8.1.1 5% Nitric Acid and Internal Standard Stock Solution

100mL concentrated nitric acid is carefully added to 500mL deionised water in a 2L plastic volumetric flask. Add 20mL of Internal Standard Stock Solution (see section 8.2.1) and make up to volume with deionised water.

8.1.2 5% Nitric Acid and Gold Wash Solution

50mL concentrated nitric acid is carefully added to 500mL deionised water in a 1L plastic volumetric flask. Add 2.5mL of gold standard (100ppm) and make up to volume with deionised water.

8.2 Standard Preparations

8.2.1 Internal Standard Stock Solution

25mL concentrated nitric acid is carefully added to 250mL deionised water in a 500mL plastic volumetric flask. Pipette 0.5mL of indium (1000ppm), 0.5mL of lutetium (1000ppm) and 0.05mL of yttrium (10000ppm) and make up to volume with deionised water.

8.2.2 Stock Standard Solution

To 50mL of 5% nitric acid/internal standard solution (8.1.1) in a 100mL plastic volumetric flask pipette the following amounts of the commercial standards and make up to volume with 5% nitric acid/internal standard solution.

Metal	Volume of Standard (mL)	Concentration (ng/mL)
Mercury (Hg)	0.025	250
Arsenic (As)	0.05	500
Nickel (Ni)	0.05	500
Selenium (Se)	0.05	500
Cadmium (Cd)	0.1	1000
Chromium (Cr)	0.1	1000
Lead (Pb)	0.1	1000

The standard is stable for 6 weeks when stored under ambient conditions.

8.2.3 Calibration Standards

Dilute the Stock Standard Solution as follows in 100mL plastic volumetric flasks and make up to volume with 5% nitric acid/internal standard solution.

Calibration Standard	Volume of Stock Standard Solution (mL)	Concentration of Hg (ng/mL)	Concentration of As, Ni & Se (ng/mL)	Concentration of Cd, Cr & Pb (ng/mL)
1	0.1	0.25	0.50	1.00
2	0.3	0.75	1.50	3.00
3	0.5	1.25	2.50	5.00
4	1.0	2.50	5.00	10.00
5	2.0	5.00	10.00	20.00

Prepare the calibration standards daily.

8.2.4 QC Stock Standard Solution

To 50mL of 5% nitric acid/internal standard solution (8.1.1) in a 100mL plastic volumetric flask pipette the following amounts of the commercial standards and make up to volume with 5% nitric acid/internal standard solution.

Metal	Volume of Standard (mL)	Concentration (ng/mL)
Mercury (Hg)	0.1	1000
Arsenic (As)	0.1	1000
Nickel (Ni)	0.1	1000
Selenium (Se)	0.1	1000
Cadmium (Cd)	0.2	2000
Chromium (Cr)	0.2	2000
Lead (Pb)	0.2	2000

The standard is stable for 6 weeks when stored under ambient conditions.

8.2.5 QC Standard

Dilute the QC Stock Standard Solution as follows in a 100mL plastic volumetric flask and make up to volume with 5% nitric acid/internal standard solution.

Standard	Volume of Stock Standard Solution (mL)	Concentration of Hg, As, Ni & Se (ng/mL)	Concentration of Cd, Cr & Pb (ng/mL)
QC	0.4	4.00	8.00

Prepare the QC standard daily.

9 ANALYTICAL PROCEDURE – SAMPLE PREPARATION

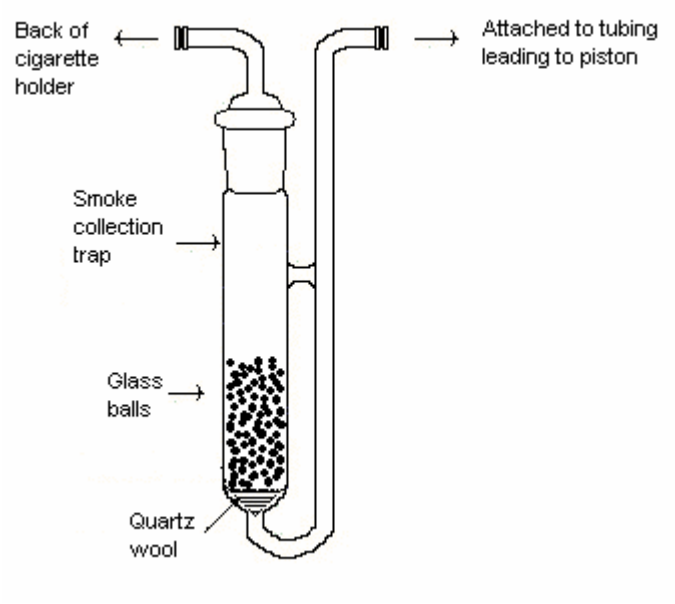
9.1 Sample Collection

This method utilises an impinger attached to the back of each smoking port. This is a deviation from the ISO Method 3308:2000.

Prior to smoking allow the smoking machine to warm up for 30 minutes and measure airflow in ports 1, 10 and 20 with an airflow probe. Individual port readings should be 200mm/sec (± 50mm/sec) and the average airflow across the measured ports should be 200mm/sec (± 30mm/sec).

9.1.1 Assembly of trapping system

Assemble the trapping system behind the cigarette holder as shown below, with each trap containing a small plug of quartz wool and soda lime glass balls filled to a depth of approximately 6cm. The impingers are held in a polystyrene box filled with sufficient dry-ice to cover the main body of the impinger.



Check the system for leaks by taking a puff. Check the puff volumes with the impingers in position and adjust if necessary. Puff volumes should be 35mL (± 0.3mL) (for ISO smoking).

9.1.2 Smoking

Smoke 10 conditioned cigarettes through each trapping system. One clearing puff is taken between each cigarette run, and a further five clearing puffs are taken at the end of the run to ensure any residual smoke has been collected in the trapping system. Record the number of lit puffs.

9.2 Sample Extraction

Add 25mL of 5% nitric acid/internal standard solution (8.1.1) from a preset dispenser and sonicate for 15 minutes. The solution is decanted through the quartz wool plug into a 50mL polypropylene centrifuge tube. Repeat with a further 25mL of 5% nitric acid/internal standard solution. Transfer sufficient sample to polystyrene ICP/MS autosampler test tubes.

10 ANALYTICAL PROCEDURE – INSTRUMENTAL ANALYSIS

10.1 Instrument Set Up Parameters

Analysis is performed on an Agilent *7500ce* ICP-MS.

Aspirate 5% nitric acid through the system for 30 minutes before performing tuning of the instrument.

10.2 System Suitability Criteria

- Daily performance is performed using the Agilent 1ppb tuning solution for ICP/MS. Check the following criteria are met on the tune report:
  - Mass 7 sensitivity >20000 counts/second
  - Mass 89 sensitivity >50000 counts/second
  - Mass 205 sensitivity >30000 counts/second
  - Oxide ratio <2%
  - Doubly charged ratio <2%
- R^2 of calibration curves should be greater than 0.999
- Reference cigarette – results within defined limits
- Quality control solution – results within defined limits

10.3 Run Order

Wash 5% nitric acid

Blank 5% nitric acid

Calibration standards in ascending order

Wash 5% nitric acid (x3)

QC standard

Wash 5% nitric acid (x2)

Samples

Wash 5% nitric acid (x3)

QC standard

Wash 5% nitric acid (x2)

Calibration standards in ascending order

11 CALCULATIONS

Use the instrument software to determine the concentrations of each metal as ng/mL. To convert results to ng/cigarette use the following equation:

$$\text{Metal concentration (ng/cigarette)} = \frac{\text{metal concentration (ng/mL)} \times V}{N}$$

Where: V = total volume of extract (normally 50mL)

N = Number of cigarettes smoked (normally 10)

12 PRECISION AND REPORTING LIMITS

Five replicate smokings and analyses are performed to determine the precision of the analysis. Longer term precision is monitored through the maintenance of control charts.

The method quantitation limits are defined as ten times the standard deviation of the lowest calibration standard analysed ten times and are follows:

Metal	Quantitation Limit (ng/cigarette)
Mercury (Hg)	0.13
Arsenic (As)	0.97
Nickel (Ni)	1.99
Selenium (Se)	4.10
Cadmium (Cd)	1.93
Chromium (Cr)	1.17
Lead (Pb)	12.03

13 QUALITY ASSURANCE AND CONTROL

Control charts of the QC standard and the reference cigarette are maintained to allow inspection of the method performance.

14 SPECIAL CASES

Under more intense regimes the number of cigarettes may need to be adjusted in order to avoid overloading of the impingers with smoke condensate.

Date of Issue: 31 March 2008