BS ISO 5409:2024

BSI Standards Publication

Stationary source emissions — Chemical absorption method for sampling and determining mercury species in flue gas

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National foreword

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Stationary source emissions — Chemical absorption method for sampling and determining mercury species in flue gas

Émissions de sources fixes — Échantillonnage et détermination du mercure dans les gaz de combustion en utilisant la méthode d'absorption chimique

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Foreword

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Introduction

Mercury is a highly toxic environmental pollutant that bioaccumulates in the food chain and can have an impact on neurological health. Most of the anthropogenic mercury is emitted from stationary sources such as coal combustion plants, cement kilns, non-ferrous metal smelting operations and waste incineration facilities. The monitoring and control of mercury mass emissions from stationary sources is increasingly important for preventing global environmental pollution and health damage caused by mercury.

The transformation and fate of mercury in the atmosphere is defined by its chemical and physical forms. Additionally, the development and implementation of mercury control technologies is highly dependent on the mercury speciation at different parts of the industrial process.

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Stationary source emissions — Chemical absorption method for sampling and determining mercury species in flue gas

1 Scope

This document describes a method for the sampling and determining mercury species in flue gas passing through ducts or chimney stacks. Mercury generally exists in gaseous elemental form, gaseous oxidized form and particulate-bound form. This method applies to the sampling and determination of gaseous elemental mercury (Hg^0), gaseous oxidized mercury (Hg^{2+}), particulate-bound mercury (Hg^P) and total mercury (Hg^T) in the flue gas from stationary sources.

This method is suitable at locations with high dust content, including locations upstream of the dust removal device with high particulate loadings in flue gas up to 120 g/m^3.

This method is applicable to locations with sulfur dioxide (SO_2) concentration up to 0,25 % when the sampling volume is 0,5 m^3 (on a dry basis as corrected to standard conditions).

The limit of detection and the limit of determination depend on the instrumental limit of detection, reagent blank, field blank, measurement technique and volume of sampled gas. When the sampling volume is 1,5 m^3 (on a dry basis as corrected to standard conditions), the expected limits of detection for Hg^0, Hg^P, Hg^{2+} and Hg^T are 0,103 µg/m^3, 0,011 µg/m^3, 0,035 µg/m^3 and 0,127 µg/m^3, respectively. The expected limits of determination for Hg^0, Hg^P, Hg^{2+} and Hg^T are 0,229 µg/m^3, 0,025 µg/m^3, 0,082 µg/m^3 and 0,263 µg/m^3, respectively.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 9096:2017, *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 10780:1994, *Stationary source emissions — Measurement of velocity and volume flowrate of gas streams in ducts*

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

ISO 20988:2007, *Air quality — Guidelines for estimating measurement uncertainty*

ISO 21741:2020, *Stationary source emissions — Sampling and determination of mercury compounds in flue gas using gold amalgamation trap*

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3 Terms and definitions

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

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

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

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

3.1
gaseous elemental mercury
mercury in its elemental form in flue gas

3.2
gaseous oxidized mercury
mercury in its mercurous or mercuric oxidation states in flue gas

3.3
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

3.4
particulate-bound mercury
mercury existing both as elemental or oxidized forms which are bound with particles collected by a filter having at least 99,5 % collection efficiency for 0,3 µm diameter particles

3.5
sampling train
complete setup including nozzle, probe, probe liner, filter, filter housing, impingers and connectors

3.6
total mercury
summation of *gaseous elemental mercury* (3.1), *gaseous oxidized mercury* (3.2) and *particulate-bound mercury* (3.4)

3.7
isokinetic sampling
sampling at a flowrate such that the velocity and direction of the gas entering the sampling nozzle is the same as that of the gas in the duct at the sampling point

4 Symbols and abbreviated terms

4.1 Symbols

B_{ws}	content of water vapour in the gas sample, normalized to standard temperature and pressure (STP)	g/m^3
$C_{S,Hg,a}$	concentration of mercury in the prepared sample solution aliquot digested from ash of container 1a	µg/ml
$C_{S,Hg,b}$	concentration of mercury in the prepared sample solution aliquot digested from ash of container 1b	µg/ml
$C_{RS,Hg}$	concentration of mercury in the probe rinse sample aliquot	µg/ml
$C_{KCl,Hg}$	concentration of mercury in the prepared sample solution aliquot in container 2	µg/ml
$C_{KCl,b}$	concentration of mercury in the KCl reagent blank aliquot	µg/ml

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$C_{HNO_3-H_2O_2,Hg}$	concentration of mercury in prepared sample solution aliquot in container 3	µg/ml
$C_{HNO_3-H_2O_2,b}$	concentration of mercury in HNO_3–H_2O_2 reagent blank aliquot	µg/ml
$C_{H_2SO_4-KMnO_4,Hg}$	concentration of mercury in prepared sample solution aliquot in container 4	µg/ml
$C_{H_2SO_4-KMnO_4,b}$	concentration of mercury in H_2SO_4–$KMnO_4$ reagent blank aliquot	µg/ml
$F_{D,a}$	dilution factor obtained by dividing the total mass of ash of container 1a by the mass of ash analysed	g
$F_{D,b}$	dilution factor obtained by dividing the total mass of ash of container 1b by the mass of ash analysed	g
P_{atm}	atmospheric pressure	kPa
P_{av}	average pressure difference between the sample gas before gas meter and atmosphere	kPa
T_{av}	average temperature of the sample gas before gas meter	K
V_m	volume of dry flue gas sample	m^3
V_f	final gas meter reading at the end of sampling	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 test	m^3
V_d	total volume of dry gas sampled at STP	m^3
$V_{main,d}$	volume of dry flue gas sample in the main stream, normalized to STP	m^3
$V_{side,d}$	volume of dry flue gas sample in the side stream, normalized to STP	m^3
$V_{G,d}$	volume of dry flue gas sample for gaseous mercury analysis, normalized to STP	m^3
$V_{S,d}$	volume of dry flue gas sample for Hg^P analysis, normalized to STP	m^3
$v_{S,a}$	volume of prepared sample solution digested from ash of container 1a	ml
$v_{S,b}$	volume of prepared sample solution digested from ash of container 1b	ml
v_{RS}	total volume of probe rinse sample	ml
v_{KCl}	total volume of solution in container 2 from which the sample aliquot was taken	ml
$v_{KCl,b}$	total volume of KCl reagent blank from which the sample aliquot was taken	ml
$v_{HNO_3-H_2O_2}$	total volume of solution in container 3 from which the sample aliquot was taken	ml
$v_{HNO_3-H_2O_2,b}$	total volume of HNO_3–H_2O_2 reagent blank from which the sample aliquot was taken	ml
$v_{H_2SO_4-KMnO_4}$	total volume of solution in container 4 from which the sample aliquot was taken	ml
$v_{H_2SO_4-KMnO_4,b}$	total volume of H_2SO_4–$KMnO_4$ reagent blank from which the sample aliquot was taken	ml
W_{i1}	mass of impinger after sampling	g
W_{i0}	mass of impinger before sampling	g

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$\rho_{S,Hg,d}$	mass concentration of Hg^P in the gas stream on a dry basis at STP	µg/m³
$\rho_{Hg^{2+},d}$	mass concentration of Hg^{2+} captured by KCl impinger solution in the gas stream on a dry basis at STP	µg/m³
$\rho_{Hg^0,HNO_3-H_2O_2,d}$	mass concentration of Hg^0 captured by HNO_3–H_2O_2 impinger solution on a dry basis at STP	µg/m³
$\rho_{Hg^0,H_2SO_4-KMnO_4,d}$	mass concentration of Hg^0 captured by H_2SO_4–$KMnO_4$ impinger solution on a dry basis at STP	µg/m³
$\rho_{Hg^0,d}$	mass concentration of Hg^0 in the gas stream on a dry basis at STP	µg/m³
$\rho_{Hg,d}$	mass concentration of Hg^T in the gas stream on a dry basis at STP	µg/m³
$\rho_{Hg,dry,ref}$	mass concentration of mercury on a dry basis at STP and reference oxygen concentration	µg/m³
$\rho_{Hg,dry}$	mass concentration of mercury measured during the sampling on a dry basis at STP	µg/m³
$\varphi_{O,ref}$	volume fraction of the reference oxygen	%
$\varphi_{O,dry}$	volume fraction of the average oxygen on a dry basis measured during the sampling	%

4.2 Abbreviated terms

AAS	atomic absorption spectrometry
AFS	atomic fluorescence spectrometry
CVAAS	cold vapour atomic absorption spectrometry
CVAFS	cold vapour atomic fluorescence spectrometry
FEP	perfluoro(ethylene/propylene), tetrafluoro ethylene/hexafluoropropylene
FGD	flue gas desulfurization system
PFA	perfluoroalkoxy alkane
PTFE	polytetra fluoroethylene
QA/QC	quality assurance/quality control
SCR	selective catalytic reduction unit
STP	standard temperature and pressure, 273,15 K and 101,325 kPa

5 Principle

Sampling for particulate-bound mercury is performed isokinetically and sampling for gaseous mercury is performed either isokinetically or non-isokinetically. Sampling for particulate-bound mercury is performed isokinetically in accordance with ISO 9096 or ISO 12141. When the flow rates for the measurement of gaseous mercury and particulate-bound mercury are the same, a main stream sampling is applied. If the flow rate for the measurement of gaseous mercury is lower than that for particulate-bound mercury, a side stream sampling is applied.

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Dust in the sampled gas stream is collected on a filter whereafter the gas stream is passed through a series of impingers in an ice bath. After sampling, the filter and absorber solution are prepared and analysed for mercury in laboratory. The recovery techniques include acid leaching and digestion. The analytical techniques include but are not limited to cold vapour atomic absorption spectrometry (CVAAS, see ISO 12846) or cold vapour atomic fluorescence spectrometry (CVAFS, see ISO 17852) with and without gold amalgamation.

When sampling at locations with particulate concentration higher than 100 mg/m^3, such as upstream of the dust removal device, a cyclone separator is used before the filter, the cyclone separator and filter are placed in the heated filter box. The particles fall into the ash storage flask of cyclone separator under gravity to avoid the influence of too much ash on sampling, and ensure the sampling time and speed.

6 Reagents

6.1 Purity of reagents

Unless otherwise indicated, the reagents in 6.3 are required to be of guaranteed purity.

6.2 Purity of water

Unless otherwise indicated, references to water shall be conform with grade 1 specified in ISO 3696:1987 for all sample preparations and dilutions.

6.3 Reagents

6.3.1 Concentrated hydrochloric acid, ω(HCl) = 37 %, ρ(HCl) = 1,19 g/ml.

6.3.2 Hydrogen peroxide, of a volume fraction of 30 %.

6.3.3 Concentrated nitric acid, $\omega(HNO_3)$ = 65 %, $\rho(HNO_3)$ = 1,4 g/ml.

6.3.4 Concentrated sulfuric acid, $\omega(H_2SO_4)$ = 98,3 %, $\rho(H_2SO_4)$ = 1,84 g/ml.

6.3.5 Potassium chloride solution, c(KCl) = 1 mol/l.

Add 74,56 g of KCl slowly to a 1 000 ml volumetric flask containing approximately 500 ml of water with stirring, and then add water to make a volume of 1 000 ml with stirring. A new batch of solution should be made prior to each field test.

6.3.6 HNO_3-H_2O_2 solution, of a volume fraction of 5 % HNO_3 and of 10 % H_2O_2.

Add 50 ml of concentrated HNO_3 (6.3.3) to a 1 000 ml volumetric flask containing approximately 500 ml of water slowly with stirring, and then add 333 ml of a volume fraction of 30 % of H_2O_2 (6.3.2) with stirring. Dilute with water to make a volume of 1 000 ml with stirring. A new batch of solution should be made prior to each field test.

6.3.7 H_2SO_4-$KMnO_4$ solution, $\omega(KMnO_4)$ = 4 %, and a volume fraction of 10 % of H_2SO_4.

Add slowly 100 ml of concentrated sulfuric acid (6.3.4) to a 1 000 ml volumetric flask containing approximately 600 ml of water while cooling and stirring, and then add water with stirring to make a volume of 1 000 ml. This solution is a volume fraction of 10 % of H_2SO_4.

Mix slowly 40 g of $KMnO_4$ to a 1 000 ml volumetric flask containing approximately 800 ml of a volume fraction of 10 % of H_2SO_4 with stirring, and then add a volume fraction of 10 % of H_2SO_4 with stirring to make a volume of 1 000 ml.

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6.3.8 Concentrated hydrofluoric acid, ω(HF) = 40 %, ρ(HF) = 1,16 g/ml.

6.3.9 Rinse solution, $\omega(HNO_3)$ = 50 g/kg.

In accordance with ISO 21741, take 77 g of concentrated nitric acid (6.3.3) in a fluoroplastic bottle made of PTFE, PFA or FEP, and add water to make a total weight of 1 kg.

6.3.10 Potassium permanganate solution, of ω = 5 %.

Mix 25 g of $KMnO_4$ into water, dilute to 500 ml and stir vigorously.

6.3.11 Hydroxylamine hydrochloride solution, of ω = 10 %.

Mix 50 g of $NH_2OH{\cdot}HCl$ slowly to a 500 ml volumetric flask containing approximately 300 ml of water with stirring and then add water while stirring to make a volume of 500 ml.

6.3.12 Mercury stock solution, conforming with mercury standard solution as specified in ISO 12846 and ISO 17852.

6.3.13 Silica gel, of a self-indicating coarse grade.

6.3.14 Boric acid (H_3BO_3), solid.

7 Apparatus

7.1 General

Two types of sampling systems, a main stream arrangement and a side stream arrangement, can be employed. Schematics of both systems are given in Figure 1. In the main stream system all the sampled flue gas is passed through the filter and impinger solution, while in the side stream arrangement only a part of the sampled flue gas is passed through the impingers. The main stream sampling is used if the flow rate and total sampling volume for the measurements of gaseous mercury and particulate-bound mercury are the same. The side stream sampling is used when the flow rate or total sampling volume for the measurements of gaseous mercury and particulate-bound mercury is different. For example, to some measurement objects, such as non-ferrous metal smelting industry, the concentration of SO_2 and mercury is extremely high, and this can cause the sampling train to be over-loaded even with small amount of sampled flue gas.

The apparatus consists of a sampling probe including a nozzle and filter assembly that shall be heated if the flue gas temperature is lower than 393 K. The absorbing system consists of eight impingers immersed in an ice bath, a manometer, a pump, a gas meter and a rotameter. 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 STP condition.

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