International Standard

ISO 5409

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

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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.

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 $\mu g/m^3$, 0,011 $\mu g/m^3$, 0,035 $\mu g/m^3$ and 0,127 $\mu g/m^3$, respectively. The expected limits of determination for Hg^0, Hg^P, Hg^{2+} and Hg^T are 0,229 $\mu g/m^3$, 0,025 $\mu g/m^3$, 0,082 $\mu g/m^3$ and 0,263 $\mu g/m^3$, 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*

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/m³
$C_{S,Hg,a}$	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

$C_{HNO_3-H_2O_2,Hg}$	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_{il}	mass of impinger after sampling	g
W_{i0}	mass of impinger before sampling	g

$\rho_{S,Hg,d}$	mass concentration of Hg^P in the gas stream on a dry basis at STP	µg/m^3
$\rho_{Hg^{2+},d}$	mass concentration of Hg^{2+} captured by KCl impinger solution in the gas stream on a dry basis at STP	µg/m^3
$\rho_{Hg^0,HNO_3-H_2O_2,d}$	mass concentration of Hg^0 captured by HNO$_3$–H$_2$O$_2$ impinger solution on a dry basis at STP	µg/m^3
$\rho_{Hg^0,H_2SO_4-KMnO_4,d}$	mass concentration of Hg^0 captured by H$_2$SO$_4$–KMnO$_4$ impinger solution on a dry basis at STP	µg/m^3
$\rho_{Hg^0,d}$	mass concentration of Hg^0 in the gas stream on a dry basis at STP	µg/m^3
$\rho_{Hg,d}$	mass concentration of Hg^T in the gas stream on a dry basis at STP	µg/m^3
$\rho_{Hg,dry,ref}$	mass concentration of mercury on a dry basis at STP and reference oxygen concentration	µg/m^3
$\rho_{Hg,dry}$	mass concentration of mercury measured during the sampling on a dry basis at STP	µg/m^3
$\varphi_{O,ref}$	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.

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, ω(HNO$_3$) = 65 %, ρ(HNO$_3$) = 1,4 g/ml.

6.3.4 Concentrated sulfuric acid, ω(H$_2$SO$_4$) = 98,3 %, ρ(H$_2$SO$_4$) = 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$_2$O$_2$ solution, of a volume fraction of 5 % HNO$_3$ and of 10 % H$_2$O$_2$.

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$_2$O$_2$ (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$_2$SO$_4$-KMnO$_4$ solution, ω(KMnO$_4$) = 4 %, and a volume fraction of 10 % of H$_2$SO$_4$.

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$_2$SO$_4$.

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$_2$SO$_4$ with stirring, and then add a volume fraction of 10 % of H$_2$SO$_4$ with stirring to make a volume of 1 000 ml.

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

6.3.9 Rinse solution, ω(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$_2$OH·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$_3$BO$_3$), 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.
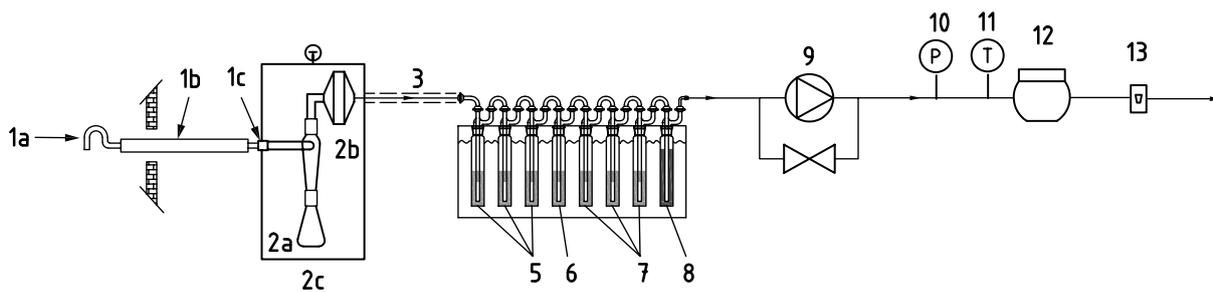
a) Main stream sampling
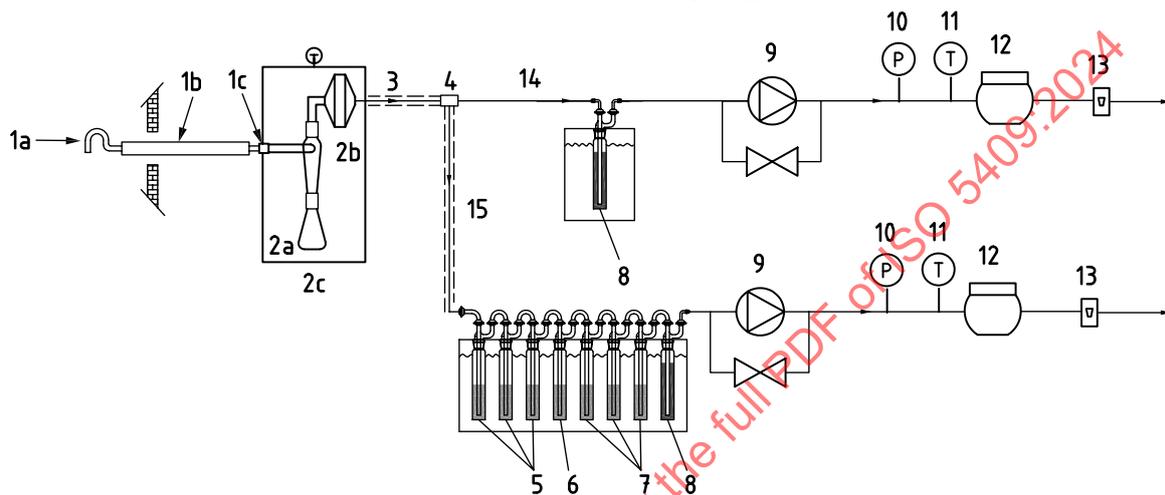
b) Side stream sampling

Key

1a	nozzle	6	HNO_3-H_2O_2 impinger
1b	probe	7	H_2SO_4-$KMnO_4$ impingers
1c	probe liner	8	silica gel impinger
2a	cyclone separator (in case the particulate concentration is >100 mg/m³)	9	pump
2b	filter and filter housing	10	manometer
2c	heated filter box	11	thermometer
3	heated transfer line	12	gas meter
4	T-piece	13	rotameter
5	KCl impingers	14	main stream
		15	side stream

Figure 1 — Schematic diagram of the sampling train

7.2 Nozzle

The diameter of nozzle shall be chosen to be compatible with the required gas sampling volume flow rate. The choice of the nozzle shall be in accordance with ISO 12141 or ISO 9096.

The nozzle shall be capable of withstanding the temperature in the duct. It shall be resistant to chemical attack from various pollutants in the duct. Suitable materials for mercury sampling are silica glass and PTFE. Glass nozzles are required unless alternate nozzles are constructed of materials that are free from contamination and will not interact with the sample. Probe fittings constructed of PTFE, polypropylene, etc., are required instead of metal fittings to prevent contamination.

7.3 Probe liner

If the sampling train is out-of-stack filtration, the probe liner should be constructed of quartz or borosilicate glass. If an in-stack filtration sampling configuration is used, the probe liner may be constructed of borosilicate glass, quartz or PTFE depending on the flue gas temperature.

7.4 Probe

In order to reduce the adsorption of gaseous mercury by dust, and prevent water and acid condensation, the probe shall be equipped with a heating system. The heating system shall increase the probe temperature to higher than 393 K or at the temperature of flue gas, whichever is greater. In the case of sampling at locations with high temperature, such as above 533 K, the heating system shall be removed to prevent damage to the heating mantle. However, note that higher temperatures can lead to the thermal degradation of mercury compounds and the overestimation of Hg^0 concentrations.

7.5 Transfer line

The transfer line should be resistant to chemical attack from gases and aerosols present in the sample gas. Suitable materials for gaseous mercury sampling are silica glass, PTFE or PFA.

The transfer line should be cleaned thoroughly using rinse solution (6.3.9) and distilled water in sequence and dried thoroughly before sampling.

The transfer line shall have a heating system capable of maintaining exit gas temperature at 393 K ± 5 K or at least 20 K above the dew point temperature, whichever is higher.

7.6 Filter

Consistent with ISO 21741, the filter shall be capable of withstanding prolonged exposures up to 40 K above the sample gas temperature to prevent a change in filter quality. The filter efficiency shall be better than 99,5 % on a test aerosol with a mean particle diameter of 0,3 μm at the maximum flow rate anticipated. The filter material shall be unreactive to SO_2 or sulfur trioxide (SO_3). A maximum mercury content in the original filter should be less than one tenth of the corresponding amounts which is calculated from the lower range of determination. Silica fibre filters without binders are recommended. The filter shall be dried, equilibrated and weighed in accordance with ISO 9096 or ISO 12141.

In the case of in-stack filtration, the filter is placed in the duct between the nozzle and the transfer line.

7.7 Cyclone separator

In the case of particulate concentration higher than 100 mg/m³, it is recommended to use a cyclone separator. Such as the sampling at upstream of dust removal device, a cyclone separator is added between the filter and the probe liner, as shown in Figure 1. Suitable material for cyclone separator is quartz or borosilicate glass.

7.8 Filter housing

The filter housing shall have an airtight seal against leakage. If the flue gas temperature is below the dew point or the filter housing cannot be inserted in the duct, the filter housing shall be placed outside the duct (out-stack filtration) in accordance with ISO 9096 or ISO 12141. The filter housing shall be cleaned thoroughly using the rinse solution (6.3.9) and distilled water in sequence and dried thoroughly before sampling.

7.9 Filter heating box

The filter heating box should have a heating system.

In the case of out-stack filtration, the cyclone separator, filter and filter housing are placed in the filter heating box. In order to reduce the adsorption of gaseous mercury by dust on the filter, and to prevent water and acid condensation, the filter heating box should be maintained at a temperature of 393 K ± 5 K or at the flue gas temperature, whichever is greater.

7.10 Absorbing system

The absorbing system consists of eight impingers immersed in an ice bath and connected in series with leak-free ground glass fittings or other non-contaminating leak-free fittings.

The first impinger, the second impinger and the third impinger contain the KCl solution (6.3.5). The fourth impinger contains the HNO_3-H_2O_2 solution (6.3.6). The fifth impinger, the sixth impinger and the seventh impinger contain the H_2SO_4-$KMnO_4$ solution (6.3.7). The last impinger contains silica gel (6.3.13) or an equivalent desiccant.

In order to ensure the complete capture of gaseous mercury, the temperature of the eight impingers should be maintained at approximately 273 K to 277 K during the entire sampling process.

The silicon grease or other greases shall not be used for this method.

7.11 Pump

The pump is used to extract the sample through the sampling train. It shall be an airtight pump capable of maintaining the selected sampling flow rate throughout the sampling period and shall be adjusted using a flow regulator.

7.12 Thermometer

It shall be fitted into the sampling train between the drying unit and the gas meter. The maximum allowable error of the thermometer shall be within 1 % of the full range.

7.13 Manometer

It shall be used to measure the pressure difference between the gas entering the gas meter and atmosphere. It shall be capable of measuring pressure difference within 1 % of the differential pressure.

7.14 Gas meter

The volume of the dried sample gas shall be measured using a calibrated gas meter. The gas meter shall be accurate within 2 % of the volume determined from the sampling system flow rate.

7.15 Rotameter

It shall be capable of measuring the flow rate to within ±10 % of the flow.

7.16 Barometer

It shall be used to measure the local atmospheric pressure in kilopascals (kPa) to within 1 % of the absolute pressure.

7.17 Ancillary equipment

Depending upon the application, other flue gas parameters can be required to convert the mercury measurements into appropriate units. This equipment may include oxygen concentration analyser.

7.18 Impinger

The recommended impingers are the Greenburg-Smith design. Other types of impingers which offer good absorption efficiency are also available and may be used.

The impingers can be made of borosilicate glass. All the connections among impingers should not use silicone grease but can be made of borosilicate glass. O-ring seals are recommended to be used at all the connections of the eight impingers.

8 Sampling

8.1 Sampling location

Sampling is carried out at a location which meets the requirements of ISO 12141 or ISO 9096. Sampling shall be conducted at a suitable access port through which the sampling probe can be passed into the duct. The port shall be capable of being sealed when not in use.

8.2 Proper differential pressure gauge

Ensure that the proper differential pressure gauge is selected for the range of velocity heads (refer to ISO 10780).

8.3 Sampling volume

The minimum sampling volume and number of samples taken depend on the nature of the process that is producing the emissions. If the sources present periodic emission characteristics, the total sampling period shall cover at least one emission cycle. If the process is operated under a steady-state condition, the minimum sampling volume can be calculated prior to sampling by using the expected emitted concentration. The minimum sampling volume also needs to consider the limit of determination of the analytical method.

Generally, the volume of sampling gas between 0,5 m^3 and 1,5 m^3 normalized to STP is recommended. When the mercury concentration in flue gas is in the range of 0,4 µg/m^3 to 5 µg/m^3, the flue gas sampling volume shall be no less than 1,0 m^3 (dry flue gas normalized to STP). This usually occurs at the sampling points after efficient dust removal device and desulfurization facility.

When the mercury concentration in flue gas is more than 5 µg/m^3, the flue gas sampling volume shall be no less than 0,5 m^3 (dry flue gas normalized to STP) to ensure the representativeness of the samples.

8.4 Preparation of the sampling train

Assemble the sampling train as shown in Figure 1. Place a weighed filter in the filter housing using tweezers or clean disposable surgical gloves. Install the selected nozzle using a non-contaminating rubber-type O-ring or equivalent when stack temperature is less than 533 K and an alternative gasket material when temperature is higher. Other connecting systems, such as PTFE ferrules or ground glass joints, may also be used on the probe and nozzle.

Place 100 ml KCl solution (6.3.5) in each of the first impinger, second impinger and third impinger. Place 100 ml of the HNO$_3$-H$_2$O$_2$ solution (6.3.6) in the fourth impinger. Place 100 ml of the H$_2$SO$_4$-KMnO$_4$ solution (6.3.7) in each of the fifth impinger, sixth impinger and seventh impinger. Transfer approximately 200 g to 300 g of silica gel from its container to the last impinger. Place crushed or cubed ice around the impingers.

Prior to final train assembly, weigh and record the weight of each impinger. This information is required to calculate the water vapour content of the sampled flue gas.

8.5 Other measurements prior to sampling

8.5.1 Volumetric gas flow through duct at the sampling plane

The measurement of the volumetric gas flow at the sampling plane is necessary if the results are to be reported in terms of mass of pollutant emitted per unit time. The measurements shall be carried out in accordance with ISO 10780.

8.5.2 Water vapour content

The water vapour content of flue gas is necessary to calculate the mercury concentration on wet basis and the isokinetic flow rate.

8.5.3 Oxygen content

If the results are to be reported after correction to a particular oxygen concentration, the measurement of the flue gas oxygen concentration is necessary during the sampling period.

9 Calibration and standardization

9.1 Calibration of probe nozzle

Refer to ISO 9096:2017, 6.2.3.

9.2 Calibration of pitot tube

Refer to ISO 10780:1994, 5.2.

9.3 Calibration of metering system

Refer to ISO 9096:2017, 6.2.8.

9.4 Calibration of thermometer

Refer to ISO 10780:1994, 5.3.

9.5 Leak check of the metering system

Refer to ISO 9096:2017, 7.4.2.

10 Measurement procedure

10.1 Sampling operation

A safe working platform shall be provided at the sampling position so that all the sampling points can be reached with safety in accordance with ISO 10396.

Carefully insert the probe into the duct with the nozzle facing downstream, avoiding contact with any parts of the duct. Seal the opening of the access port to minimize air ingress.

Record the time and the current gas meter reading (V_i). Turn the sampling probe until the entry nozzle is facing upstream within ±10°, start the pump, open the shut-off valve and adjust the flow rate in order to obtain isokinetic sampling. When moving points, it is required that the pump remains switched on and that the isokinetic flow rate is immediately checked and adjusted if necessary. The sampling flow rate shall be sufficient to allow vigorous bubbling within the impingers of the sampling train but not so vigorous that the solution is carried over from one impinger into another one. Metered temperature and ambient pressure should be recorded periodically.

At the end of the sampling period, the suction control valve shall be closed and the sampling pump switched off. The gas meter shall be read (V_f). A post-test leak test of the equipment should then be carried out.

10.2 Sample recovery

10.2.1 General

Withdraw the probe from the duct and allow it to cool so that it can be handled.

10.2.2 Recovery of ash sample

Remove the probe and filter heating box from the sampling train.

In the case of sampling at upstream of the dust removal device, with high particulate loadings in flue gas, the cyclone separator shall be used. Remove the filter from the filter housing. Then, transfer the ash from the filter and storage flask of cyclone separator to a labelled petri dish (i.e. container 1a) carefully. A non-metallic brush should be used for removing particulate matter. Wash the nozzle, probe liner, cyclone separator, storage flask and filter housing with approximately 30 ml of the rinse solution (6.3.9). Repeat this washing process twice. If a long transfer line is used, increase the number of washing process. Then, transfer all the probe rinse solution into a sample bottle.

In the case of sampling at downstream of the dust removal device, remove the filter from the filter housing and place it in a labelled petri dish (i.e. container 1a). It is necessary to fold the filter and make certain the particulate cake is inside the fold. Wash the nozzle, probe liner and filter housing with approximately 25 ml of the rinse solution (6.3.9). Repeat this washing process twice. If a long transfer line is used, increase the number of washing process. Then, transfer all the probe rinse solution into a sample bottle. The sample bottle should be fluoroplastic bottle made of PTFE, PFA or FEP.

10.2.3 Recovery of absorber samples

Dry the exterior surfaces of impingers 1, 2, 3, 4, 5, 6 and 7. Then, weigh and record the weight of each impinger.

Pour all the liquid from the three KCl impingers into container 2. Rinse the three KCl impingers and connecting glassware with the rinse solution (6.3.9) for at least three times, and pour the rinses into container 2.

Pour all the liquid from HNO_3-H_2O_2 impinger into container 3. Rinse the HNO_3-H_2O_2 impinger and connecting glassware with the rinse solution (6.3.9) two times and pour the rinses into container 3.

Pour all the liquid from the three H_2SO_4-$KMnO_4$ impingers into container 4. Rinse the three H_2SO_4-$KMnO_4$ impingers and connecting glassware two times with the rinse solution (6.3.9) and pour the rinses into container 4.

Mark the height of the fluid level in containers 2, 3 and 4, seal and clearly label the contents.

10.2.4 Recovery of silica gel impinger

Dry the exterior surfaces of impinger 8, then weigh and record the weight of this impinger.

Note the colour of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition.

10.2.5 Storage of recovered samples

Store the samples out of direct sunlight and complete chain-of-custody forms as applicable. The samples should be analysed within 45 days. Report the time between sample acquisition and analysis.

10.3 Sample preparation

10.3.1 Preparation of ash sample

In the case of sampling at upstream of the dust removal device, filter the probe rinse solution using an acid-resistant filter paper (0,45 μm). Dilute to the appropriate volume for the expected mercury concentration with water. Record the volume of the sample. Collect the filtered particulate on the filter paper and dry at the temperature of less than 323 K, and then place the dry particulate into a labelled petri dish (container 1b) carefully. Take the ash sample from container 1a and container 1b respectively, to create representative-weighed aliquots for digestion.

In the case of sampling at downstream of the dust removal device, the mass of ash collected is small, digest the entire filter along with the ash from container 1a and take the ash sample from container 1b for digestion.

Place 0,1 g of ash sample in a closed pressurized fluoroplastic vessel made of PTFE, PFA or FEP. Add 5 ml of concentrated HNO_3 (6.3.3), 2 ml of concentrated HCl (6.3.1) and 1 ml of concentrated HF (6.3.8) to the vessel. Heat the closed pressurized vessel at 473 K for 25 min, keep warm for 20 min, and then cool to 343 K. Take out the digestion vessel, add 0,2 g of H_3BO_3 (6.3.14). Heat the closed pressurized vessel at 423 K for 18 min and keep warm for 20 min. If the actual mass of ash digested differs significantly from 0,1 g, the amounts of acids shall be changed proportionally.

10.3.2 Preparation of solution samples

To neutralize any SO_2 that can have dissolved in KCl solution, add small amounts (1 ml increments) of the solution of $\omega(KMnO_4)$ = 5 % (6.3.10) very slowly to container 2, and gently mix the solution until a purple colour is obtained. Let the container sit for approximately 15 min and verify that the purple colour remains. If the solution in container 2 becomes clear, add a small amount of the solution of $\omega(KMnO_4)$ = 5 % (6.3.10) until a pink or slightly purple colour is obtained. Check again after 90 min to ensure the purple colour remains. If the purple colour of the solution is too dark, use hydroxylamine hydrochloride solution (6.3.11) to drip back, and finally add 1 ml of the solution of $\omega(KMnO_4)$ = 5 % (6.3.10) for storage.

Add small amounts (1 ml increments) of the solution $\omega(KMnO_4)$ = 5 % (6.3.10) very slowly to the nitric acid-hydrogen peroxide solution in container 3, and gently mix the solution until a purple colour is obtained. If the purple colour of the solution is too dark, use hydroxylamine hydrochloride solution (6.3.11) to drip back, and finally add 1 ml of the solution of $\omega(KMnO_4)$ = 5 % (6.3.10) for storage.

Add several drops of a hydroxylamine hydrochloride solution of ω = 10 % (6.3.11) to the three H_2SO_4-$KMnO_4$ impingers until the brown stains are completely gone. Add this rinse to container 4. If the solution in container 4 becomes clear, add small amounts of H_2SO_4-$KMnO_4$ solution (6.3.7) until a pink or slightly purple colour is obtained. Finally, preserve the solution by adding 1 ml of the solution of $\omega(KMnO_4)$ = 5 % (6.3.10) to container 4.

Mark the height of the fluid level in containers 2, 3 and 4, seal and clearly label the contents.

10.4 Analytical procedures

10.4.1 Reagent blank

Refer to 11.2.1.

10.4.2 Analytical procedure for mercury in prepared solution

10.4.2.1 General

In accordance with ISO 21741, the standard method for the determination of mercury in the rinse solution and digested solution is CVAAS or CVAFS.

The described digestion step for the liquid solution in ISO 12846:2012, Clause 5 and ISO 17852:2006, Clause 7, is unnecessary and shall be omitted. After preparing the sample (see 10.3), the sample shall be analysed immediately.

10.4.2.2 Atomic absorption spectrometry

Analyse the mercury concentration in the samples in accordance with ISO 12846.

10.4.2.3 Atomic fluorescence spectrometry

Analyse the mercury concentration in the samples in accordance with ISO 17852.

11 Quality assurance/quality control

11.1 General

Quality assurance/quality control (QA/QC) using this document requires high-level sampling and analytical experience to obtain defensible and scientifically valid data. It is important that both the sampling team and analytical people are very well trained in the procedures.

11.2 QA/QC for the sampling

11.2.1 Absorbing system

Throughout the sampling process, the temperature of the impingers should be maintained at approximately 273 K to 277 K.

The geometry of the impingers and the quantity of absorber solution shall ensure a gaseous mercury absorption efficiency of no less than 90 % at the chosen sampling flow rate and in the concentration range examined.

If the flue gas is known to contain high SO_2 (i.e. of a volume fraction greater than 0,25 %), the verification test of gaseous mercury absorption efficiency shall be carried out. The solution in each impinger should be separately recovered, digested and tested. If the Hg^0 mass concentration of the seventh impinger is more than 10 % of total elemental mercury concentration in the sampled gas, the overall result shall be rejected. In this case, it is recommended to shorten the sampling time and increase the sampling frequency, or to add a second HNO_3-H_2O_2 impinger.

If the potassium permanganate is consumed during sampling or on receipt of samples in the laboratory or after storage, the data should be flagged as suspect and the result is invalid.

11.2.2 Operation prior to sampling and during sampling

Prior to sampling, record the time and the current gas meter reading.

During sampling, operators shall periodically check and correct the following.

— The flow rate for gas sampling has not drifted by more than ±10 % of the chosen flow rate.

— The flow rate for particulate sampling has been within ±10 % under the condition of ISO 9096 or −5 % to +15 % under the condition of ISO 12141 of the isokinetic sampling rate.

— The silica gel shall not be exhausted. If the colour of silica gel indicates that it is nearly exhausted, then the pump shall be switched off and the probe shall be withdrawn from the duct. The leak test shall be performed before a new bottle of silica gel is fitted into the system.

— Check the purple colour of H_2SO_4-$KMnO_4$ absorbing solution in the seventh impinger remains throughout the sampling. If not, repeat sampling and reduce the total sampling volume.

If any of the components are replaced, then the leak test shall be performed again.

11.2.3 Field blank

To check the sampling procedure and ensure that there is no contamination as a result of the sampling activities, a field blank shall be taken at least before each measurement series or at least once a day. A field blank is performed by assembling a sampling train, transporting it to the sampling location during the sampling period without drawing flue gas through the sampling equipment, and recovering it as a regular sample.

The resulting solution and filter shall be treated, labelled and handled in the same manner as the test solution. The results for the field blank shall be reported along with the samples from the field site.

The field blank value shall not be subtracted from the result of measurement, if the field blank exceeds 10 % of the measured value at the corresponding location, the data should be flagged as suspect.

If the calculated result of measurement is less than the field blank value, the result of measurement shall be reported as less or equal to the field blank value.

11.2.4 Field spike

A field spike is similar to the field blank, with the addition of a predetermined amount of mercury added to each type of the three impinger solution. Perform the field spike by assembling a sampling train, transporting it to the sampling location during the sampling period, adding the spiked solution and recovering it as a regular sample. The solution should be then labelled and sent to the analytical laboratory as if they were actual samples. Conduct at least one field spike for each day of testing.

11.2.5 Leak test

The pre-sampling leak test should be carried out at the maximum vacuum expected during sampling. The post-sampling leak test should be carried out at the maximum vacuum reached during sampling.

The leakage flow rate, determined by pressure variation or a calibrated rotameter with appropriate scale after evacuation of the train at the maximum vacuum, shall be below 2 % of the normal flow rate. During sampling, a leak test can be monitored by measuring continuously the concentration of a relevant gas component (O_2, etc.) directly in the duct and downstream of the sampling train. Any detectable difference between those concentrations indicates a leak in the sampling equipment parts located out of the stack. The leak shall then be investigated and rectified.

11.2.6 Sampling in flue gas with high concentration of SO_2

If the flue gas is known to contain large amounts of SO_2 (i.e. of a volume fraction greater than 0,25 %) or breakthrough has occurred in previous sampling runs, then the volume of HNO_3-H_2O_2 (6.3.6) in the fourth impinger should be doubled, or add an additional HNO_3-H_2O_2 impinger, to increase the oxidation capacity for SO_2 prior to the H_2SO_4-$KMnO_4$ impingers.

Monitor the colour of the $KMnO_4$ impingers. If the purple colour of the first two H_2SO_4-$KMnO_4$ impingers is too light or even clear, the sample should be invalidated. Then, the sampling time for the next sample collected should be shortened so that it becomes less than 30 min.

11.3 QA/QC for the analysis

11.3.1 Reagent blank

A reagent blank test should be done before sample analysis. Two reagent blank tests should be conducted at least for each batch of samples. The results for the reagent blank should be reported along with the samples. The blank value should not exceed 0,1 ng/ml or less than the minimum level of quantification. If contamination of the reagent blank is suspected, the source of contamination should be identified and corrective measures should be taken.

11.3.2 Separate mercury standard solutions

The separate mercury standard solutions are prepared from mercury stock solution (6.3.12) or use commercially available quantitative standard solutions. The QC standard should be prepared at a concentration of approximately half of the calibration range.

11.3.3 Parallel analysis

Every sample should be analysed in triplicate. These results should be within 10 % of each other. If they are not, the instrument should be recalibrated and the samples re-analysed.

11.3.4 Independent QA/QC checks for ash samples

For the ash samples, a certified reference ash sample is to be analysed at least once during the test program. The measured mercury content of reference samples should be within 15 % of the certified value. If this limit is exceeded, corrective action (e.g. re-calibration) should be taken and the samples re-analysed.

12 Expression of results

12.1 Dry gas volume

Calculate the volume of dry flue gas sample using Formula (1):

$$V_m = V_f - V_i - V_l \tag{1}$$

where

V_m is the volume of dry flue gas sample (m^3);

V_f is the final gas meter reading at the end of sampling (m^3);

V_i is the initial gas meter reading at the beginning of sampling (m^3);

V_l is the volume of air drawn through the gas meter during any intermediate leak test (m^3).

Calculate the volume of dry gas sample at STP using Formula (2):

$$V_d = V_m \times \frac{(P_{atm} + P_{av}) \times 273,15}{T_{av} \times 101,325} \tag{2}$$

where

V_d is the total volume of dry gas sampled at STP (m^3);

V_m is the volume of dry flue gas sample (m^3);

P_{atm} is the atmospheric pressure (kPa);

P_{av} is the average pressure difference between the sample gas before gas meter and atmosphere (kPa);

T_{av} is the average temperature of the sample gas before the gas meter (K).

12.2 Content of water vapour

Methods to determine the molecular composition of the stack gas are readily available, as are methods for measuring the moisture content, for example, silica gel, a psychrometer (wet-and-dry-bulb thermometer), a condenser or a set of ice-cooled impingers.

In the event that the CO_2 absorption is negligible, the content of water vapour can be calculated using Formula (3):

$$B_{ws} = \sum_{i=1}^{8} \frac{W_{i1} - W_{i0}}{V_d} \tag{3}$$

where

B_{ws} is the content of water vapour in the gas sample, normalized to STP (g/m^3);

W_{i1} is the mass of impinger after sampling (g);

W_{i0} is the mass of impinger before sampling (g);

V_d is the total volume of dry gas sampled at STP (m^3).

12.3 Mass concentration of Hg^P

The mass concentration of Hg^P on a dry basis at STP is calculated using Formula (4) and Formula (5).

For the main stream arrangement,

$$\rho_{S,Hg,d} = \frac{C_{S,Hg,a} \times v_{S,a} \times F_{D,a} + C_{S,Hg,b} \times v_{S,b} \times F_{D,b} + C_{RS,Hg} \times v_{RS}}{V_{S,d}} \tag{4}$$

where

$\rho_{S,Hg,d}$ is the mass concentration of Hg^P in the gas stream on a dry basis at STP (µg/m^3);

$C_{S,Hg,a}$ is the concentration of mercury in the prepared sample solution aliquot digested from ash of container 1a (µg/ml);

$C_{S,Hg,b}$ is the concentration of mercury in the prepared sample solution aliquot digested from ash of container 1b (µg/ml);

$C_{RS,Hg}$ is the concentration of mercury in the probe rinse sample aliquot for Hg^P analysis (µg/ml);

$v_{S,a}$ is the volume of the prepared sample solution digested from ash of container 1a (ml);

$v_{S,b}$ is the volume of the prepared sample solution digested from ash of container 1b (ml);

v_{RS} is the total volume of the probe rinse sample from which the sample aliquot was taken (ml);

$V_{S,d}$ is the volume of dry flue gas sample for Hg^P analysis, normalized to STP (m^3);

$F_{D,a}$ is the dilution factor, which is the total mass of ash of container 1a divided by the mass of ash analysed;

$F_{D,b}$ is the dilution factor, which is the total mass of ash of container 1a divided by the mass of ash analysed.

For the side stream arrangement,

$$\rho_{S,Hg,d} = \frac{C_{S,Hg,a} \times v_{S,a} \times F_{D,a} + C_{S,Hg,b} \times v_{S,b} \times F_{D,b} + C_{RS,Hg} \times v_{RS}}{V_{main,d} + V_{side,d}} \tag{5}$$

where

$\rho_{S,Hg,d}$ is the mass concentration of Hg^P in the gas stream on a dry basis at STP (µg/m^3);

$C_{S,Hg,a}$ is the concentration of mercury in the prepared sample solution aliquot digested from ash of container 1a (µg/ml);

$C_{S,Hg,b}$ is the concentration of mercury in the prepared sample solution aliquot digested from ash of container 1b (µg/ml);

$C_{\text{RS,Hg}}$ is the concentration of mercury in the probe rinse sample aliquot for Hg^P analysis (µg/ml);

$v_{\text{S,a}}$ is the volume of prepared sample solution digested from ash of container 1a (ml);

$v_{\text{S,b}}$ is the volume of prepared sample solution digested from ash of container 1b (ml);

v_{RS} is the total volume of probe rinse sample from which the sample aliquot was taken (ml);

$V_{\text{S,d}}$ is the volume of the dry flue gas sample for Hg^P analysis, normalized to STP (m^3);

$F_{\text{D,a}}$ is the dilution factor, which is the total mass of ash of container 1a divided by the mass of ash analysed;

$F_{\text{D,b}}$ is the dilution factor, which is the total mass of ash of container 1a divided by the mass of ash analysed;

$V_{\text{main,d}}$ is the volume of dry flue gas sample in the main stream, normalized to STP (m^3);

$V_{\text{side,d}}$ is the volume of dry flue gas sample in the side stream, normalized to STP (m^3).

12.4 Mass concentration of Hg^{2+}

Calculate the mass concentration of Hg^{2+} in the gas stream on a dry basis at STP using Formula (6):

$$\rho_{Hg^{2+},d} = \frac{C_{\text{KCl,Hg}} \times v_{\text{KCl}} - C_{\text{KCl,b}} \times v_{\text{KCl,b}}}{V_{\text{G,d}}} \tag{6}$$

where

$\rho_{Hg^{2+},d}$ is the mass concentration of Hg^{2+} captured by the KCl impinger solution in the gas stream on a dry basis at STP (µg/m^3);

$C_{\text{KCl,Hg}}$ is the concentration of mercury in the prepared sample solution aliquot in container 2 (µg/ml);

$C_{\text{KCl,b}}$ is the concentration of mercury in the KCl reagent blank aliquot (µg/ml);

v_{KCl} is the total volume of solution in container 2 from which the sample aliquot was taken (ml);

$v_{\text{KCl,b}}$ is the total volume of KCl reagent blank from which the sample aliquot was taken (ml);

$V_{\text{G,d}}$ is the volume of dry flue gas sample for gaseous mercury analysis, normalized to STP (m^3).

12.5 Mass concentration of Hg^0

Calculate the mass concentration of Hg^0 captured by the HNO_3-H_2O_2 impinger solution on a dry basis at STP using Formula (7):

$$\rho_{Hg^0,HNO_3-H_2O_2,d} = \frac{C_{HNO_3-H_2O_2,Hg} \times v_{HNO_3-H_2O_2} - C_{HNO_3-H_2O_2,b} \times v_{HNO_3-H_2O_2,b}}{V_{\text{G,d}}} \tag{7}$$

where

$\rho_{Hg^0,HNO_3-H_2O_2,d}$ is the mass concentration of Hg^0 captured by the HNO_3-H_2O_2 impinger solution on a dry basis at STP (µg/m^3);

$C_{HNO_3-H_2O_2,Hg}$ is the concentration of mercury in the prepared sample solution aliquot in container 3 (µg/ml);

$C_{HNO_3-H_2O_2,b}$ is the concentration of mercury in the HNO_3-H_2O_2 reagent blank aliquot (µg/ml);

$v_{HNO_3-H_2O_2}$ is the total volume of solution in container 3 from which the sample aliquot was taken (ml);

$v_{HNO_3-H_2O_2,b}$ is the total volume of $HNO_3-H_2O_2$ reagent blank from which the sample aliquot was taken (ml);

$V_{G,d}$ is the volume of dry flue gas sample for gaseous mercury analysis, normalized to STP (m^3).

Calculate the mass concentration of Hg^0 captured by the H_2SO_4-KMnO$_4$ impinger solution on a dry basis at STP using Formula (8):

$$\rho_{Hg^0,H_2SO_4-KMnO_4,d} = \frac{C_{H_2SO_4-KMnO_4,Hg} \times v_{H_2SO_4-KMnO_4} - C_{H_2SO_4-KMnO_4,b} \times v_{H_2SO_4-KMnO_4,b}}{V_{G,d}} \qquad (8)$$

where

$\rho_{Hg^0,H_2SO_4-KMnO_4,d}$ is the mass concentration of Hg^0 captured by the H_2SO_4-KMnO$_4$ impinger solution on a dry basis at STP (μg/m^3);

$C_{H_2SO_4-KMnO_4,Hg}$ is the concentration of mercury in the prepared sample solution aliquot in container 4 (μg/ml);

$C_{H_2SO_4-KMnO_4,b}$ is the concentration of mercury in the H_2SO_4-KMnO$_4$ reagent blank aliquot (μg/ml);

$v_{H_2SO_4-KMnO_4}$ is the total volume of solution in container 4 from which the sample aliquot was taken (ml);

$v_{H_2SO_4-KMnO_4,b}$ is the total volume of the H_2SO_4-KMnO$_4$ reagent blank from which the sample aliquot was taken (ml);

$V_{G,d}$ is the volume of the dry flue gas sample for gaseous mercury analysis, normalized to STP (m^3).

The mass concentration of Hg^0 in the gas stream on a dry basis at STP is determined using Formula (9):

$$\rho_{Hg^0,d} = \rho_{Hg^0,H_2SO_4-KMnO_4,d} + \rho_{Hg^0,HNO_3-H_2O_2,d} \qquad (9)$$

where

$\rho_{Hg^0,d}$ is the mass concentration of Hg^0 in the gas stream on the dry basis at STP (μg/m^3);

$\rho_{Hg^0,H_2SO_4-KMnO_4,d}$ is the mass concentration of Hg^0 captured by the H_2SO_4-KMnO$_4$ impinger solution on a dry basis at STP (μg/m^3);

$\rho_{Hg^0,HNO_3-H_2O_2,d}$ is the mass concentration of Hg^0 captured by the HNO_3-H_2O_2 impinger solution on a dry basis at STP (μg/m^3).

12.6 Mass concentration of Hg^T

The mass concentration of Hg^T in the gas stream on a dry basis at STP is determined using Formula (10):

$$\rho_{Hg,d} = \rho_{S,Hg,d} + \rho_{Hg^{2+},d} + \rho_{Hg^0,d} \qquad (10)$$

where

$\rho_{Hg,d}$ is the mass concentration of Hg^T in the gas stream on a dry basis at STP ($\mu g/m^3$);

$\rho_{S,Hg,d}$ is the mass concentration of Hg^P in the gas stream on a dry basis at STP ($\mu g/m^3$);

$\rho_{Hg^{2+},d}$ is the mass concentration of Hg^{2+} in the gas stream on a dry basis at STP ($\mu g/m^3$);

$\rho_{Hg^0,d}$ is the mass concentration of Hg^0 in the gas stream on a dry basis at STP ($\mu g/m^3$).

12.7 Mass concentration of mercury in the gas stream on a dry basis at STP and reference oxygen volume fraction

The mass concentration of mercury in the gas stream on a dry basis at STP and reference oxygen volume fraction is determined using Formula (11):

$$\rho_{Hg,dry,ref} = \rho_{Hg,dry} \times \frac{20,9 - \varphi_{O,ref}}{20,9 - \varphi_{O,dry}}$$ (11)

where

$\rho_{Hg,dry,ref}$ is the mass concentration of mercury on a dry basis at STP and reference oxygen concentration ($\mu g/m^3$);

$\rho_{Hg,dry}$ is the mass concentration of mercury measured during the sampling on a dry basis at STP ($\mu g/m^3$);

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

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

13 Performance characteristics

13.1 Instrumental limits of detection

The instrumental limits of detection for gaseous mercury by CVAAS and CVAFS are in the order of 0,01 ng and 0,001 ng, respectively, as absolute mass of mercury. The limit of detection, limit of determination, precision and accuracy are evaluated in laboratory tests (see Annex A). 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 m³ (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 $\mu g/m^3$, 0,011 $\mu g/m^3$, 0,035 $\mu g/m^3$ and 0,127 $\mu g/m^3$, respectively. The expected limits of determination for Hg^0, Hg^P, Hg^{2+} and Hg^T are 0,229 $\mu g/m^3$, 0,025 $\mu g/m^3$, 0,082 $\mu g/m^3$ and 0,263 $\mu g/m^3$, respectively.

13.2 Evaluation of the measurement uncertainty

Calculate the measurement uncertainty in accordance with ISO 20988 (see Annex B).

14 Test report

The test report shall include at least the following information:

a) a reference to this document (i.e. ISO 5409:2024);

b) a description of the whole sampling system and the analytical system;

c) identification of the sampling test, including

— the date,

— the time and duration of sampling, and

— the sampling and analytical personnel;

d) a description of the plant or process operation conditions, including:

— any variation to the process that occurred during sampling,

— the load on the plant during monitoring,

— the maximum loading conditions of the plant;

e) identification of the sampling location, including

— duct dimensions,

— sampling position, and

— number and position of sampling points;

f) flue gas characteristics at the sampling location, including

— flue gas velocity,

— flue gas static pressure,

— temperature and oxygen profiles, and

— flue gas water vapour content;

g) the measurement procedure:

— whether sampling was carried out iso-kinetically at sampling points in accordance with ISO 9096 or ISO 12141 with justification or at a single point with justification,

— entry nozzle diameter,

— location of filter,

— filtration temperature, and

— duration for each sample;

h) the test results:

— sampled flue gas volume at sampling conditions,

— average sample gas flow rate, any special circumstances or incidents,

— the portion of prepared sample solution submitted for analysis,

— the concentration of mercury in the sample measured in the laboratory, and

— the normalized concentration at STP;

i) QA/QC:

— the leak test result,

— the reagent blank,

— the field blank,

— information on measurement uncertainty,

— collection efficiency,

— quality control results for all replicates, blanks and spikes,

— the limit of detection of the method;

j) comments:

— any special circumstances that can have influenced the results,

— report of any modification to the method.

Annex A
(informative)

Evaluation of limit of detection, limit of determination, precision and accuracy in laboratory tests

A.1 General

Due to the uneven mercury content in fuel and raw materials and the unstable flue gas conditions in the actual production process, mercury concentration in flue gas fluctuates greatly over time. Therefore, it is impossible to evaluate the limit of detection, limit of determination, precision and accuracy by using actual flue gas.

This method used the Hg^0 permeation device to generate standard Hg^0 gas. The Hg^0 permeation device was placed in a sealed U-shaped quartz tube immersed in a temperature-controlled water bath. A regulated volume of nitrogen gas was introduced into the inlet of the U tube serving as carrier gas.

A fixed concentration of mercury sample gas was produced under a fixed water temperature and nitrogen gas flow. As to Hg^{2+}, considering that the existing Hg^{2+} generators are still in the experimental exploration stage, this method used the oxidation products of Hg^0 and other flue gas components (such as SO_2 and nitric oxide) as the simulated flue gas containing Hg^{2+}. However, since the accurate Hg^{2+} compound compositions are still unknown, the precision and accuracy for Hg^{2+} are only for reference. The specific experimental scheme and results are as follows.

A.2 Limit of detection and limit of determination for Hg^0, Hg^P, Hg^{2+} and Hg^T (see [Table A.1](#))

The limit of detection is calculated from the summation of the average blank value plus three times standard deviation. The limit of determination is calculated from the summation of average blank value plus 10 times standard deviation.

This document used blank flue gas with high-purity nitrogen as the diluent gas. The concentration of SO_2 is 143 mg/m³ and the concentration of nitric oxide is 134 mg/m³. Six different laboratories conducted seven tests using CVAAS separately and finally 42 parallel tests in total are obtained.

When the sampling volume is 1,5 m³ (on a dry basis as corrected to standard conditions), the average limits of detection for Hg^0, Hg^P, Hg^{2+} and Hg^T are 0,103 µg/m³, 0,011 µg/m³, 0,035 µg/m³ and 0,127 µg/m³, respectively. The average limits of determination for Hg^0, Hg^P, Hg^{2+} and Hg^T are 0,229 µg/m³, 0,025 µg/m³, 0,082 µg/m³ and 0,263 µg/m³, respectively.

A.3 Accuracy and precision for Hg^0 (see [Table A.2](#))

The relative error and relative standard deviation of the data in each verification laboratory are calculated as the accuracy and precision, respectively.

In order to examine the accuracy and precision of tested Hg^0, the simulated flue gas with three different Hg^0 concentration levels (5 µg/m³, 15 µg/m³ and 50 µg/m³) were prepared. Six different laboratories conducted six tests using CVAAS separately, and finally 36 parallel tests in total were obtained.

When the generated Hg^0 concentration is 5 µg/m³, the mean accuracy expressed as a relative error (%) is found to be −2,52 % and the average precision expressed as relative standard deviation is found to be 6,51 %. When the generated Hg^0 concentration is 15 µg/m³, the mean accuracy expressed as a relative error (%) is found to be −6,65 % and the average precision expressed as a relative standard deviation is found to

be 10,98 %. When the generated Hg^0 concentration is 50 μg/m^3, the mean accuracy expressed as relative error (%) is found to be −9,36 % and the average precision expressed as a relative standard deviation is found to be 5,50 %.

A.4   Accuracy and precision for Hg^{2+} and Hg^T (see <u>Table A.3</u>)

In order to investigate the accuracy and precision for Hg^{2+} and Hg^T, simulated flue gas with three different Hg^0 concentration levels (5 μg/m^3, 15 μg/m^3, 50 μg/m^3) were prepared. SO_2 (286 mg/m^3), nitric oxides (67 mg/m^3), and hydrogen chloride (41 mg/m^3) were added to the Hg^0-containing flue gas as oxidizing component. After oxidative conversion, a continuous emission monitoring system of mercury (HgCEM) was used to determine the concentration of Hg^{2+} and Hg^0 continuously, when the flue gas was sampled using the method of this document. The concentrations of Hg^{2+} were 1,45 μg/m^3, 5,00 μg/m^3, and 15,0 μg/m^3, respectively. The concentrations of Hg^0 were 3,55 μg/m^3, 10,0 μg/m^3, 35,0 μg/m^3, respectively.

The above concentrations of Hg^{2+} and Hg^0 tested by HgCEM are regarded as the actual value in the flue gas. There will be bias between actual value and the concentration tested by the HgCEM. Thus, the precision and accuracy of both Hg^{2+} and Hg^0 from oxidation experiment are just for reference. The relative error of this method is calculated against the HgCEM results. Since the accuracy and precision of Hg^0 provided in <u>Table A.2</u> are more accurate, the statistical data of Hg^0 are not provided in <u>Table A.3</u>.

Six different laboratories conducted six tests using CVAAS separately, and finally 36 parallel tests in total were obtained. The corresponding test data and statistical results are listed in <u>Table A.3</u>.

When the concentration of Hg^{2+} after oxidation experiment is 1,45 μg/m^3, the average accuracy and precision for Hg^{2+} is found to be 4,08 % and 2,51 %, respectively, and the accuracy and precision for Hg^T is found to be 2,63 % and 1,89 %, respectively.

When the concentration of Hg^{2+} after oxidation experiment is 5,00 μg/m^3, the accuracy and precision for Hg^{2+} are 5,00 % and 1,64 %, respectively, and the accuracy and precision for Hg^T are 3,01 % and 1,21 %, respectively.

When the concentration of Hg^{2+} after oxidation experiment is 15,0 μg/m^3, the accuracy and precision for Hg^{2+} are 3,38 % and 1,84 %, respectively, and the accuracy and precision for Hg^T are 2,05 % and 1,40 %, respectively.

Table A.1 — Limit of detection and limit of determination for Hg^0, Hg^P, Hg^{2+} and Hg^T

Laboratory	Blank value µg/m³				Average value µg/m³				Standard deviation µg/m³				Limit of detection µg/m³				Limit of determination µg/m³			
	Hg^0	Hg^P	Hg^{2+}	Hg^T	Hg^0	Hg^P	Hg^{2+}	Hg^T	Hg^0	Hg^P	Hg^{2+}	Hg^T	Hg^0	Hg^P	Hg^{2+}	Hg^T	Hg^0	Hg^P	Hg^{2+}	Hg^T
A	0,080	0,010	0,020	0,110	0,053	0,008	0,012	0,073	0,016	0,001	0,009	0,018	0,101	0,012	0,038	0,128	0,213	0,022	0,098	0,255
	0,040	0,008	0,000	0,048																
	0,050	0,008	0,015	0,073																
	0,070	0,008	0,020	0,098																
	0,050	0,008	0,015	0,073																
	0,040	0,005	0,015	0,060																
	0,040	0,008	0,000	0,048																
B	0,050	0,005	0,015	0,070	0,044	0,005	0,011	0,060	0,021	0,001	0,008	0,022	0,106	0,008	0,035	0,127	0,251	0,014	0,092	0,283
	0,020	0,004	0,000	0,024																
	0,050	0,005	0,015	0,070																
	0,020	0,003	0,000	0,023																
	0,040	0,005	0,015	0,060																
	0,050	0,005	0,015	0,070																
	0,080	0,006	0,020	0,106																
C	0,050	0,005	0,015	0,070	0,059	0,005	0,016	0,080	0,012	0,000	0,002	0,012	0,095	0,006	0,024	0,117	0,180	0,010	0,041	0,204
	0,070	0,004	0,020	0,094																
	0,060	0,005	0,015	0,080																
	0,080	0,004	0,020	0,104																
	0,050	0,005	0,015	0,070																
	0,050	0,005	0,015	0,070																
	0,050	0,005	0,015	0,070																
D	0,020	0,004	0,020	0,044	0,047	0,006	0,016	0,070	0,020	0,003	0,009	0,022	0,106	0,014	0,043	0,135	0,245	0,034	0,106	0,289
	0,050	0,005	0,015	0,070																
	0,070	0,010	0,020	0,100																
	0,060	0,010	0,030	0,100																
	0,060	0,005	0,015	0,080																
	0,050	0,005	0,015	0,070																
	0,020	0,003	0,000	0,023																

Table A.1 *(continued)*

Laboratory	Blank value μg/m³				Average value μg/m³				Standard deviation μg/m³				Limit of detection μg/m³				Limit of determination μg/m³			
	Hg^0	Hg^P	Hg^{2+}	Hg^T	Hg^0	Hg^P	Hg^{2+}	Hg^T	Hg^0	Hg^P	Hg^{2+}	Hg^T	Hg^0	Hg^P	Hg^{2+}	Hg^T	Hg^0	Hg^P	Hg^{2+}	Hg^T
E	0,050	0,005	0,015	0,070	0,044	0,005	0,014	0,063	0,018	0,003	0,006	0,019	0,099	0,014	0,032	0,121	0,226	0,034	0,076	0,257
	0,020	0,000	0,000	0,020																
	0,050	0,005	0,015	0,070																
	0,020	0,005	0,015	0,040																
	0,050	0,005	0,015	0,070																
	0,050	0,005	0,015	0,070																
	0,070	0,010	0,020	0,100																
F	0,020	0,002	0,000	0,022	0,050	0,006	0,014	0,070	0,021	0,003	0,007	0,022	0,112	0,015	0,034	0,137	0,258	0,035	0,082	0,291
	0,050	0,005	0,015	0,070																
	0,030	0,005	0,015	0,050																
	0,080	0,010	0,020	0,110																
	0,050	0,005	0,015	0,070																
	0,050	0,005	0,015	0,070																
	0,070	0,010	0,020	0,100																

Table A.2 — Accuracy and precision for Hg⁰

Laboratory	Tested concentration µg/m³						Average value µg/m³	Relative error %	Standard deviation µg/m³	Relative standard deviation %
	1	2	3	4	5	6				
Generated Hg⁰: 5 µg/m³										
A	4,50	4,76	5,15	4,69	5,09	4,94	4,86	−2,90	0,25	5,14
B	4,39	4,60	4,80	5,22	4,78	5,29	4,85	−3,07	0,35	7,22
C	4,56	4,80	5,21	4,77	5,12	5,05	4,92	−1,63	0,25	5,04
D	4,39	4,68	4,83	5,29	4,81	5,30	4,88	−2,33	0,36	7,28
E	4,49	4,72	5,05	4,65	5,03	5,57	4,92	−1,63	0,39	7,87
F	4,45	4,72	4,84	4,64	4,91	5,37	4,82	−3,57	0,31	6,49
Generated Hg⁰: 15 µg/m³										
A	12,0	13,5	14,4	14,3	14,2	15,7	14,0	−6,67	1,21	8,64
B	11,1	12,9	13,9	13,3	16,0	14,6	13,6	−9,29	1,66	12,2
C	12,1	13,6	14,5	15,8	14,4	15,9	14,4	−4,07	1,43	9,93
D	11,2	13,0	14,2	13,9	16,1	15,0	13,9	−7,38	1,69	12,1
E	11,6	13,2	14,3	14,2	16,3	15,2	14,1	−5,74	1,61	11,4
F	11,5	13,0	14,2	13,9	16,2	15,0	14,0	−6,77	1,61	11,6
Generated Hg⁰: 50 µg/m³										
A	42,9	46,5	43,6	45,9	49,6	48,6	46,2	−7,67	2,68	5,81
B	41,2	43,2	47,0	44,3	46,8	49,8	45,4	−9,24	3,09	6,82
C	42,4	46,1	43,5	45,5	45,8	48,4	45,3	−9,43	2,11	4,65
D	41,6	43,8	48,3	44,3	49,3	46,6	45,7	−8,68	2,94	6,43
E	42,2	45,5	42,3	45,1	45,4	45,6	44,3	−11,3	1,63	3,67
F	41,8	43,8	48,7	44,5	44,4	47,4	45,1	−9,82	2,53	5,62

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Annex B
(informative)

Results of evaluation of measurement uncertainties in field tests

The precision of data using this sampling method is influenced by many factors: flue gas concentration, source, procedural and equipment variables. Strict adherence to the method is necessary to reduce the effect of these variables. Failure to ensure a leak-free system, failure to accurately calibrate all indicated system components, failure to select a proper sampling location, failure to thoroughly clean all glassware, and failure to follow prescribed sample recovery, preparation and analysis procedures can seriously affect the precision of the results.

The onsite tests using this method were conducted in a coal-fired power plant equipped with selective catalytic reduction unit (SCR), electrostatic precipitator (ESP) and flue gas desulfurization system (FGD). The onsite sampling positions are shown in Figure B.1. Four groups of repeated sampling tests were carried out at each sampling location. Two sets of sampling trains were used for each sampling test simultaneously. The standard uncertainty and the expanded uncertainty of the measurement were calculated from the results of paired measurements for flue gases from coal-fired power plants before and after dust removal device using Formula (B.1) according to ISO 20988:2007, Table 1, type A6 (paired measurement of two identical measurement systems).

$$u(y)=\sqrt{\frac{1}{2n}\sum\nolimits_{j=1}^{n}\left(y_{1,j}-y_{2,j}\right)^{2}} \tag{B.1}$$

where

$u(y)$ is the standard uncertainty;

$y_{1,j}$ is the jth concentration value of the first measuring system;

$Y_{2,j}$ is the jth concentration value of the second measuring system;

n is the number of paired measured values.