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Analysis of mercury in Platform 1 aerosol

PRODUCT TESTING LABORATORY AND GOVERNANCE

Contents

1. DETERMINATION OF MERCURY IN PLATFORM 1 AEROSOL 3
1.1. Abstract 3
1.2. Applicability 3
1.3. Reagents 3
1.4. Aerosol generation 3
1.5. Samples preparation 4
1.6. Internal standard solution 4
1.7. Extraction solution 4
1.8. Calibration solutions preparation 5
1.8.1. Mercury stock solutions 5
1.8.2. Calibration standards 5
1.9. Instrumental Conditions 6
1.10. Testing procedure 7
1.11. Verification of results 7
1.11.1. Calibration curve 7
1.11.2. Quality Check 7
1.12. Example Spectra 8
1.13. Limit of Detection (LOD) / Lower Limit of Quantitation (LLOQ) 9
1.14. Repeatability limit (r) and Intermediate precision limit (IP) 10
1.15. NORMATIVE REFERENCES 10

Tables

Table 1: Aerosol Collection Condition 4
Table 2: Typical standard solution concentrations for mercury 5
Table 3: Sample introduction settings 6
Table 4: Plasma conditions 6
Table 5: Paramenters used for calibration curve 7
Table 6: LOD and LLOQ for ISO and HC smoking regimens 9
Table 7: Repeatability (r) and intermediate precision (IP) for HC and ISO smoking regimens 10

Figures

N/A

1. DETERMINATION OF MERCURY IN PLATFORM 1 AEROSOL

1.1. Abstract

The aerosol samples are generated with a rotary smoking machine. The aerosol is firstly freed from particulate matter with a glass fiber Cambridge Filter Pad (CFP) and then trapped in two impingers filled of a nitric acid-hydrochloric acid solution containing the internal standard, gold and hydrogen peroxide. At the end of the smoking process, an aliquot of the trapping solution is taken from the two impingers and diluted with ultrapure water.

The resulting solutions are analyzed by Inductively Coupled Plasma (ICP) Mass Spectrometry (MS).

Results are expressed as ng/item for P1.

1.2. Applicability

The method described is used for the determination of mercury in Platform 1 (P1) aerosols generated under International Organization for Standardization (ISO) or Health Canada (HC) conditions.

1.3. Reagents

- Nitric acid
- Hydrochloric acid
- Hydrogen peroxide
- Sodium bicarbonate
- Argon
- Ultrapure water
- Mercury ICP standard solution
- Gold ICP standard solution
- Indium ICP standard solution

1.4. Aerosol generation

P1 items are conditioned in opened packs for at least 48 hours at target conditions of 22 ± 1°C and relative humidity of 60 ± 3% before to be used for aerosol generation.

The aerosol samples are generated on a rotary smoking machine (Butkhart RMB20 or equivalent) under ISO or HC smoking regimens. The collection conditions for the different smoking regimes are summarized in Table **1**.

Table 1: Aerosol Collection Condition

Regimen	Accumulation number	Puff number	Regimen Condition [puff volume/Puff duration/Puff Interval] [ml/s/s]
ISO	20	6	35/2/60
HC	10	12	55/2/30

The collection of aerosol particles is performed in two impingers filled respectively with 20 mL and 10 mL of a nitric acid-hydrochloric acid-internal standard (ISTD)-gold solution. Moreover, respectively 2 mL and 1 mL of hydrogen peroxide are added to the two impingers right before sample collection in order to improve the oxidizing reaction of mercury. Gold acts as well as strong oxidizing agent and converts or maintains mercury in ionic form in solution.

In order to protect the pump of the machine from the nitric vapours, the two impingers are followed by a third one, filled with 100 mL of a saturated sodium bicarbonate solution. Moreover, a glass fiber Cambridge Filter Pad (CFP) is placed before the first impinger in order to remove the aerosol particulate matter.

Four replicates for each sample are generated. Within each series of aerosol collection, three blanks are performed and analyzed to ensure that no contamination is carried out. These blanks are generated before sample generation by performing the entire procedure described above while any item is charged on the smoking machine.

1.5. Samples preparation

The following sample preparation steps and the ICP-MS analysis are performed in a clean room under the ISO 7 classification.

After aerosol collection, 5 mL of solution from the first impinger are mixed with 2.5 mL of solution from the second impinger and 50 µL of a 1000 mg/mL gold ICP standard solution; the resulting solution is brought up to 50 mL with ultrapure water and analyzed by ICP-MS.

1.6. Internal standard solution

The internal standard solution is prepared by dilution of an indium ICP standard solution with a 2% nitric acid solution.

1.7. Extraction solution

The extraction solution consists in a 54.6% nitric acid and 0.6% hydrochloric acid solution containing 200 pg/mL of indium (internal standard) and 1 µg/mL of gold.

1.8. Calibration solutions preparation

1.8.1. Mercury stock solutions

An intermediary mercury stock solution is prepared by dilution of the mercury ICP standard solutions with a 2% nitric acid solution.

The mercury stock solution is prepared by dilution of the intermediary mercury stock solution with a 2% nitric acid solution and addition of a precise amount of gold ICP standard solution. The final concentrations are 25000 pg/mL for mercury and 1 µg/mL for gold.

1.8.2. Calibration standards

Six standard (STD) solutions are prepared by dilution of the mercury stock solution with the extraction solution and addition of gold. The range of concentrations covers the range relevant for analysis and is provided in Table 2. Standard level 4 is also used as quality check.

Table 2: Typical standard solution concentrations for mercury

Standard level	Conc. of Hg [pg/mL]
1	25
2	50
3	100
4	250
5	500
6	1000

1.9. Instrumental Conditions

The samples are analyzed by Inductively Coupled Plasma (ICP) mass spectrometry (MS) following tables below:

Table 3: Sample introduction settings

Spray chamber temperature	2°C
Carrier gas flow	~ 1.05 L/min, optimized daily with auto-tune
Nebulizer pump speed	0.10 rps

Table 4: Plasma conditions

ICP RF Power	~ 1550 Watts
Plasma gas flow	~ 15 L/min
Cones material and dimensions	Platinum, Ø 0.9 and 1.1 mm

1.10. Testing procedure

The following typical analytical sequence is used for the determination of mercury:

- 3 calibration blanks (diluted extraction solution containing internal standard and gold)
- Calibration curve (STD 1 to 6)
- Blanks and samples
- After every 15-20 samples, inject a quality check (STD level 4)
- Sequence ends with a quality check (STD level 4)

1.11. Verification of results

1.11.1. Calibration curve

A calibration curve is used to quantify the unknown samples using the response ratio of analyte to the internal standard. The peak intensity ratio is applied to generate the curve. The linear regression is calculated automatically by MassHunter software. Specific information about the regression are provided in Table 5.

Table 5: Paramenters used for calibration curve

Compound	Internal standard	Regression type	Weighting factor
Mercury	Indium	linear	1/x

1.11.2. Quality Check

The validity of the calibration is continuously verified during the batch analysis by analysing the calibration control standard injections. All quality checks must be within ±10% of its theoretical value.

1.12. Example Spectra

N/A

1.13. Limit of Detection (LOD) / Lower Limit of Quantitation (LLOQ)

The LOD and LLOQ were both calculated in terms of the standard deviation of five different measurements of the lowest calibration standard for all other analytes produced under intermediate precision conditions (five different preparations from at least two different operators and analyzed on five different days).

$$LOD = 3 \times SD_{level1}$$

$$LLOQ = 10 \times SD_{level1}$$

Level 1 is the lowest calibration level.

Detailed values are provided in Table 6.

Table 6: LOD and LLOQ for ISO and HC smoking regimens

Compound	P1, HC smoking regimen			P1, ISO smoking regimen		
	LOD	LLOQ	STD1	LOD	LLOQ	STD1
	(ng/item)	(ng/item)	(ng/item)	(ng/item)	(ng/item)	(ng/item)
Mercury	0.0919	0.306	0.500	0.0460	0.153	0.250

1.14. Repeatability limit (r) and Intermediate precision limit (IP)

$$r = 2 \cdot \sqrt{2} \cdot s_r$$

$$IP = 2 \cdot \sqrt{2} \cdot s_{IP}$$

s_r is the standard deviation of repeatability.

s_{IP} is the standard deviation of intermedidate precision.

Repeatability limit and intermediate precision limit are determined during four different days using different standard solutions preparation. Different operators are involved in the aerosol generation and analysis.

Table 7: Repeatability (r) and intermediate precision (IP) for HC and ISO smoking regimens

Compound	P1, HC smoking regimen			P1, ISO smoking regimen		
	r	IP	Mean	r	IP	Mean
	(ng/item)	(ng/item)	(ng/item)	(ng/item)	(ng/item)	(ng/item)
Mercury	0.143	0.229	1.05	0.063	0.063	0.480

1.15. 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 14644-1:2015 – Classification of air cleanliness