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Stationary source emissions — Sampling and determination of mercury compounds in flue gas using gold amalgamation trap

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National foreword

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 1, *Stationary source emissions*.

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Introduction

Because mercury is exhausted from stationary sources such as coal combustion plants, cement kilns, non-ferrous metal smelting operations and roasting plants, and waste incineration facilities, the monitoring of the stationary source mercury mass emissions is increasingly important for preventing global environmental pollution and health damage caused by mercury.

This document describes a method for the sampling and determination of mercury concentrations in a flue gas passing through ducts or chimney stacks. Mercury generally exists as elemental (Hg^0) and oxidized (Hg^{2+}) forms, both in vapour and in solid phases in flue gases, this method allows the determination of both total vapour-phase mercury and total solid-phase mercury concentrations in flue gases.

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Stationary source emissions — Sampling and determination of mercury compounds in flue gas using gold amalgamation trap

1 Scope

This document describes a method for the sampling and measurement of mercury of both vapour and solid phases on stationary source flue gas streams. Mercury generally exists as elemental (Hg^0) and oxidized (Hg^{2+}) forms, both in the vapour and solid phases in flue gases. The vapour-phase (gaseous) mercury is captured either isokinetically or non-isokinetically with a gold amalgamation trap after removing solid-phase (particulate) mercury with a filter. Because gold amalgamation trap captures only gaseous elemental mercury, the oxidized mercury (Hg^{2+}) in the vapour phase is converted to elemental mercury (Hg^0) prior to the gold amalgamation trap. The concentration of gaseous mercury is determined using atomic absorption spectrometry (AAS) or atomic fluorescence spectrometry (AFS) after releasing mercury by heating the gold amalgamation trap. Separately, particulate mercury is collected isokinetically on a filter and the concentration is determined using cold vapour AAS or cold vapour AFS after dissolving the particulate mercury into solution.

The total concentration of mercury in flue gas is expressed as the sum of both gaseous and particulate mercury concentrations.

The gold amalgamation method is intended for short-term (periodic) measurements of gaseous mercury ranging from 0,01 µg/m^3 to 100 µg/m^3 with sampling volumes from 0,005 m^3 to 0,1 m^3 and sample gas flow rate between 0,2 l/min to 1 l/min. The measurement range of particulate mercury is typically from 0,01 µg/m^3 to 100 µg/m^3 with sampling volume from 0,05 m^3 to 1 m^3.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 9096, *Stationary source emissions — Manual determination of mass concentration of particulate matter*

ISO 10396, *Stationary source emissions — Sampling for the automated determination of gas emission concentrations for permanently-installed monitoring systems*

ISO 12141, *Stationary source emissions — Determination of mass concentration of particulate matter (dust) at low concentrations — Manual gravimetric method*

ISO 12846:2012, *Water quality — Determination of mercury — Method using atomic absorption spectrometry (AAS) with and without enrichment*

ISO 16911-1, *Stationary source emissions — Manual and automatic determination of velocity and volume flow rate in ducts — Part 1: Manual reference method*

ISO 17852:2006, *Water quality — Determination of mercury — Method using atomic fluorescence spectrometry*

ISO 20988, *Air quality — Guidelines for estimating measurement uncertainty*

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3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
gaseous mercury
mercury existing both as elemental and oxidized forms passing through a filter having at least 99,5 % collection efficiency for 0,3 µm diameter particles

3.2
particulate mercury
mercury existing both as elemental and oxidized forms contained in a solid phase particle collected by a filter having at least 99,5 % collection efficiency for 0,3 µm diameter particles

3.3
isokinetic sampling
sampling at a flow rate such that the velocity and direction of the gas entering the sampling nozzle are the same as those of the gas in the duct at the *sampling point* (3.4)

3.4
sampling point
specific position on the sampling section at which a sample is extracted

3.5
STP
standard conditions for temperature, 273,15 K, and pressure, 101,325 kPa

4 Symbols and abbreviated terms

4.1 Symbols

$M_{A1,Hg}$ amounts of mercury in the first gold amalgamation trap (µg)

$M_{A2,Hg}$ amounts of mercury in the second gold amalgamation trap (µg)

$C_{R,Hg}$ concentration of mercury in a prepared sample of rinse solution that washed the transfer line from the filter housing to the impinger nozzle of stannous chloride solution or the inlet of catalytic reduction unit in main-stream sampling (µg/ml). Ref. Figure 1 and 2.

$C_{R1,Hg}$ concentration of mercury in a prepared sample of rinse solution that washed transfer line from the filter housing to the T-piece in side-stream sampling (µg/ml). Ref. Figure 3.

$C_{R2,Hg}$ concentration of mercury in a prepared sample of rinse solution that washed transfer line after the T-piece to the impinger nozzle of stannous chloride solution or the inlet of catalytic reduction unit in side-stream sampling (µg/ml). Ref. Figure 3.

$C_{S,Hg}$ concentration of mercury in a prepared sample solution for particulate mercury analysis (µg/ml)

d density of reagent solution (g/ml)

p_{atm} atmospheric pressure (kPa)

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p_{av}	average pressure difference between the sample gas before the gas meter and the atmosphere (kPa)
$q_{m,Hg}$	rate of mass discharge of mercury expressed as elemental mercury (mg/s)
$q_{V,fg,i}$	volume flow rate of flue gas through the sampling plane at conditions i of temperature, pressure, moisture and oxygen content (m^3/s)
T_{av}	average temperature of the sample gas before the gas meter (K)
$u(y)$	standard uncertainty ($\mu g/m^3$)
V_d	volume of dry flue gas sample normalized to STP (m^3)
V_f	final gas meter reading at the end of sampling (m^3)
$V_{G,d}$	volume of dry flue gas sample for gaseous mercury analysis normalized to STP (m^3)
V_i	initial gas meter reading at the beginning of sampling (m^3)
V_l	volume of air drawn through the gas meter during any intermediate leak tests (m^3)
V_m	volume of dry flue gas sample (m^3)
$V_{main,d}$	volume of dry flue gas sample in main stream, normalized to STP, in side-stream sampling (m^3)
$V_{S,d}$	volume of dry flue gas sample for particulate mercury analysis normalized to STP (m^3)
$V_{side,d}$	volume of dry flue gas sampled in side stream, normalized to STP, in side-stream sampling (m^3)
v_R	volume of a recovered sample of rinse solution that washed transfer line from the filter housing to the impinger nozzle of stannous chloride solution or the inlet of catalytic reduction unit in main-stream sampling (ml). Ref. Figure 1 and 2.
v_{R1}	volume of a recovered sample of rinse solution that washed transfer line from the filter housing to the T-piece in side-stream sampling (ml). Ref. Figure 3.
v_{R2}	volume of a recovered sample of rinse solution that washed transfer line after the T-piece to the impinger nozzle of stannous chloride solution or the inlet of catalytic reduction unit in side-stream sampling (ml). Ref. Figure 3.
v_S	volume of a prepared sample solution for particulate mercury analysis (ml)
w_W	average moisture content of the flue gas at the sampling plane during the sampling period (%)
$y_{1,j}$	j th concentration value of the first measuring system ($\mu g/m^3$)
$y_{2,j}$	j th concentration value of the second measuring system ($\mu g/m^3$)
$\rho_{G,Hg,dry}$	mass concentration of gaseous mercury expressed as elemental mercury in the flue gas on a dry basis at STP ($\mu g/m^3$)
$\rho_{S,Hg,dry}$	mass concentration of particulate mercury expressed as elemental mercury in the flue gas on a dry basis at STP ($\mu g/m^3$)
$\rho_{Hg,dry}$	mass concentration of total mercury expressed as elemental mercury in the flue gas on a dry basis at STP ($\mu g/m^3$)

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$\rho_{Hg,dry,O}$ mass concentration of mercury expressed as elemental mercury in the flue gas on a dry basis at STP and reference oxygen concentration (μg/m^3)

$\rho_{Hg,i}$ mass concentration of mercury expressed as elemental mercury at conditions *i* of temperature, pressure, oxygen and moisture conditions (μg/m^3)

$\rho_{Hg,wet}$ mass concentration of mercury expressed as elemental mercury in the flue gas on a wet basis at STP (μg/m^3)

$\rho_{Hg,wet,O}$ mass concentration of mercury expressed as elemental mercury in the flue gas on a wet basis at STP and reference oxygen concentration (μg/m^3)

$\varphi_{O,d}$ volume fraction of the oxygen on a dry basis measured during the sampling (%)

$\varphi_{O,ref}$ volume fraction of the reference oxygen for the process (%)

4.2 Abbreviated terms

AAS atomic absorption spectrometry

AFS atomic fluorescence spectrometry

FEP perfluoro(ethylene/propylene), tetrafluoroethylene/hexafluoropropylene

PFA perfluoroalkoxy alkane

PTFE polytetrafluoroethylene

5 Principle

In flue gases, mercury commonly exists in both the vapour phase and solid phase. In this method, particulate mercury is captured on a filter, and gaseous mercury is captured on a gold amalgamation trap. The total concentration of mercury in a flue gas is expressed as the sum of both concentrations.

To determine particulate mercury contents in a flue gas, a sample is taken isokinetically and particles are collected on a filter in accordance with ISO 9096 or ISO 12141. The particulate mercury on the filter is dissolved into solution from the filter and the mercury concentration is determined using cold vapour atomic absorption spectrometry (CV AAS, ISO 12846) or cold vapour atomic fluorescence spectrometry (CV AFS, ISO 17852). The described digestion step for the liquid solutions in ISO 12846:2012, Clause 5, and ISO 17852:2006, Clause 7, is unnecessary and shall be omitted. After sample preparation (see 9.2 in this document), the samples are analysed immediately.

To determine gaseous mercury contents in a flue gas, a sample is taken either isokinetically or non-isokinetically. Gaseous elemental mercury that passes through the filter is captured on a gold amalgamation trap and gaseous oxidized mercury is converted to elemental mercury using either a stannous chloride solution or a heated catalytic reduction unit, and then collected on the gold amalgamation trap. The mercury amalgamated with the gold trap is released by heating the trap and determined using atomic absorption spectrometry (AAS) or atomic fluorescence spectrometry (AFS).

Particulate and gaseous sampling is performed simultaneously by the isokinetic sampling procedure if the flow rates and the total sampling volumes for the measurements of particulate and gaseous mercury are the same.

6 Reagents

6.1 General

To carry out the method, the following reagents are required to be of a recognized analytical grade.

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6.2 Water

Conforming with grade 1 specified in ISO 3696 for all sample preparation and dilutions.

6.3 Nitric acid

$w(HNO_3)$ = 65%, $d(HNO_3)$ = 1,4 g/ml.

NOTE Nitric acid is available both as $d(HNO_3)$ = 1,40 g/ml [$w(HNO_3)$ = 650 g/kg] and $d(HNO_3)$ = 1,42 g/ml [$w(HNO_3)$ = 690 g/kg].

6.4 Sulfuric acid

$c(H_2SO_4)$ = 0,5 mol/l.

Add slowly 28 ml of concentrated sulfuric acid [$d(H_2SO_4)$ = 1,84 g/ml] to a 1 000 ml volumetric flask containing approximately 500 ml of water while cooling and stirring, and then add water with stirring to make a volume of 1 000 ml.

6.5 Stannous chloride solution

$\rho(SnCl_2)$ = 100 g/l.

Add 60 ml of sulfuric acid (6.4) onto 10 g of tin (II) chloride dehydrate and heat it to dissolve while stirring them. After cooling, add sulfuric acid (6.4) to make a volume of 100 ml. This solution should be purged with inert gas such as argon and nitrogen prior to use to remove traces of Hg. This solution shall be used up within one week from preparation.

6.6 Phosphate buffer solution

$c(KH_2PO_4)$ = 0,025 mol/l and $c(Na_2HPO_4)$ = 0,025 mol/l, pH6, 86 at 298 K.

Take 3,39 g of potassium dihydrogen phosphate and 3,54 g of disodium hydrogen phosphate in a beaker and add water to dissolve them. Transfer the solution from the beaker to a 1 000 ml volumetric flask and add water to make a volume of 1 000 ml. Store it in a fluoroplastic bottle made of PTFE, PFA or FEP.

6.7 Hydrofluoric acid

$w(HF)$ = 40 %, $d(HF)$ = 1,16 g/ml.

6.8 Hydrochloric acid

$w(HCl)$ = 37 %, $d(HCl)$ = 1,19 g/ml.

6.9 Mercury stock solution

Conforming with mercury standard solutions as specified in ISO 12846 and ISO 17852.

6.10 Rinse solution

$w(HNO_3)$ = 50 g/kg.

Take 77 g of nitric acid [$w(HNO_3)$ = 650 g/kg] or 72 g of nitric acid [$w(HNO_3)$ = 690 g/kg] in a fluoroplastic bottle made of PTFE, PFA or FEP, and add water to make a total weight of 1 kg.

6.11 Sample gas drying agent

Self-indicating coarse grade silica gel.

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6.12 Trapping agent of mercury

Supporting materials, such as diatomaceous earth and silica beads, coated with gold thin layer or gold nanoparticles are used as trapping agent of mercury. Since the capacity of amalgamation is dependent on the surface area of gold, supporting materials and a gold coating method shall be selected that gives a sufficient surface area for the targeted determination range of mercury. The trapping agents are commercially available or can be prepared in the laboratory.

An example of preparation of trapping agent is as follows: onto 3 g of diatomaceous earth with 420 µm to 590 µm grain size, add the solution prepared by dissolving 1 g of tetrachloroauric(III) acid in 20 ml to 30 ml of water, and mix them to make uniform. Heat it at about 353 K to dry it, put it in a furnace, and heat it at about 1 073 K for 30 min while air is being flowed. Gold nanoparticles (average diameter; ca. 10 nm) dispersed in water or ethanol are also available for preparation of trapping agent as well as tetrachloroauric(III) acid. In this case, use the solution prepared by adding 0,3 g of aqueous or ethanol solution of gold nanoparticles at 10% in 20 ml to 30 ml of water instead of tetrachloroauric(III) acid solution. In general, supporting materials coated with gold nanoparticles are able to collect larger amounts of mercury than those coated with gold thin layer prepared with tetrachloroauric(III) acid.

7 Apparatus

7.1 General

Two types of sampling systems, a main-stream and a side-stream arrangement, can be employed. In the main-stream system all the sampled flue gas is passed though the gold amalgamation traps, while in the side-stream arrangement only a part of the sampled flue gas is passed through the gold amalgamation traps. The main-stream sampling is used when the flow rate and total sampling volume for the measurements of gaseous and particulate mercury are the same. The side-stream sampling is used when the flow rate or total sampling volume for the measurements of gaseous and particulate mercury is different.

It is also possible to use two sampling trains, one for particulate mercury and one for gaseous mercury, even when the flow rate or total sampling volume is different. Two sampling nozzles, for particulate mercury and gaseous mercury respectively, are placed at neighbouring points in which the physicochemical parameters such as mercury concentration and gas flow rate are considered to be equivalent. Particulate mercury is collected on the filter isokinetically. Gaseous mercury is captured on the gold amalgamation traps non-isokinetically after particles are removed. Non-isokinetic sampling of gaseous mercury is possible only when no water droplets occurs in the flue gas.

7.1.1 Main-stream sampling

Schematic diagram of main-stream sampling system using a stannous chloride reduction unit is given in Figure 1. The apparatus consists of a sampling probe including a nozzle and filter assembly that may be heated if required, a heated transfer line, two impingers containing stannous chloride solution to reduce Hg^{2+} to Hg^0, a gas-washing impinger containing phosphate buffer solution, a dehumidifying impinge (empty), two gold amalgamation traps to capture gaseous mercury, a drying unit containing silica gel, a suction pump, a gas meter, and a sample gas flow rate measurement system. A thermometer and manometer shall be included in the sampling train to measure the temperature and pressure of the metered gas. A barometer shall be used to measure atmospheric pressure during the test in order that the volume of the gas sampled can be normalized to the standard condition of 273,15 K and 101,325 kPa.

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