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

Émissions de sources fixes — Échantillonnage et détermination de la teneur en mercure dans les gaz de combustion en utilisant un piège d'amalgamation de l'or

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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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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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*.

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

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.

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*

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)

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 ($\mu g/m^3$)

$\rho_{Hg,dry,O}$ 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.

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.

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

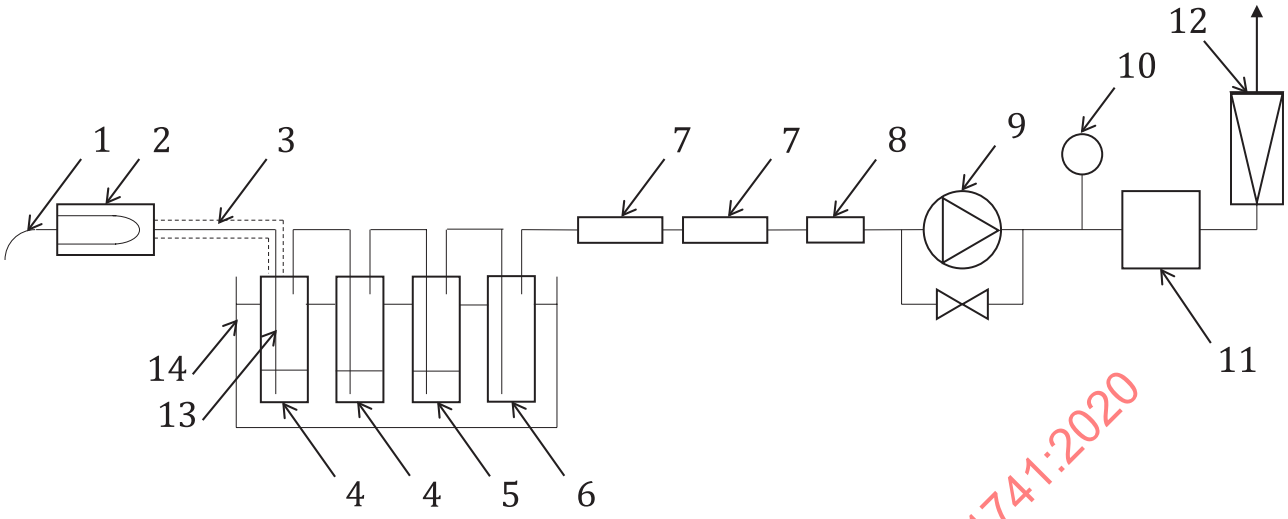
7.1 General

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.

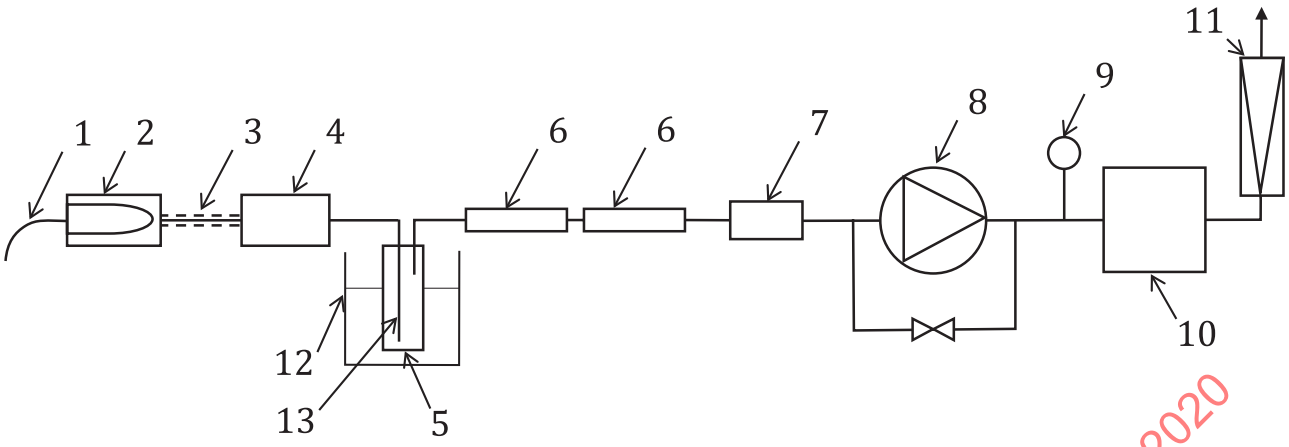


Key

1	nozzle	8	drying unit (silica gel)
2	filter and filter housing	9	pump
3	heated transfer line	10	thermometer and manometer
4	$SnCl_2$ impinger	11	gas meter
5	gas-washing impinger	12	flowmeter
6	dehumidifying impinger (empty)	13	impinger nozzle
7	gold amalgamation trap	14	cooling bath

Figure 1 — Schematic diagram of a main-stream sampling train with stannous chloride reduction unit

Schematic diagram of main-stream sampling system using a heated catalytic reduction unit is given in Figure 2. A solid reductant is used instead of stannous chloride solution to reduce Hg^{2+} to Hg^0. The gas-washing impinger containing phosphate buffer solution is not necessary because the solid reductant also removes interfering gases like SO_2, NO_x and HCl. An empty impinger is used to remove moisture.



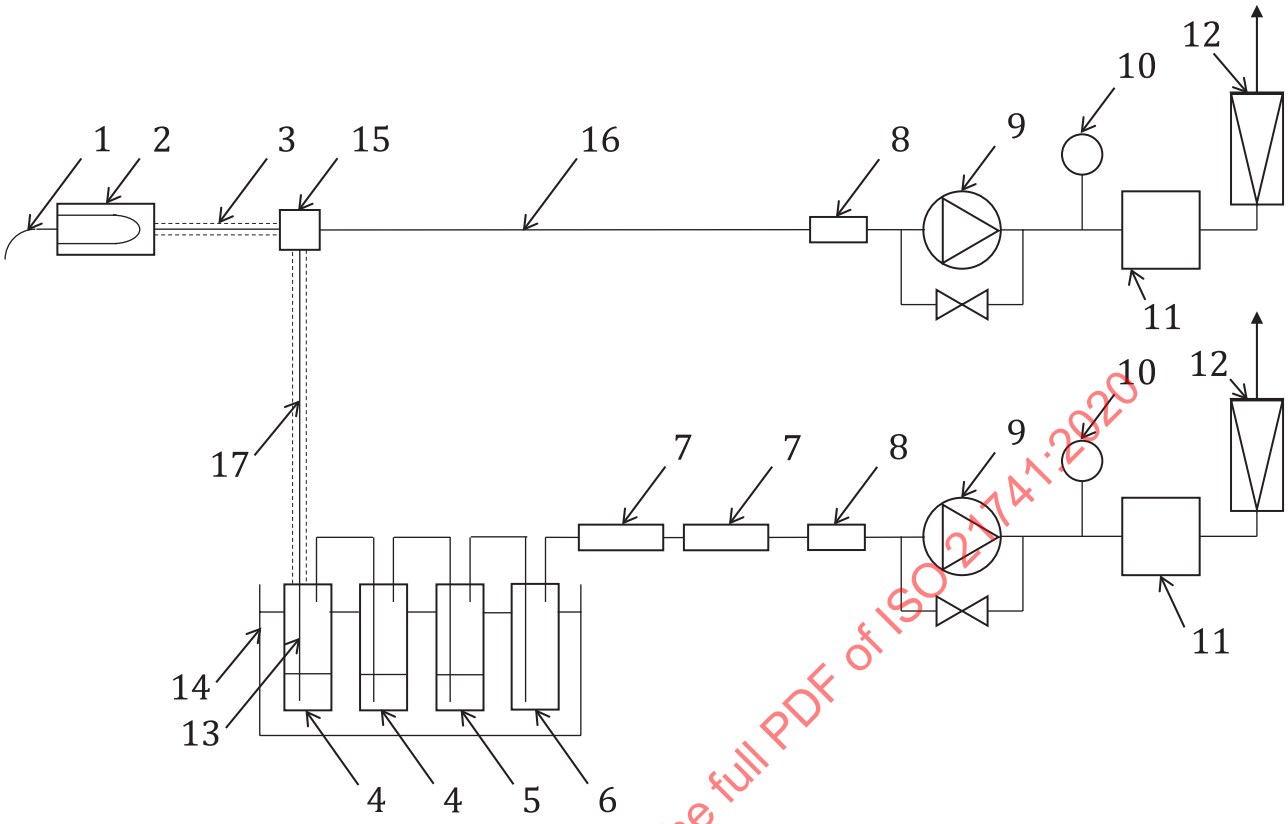
Key

1	nozzle	8	pump
2	filter and filter housing	9	thermometer and manometer
3	heated transfer line	10	gas meter
4	solid reductant	11	flowmeter
5	dehumidifying impinger (empty)	12	cooling bath
6	gold amalgamation trap	13	impinger nozzle
7	drying unit (silica gel)		

Figure 2 — Schematic diagram of a main- stream sampling train with heated catalytic reduction unit

7.1.2 Side-stream sampling

Schematic diagram of side-stream sampling system using a stannous chloride reduction unit is given in Figure 3. The apparatus consists of almost the same components except for T-piece which splits the gas stream to obtain an appropriate gas flow rate between 0,2 l/min to 1,0 l/min for gaseous mercury sampling. The heated catalytic reduction unit is also used instead of the stannous chloride reduction unit.



Key

1	nozzle	10	thermometer and manometer
2	filter and filter housing	11	gas meter
3	heated transfer line	12	flowmeter
4	$SnCl_2$ impinger	13	impinger nozzle
5	gas-washing impinger	14	cooling bath
6	dehumidifying impinger (empty)	15	T-piece
7	gold amalgamation trap	16	main stream
8	drying unit (silica gel)	17	side stream (heated)
9	pump		

Figure 3 — Schematic diagram of a side-sampling train with stannous chloride reduction unit

7.2 Nozzle

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

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, PTFE and titanium.

The nozzle shall be cleaned thoroughly before each sample run by rinsing with rinse solution (6.10) and distilled water. The rinse shall be repeated until the rinse water shows no evidence of particulate matter.

7.3 Filter and filter housing

The filter shall be capable of withstanding prolonged exposures up to 40 K above the sample duct 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. 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. The filter shall be dried, equilibrated and weighed in accordance with ISO 9096 or ISO 12141.

The silica fibre filter is placed in the duct between the nozzle and the transfer line (in-stack filtration). Silica fibre filters without binders are recommended. The filter holder 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 (6.10) and distilled water in this order and dried thoroughly before sampling.

NOTE Distribution of mercury in vapour phase and in solid phase depends on the temperature of filtration and adsorption of gaseous mercury and re-vaporization of particulate mercury on the filter will occur. Therefore, especially if the out-stack filtration is employed, an accurate determination of particulate mercury and gaseous mercury as they exist at stack conditions is difficult, but the total mercury concentration can still be determined.

7.4 Transfer line

The transfer line shall be resistant to chemical attack from gases and aerosols present in the sample gas. Suitable materials for gaseous mercury sampling are silica glass, PTFE and titanium. When using titanium transfer line, gas temperature shall be maintained above 453 K as mercury creates amalgam with titanium at temperature below 453 K.

The transfer line shall be cleaned thoroughly using rinse solution (6.10) and distilled water in this order and dried thoroughly before sampling.

The transfer line shall have a heating system capable of maintaining a gas temperature at its exit of at least 423 K or >20 K above the dew point temperature, whichever is higher.

7.5 Pretreatment unit

The oxidized mercury (Hg^{2+}) in vapour phase must be converted to elemental mercury (Hg^0) and interfering gases which deteriorate the efficiency of gold amalgamation trap must be removed prior to the gold amalgamation trap. The pre-treatment unit for these purposes consists of a series of impingers or a heated catalytic reduction unit.

When using the impingers, the first and second impingers shall contain stannous chloride solution (6.5) to reduce Hg^{2+} to Hg^0. The third gas-washing impinger containing phosphate buffer solution (6.6) shall be used when flue gas contains acidic gases like HCl typically at higher than 10 ppm. Sulfur dioxide (SO_2) at 1 000 ppm, NO_x at 500 ppm and CO at 100 ppm do not interfere the efficiency of gold amalgamation trap irrespective of the presence or absence of the gas-washing impinger. The fourth impinger shall be empty to catch any carryover from the gas-washing impinger. This impinger also works to remove moisture. These impingers shall be kept in a cooling bath as shown in Figure 1.

For high reduction and removal efficiency it is advisable to distribute the gas stream in these solutions as homogeneously as possible and have reasonably long contact time between gas and solution. These solutions should not be carried over to the next impinger by the gas stream. In practice, sufficient free space will also break down any foam which can be formed while the gas is bubbling through the solution. A typical size for impingers is 250 ml and the optimum volume of these solution is 100 ml. The impinger nozzle has fritted glass or PTFE tip.

The impingers can be made of silica glass, borosilicate glass or PTFE and shall be rinsed and cleaned with the rinse solution (6.10) and distilled water in this order and shall be dried thoroughly before sampling.

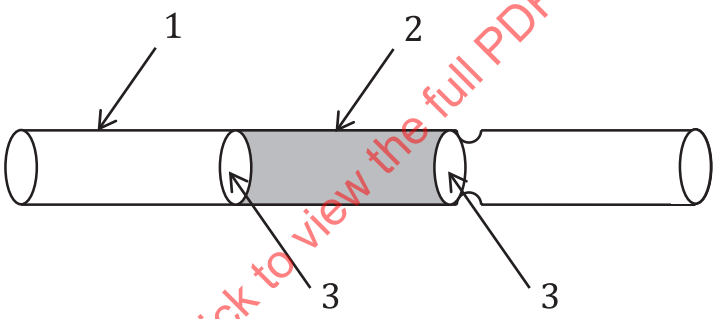
When using the catalytic reduction unit, solid reductant is used to reduce Hg^{2+} to Hg^0. In general, sulphite or phosphate of alkali metals (Na or K) or alkaline-earth metals (Mg or Ca) is used as reductant and it also removes interfering gases like SO_2, NO_x and HCl. Solid reductant is typically operated at elevated temperatures from 573 K to 773 K to provide a thermal conversion of oxidised mercury to

elemental mercury. A dehumidifying impinger (empty) kept in a cooling bath or an electric cooling unit shall be connected to remove moisture as shown in Figure 2.

7.6 Gold amalgamation trap

In this method, for the efficient collection of mercury, two gold amalgamation traps are placed in series. The traps can be made of silica glass. The geometry of the traps and quantity of gold amalgamation materials shall be such that an elemental mercury collection efficiency of not less than 95 % is achieved at the chosen sampling flow rate and in the concentration range examined. If the absolute amounts of mercury trapped with the second trap is more than 5 % of those with the first trap, then the overall result shall be rejected. The gold traps are commercially available from mercury vendors that use amalgamation techniques or can be constructed in the laboratory.

An example of gold amalgamation trap is shown in Figure 4. For preparation of the trap, pack silica wool, 80 mg to 200 mg of mercury-trapping agent (6.12), and silica wool in this order into silica glass tube which has a dent. Heat the gold amalgamation trap at 873 K to 1 073 K for 5 min while mercury-free carrier gas is being flowed at the rate of 0,2 l/min to 0,5 l/min in it, and then place the gold amalgamation trap in a glass test tube, close it hermetically with a stopper made of butyl rubber, and store it. After long storage, the trap should be cleaned by heating before using it for sampling, especially when analysing mercury at very low concentration levels. Storing limit shall be 6 months from its preparation.



Key

1 silica tube
2 mercury-trapping agent
3 silica wool

Figure 4 — Gold amalgamation trap (example)

7.7 Drying unit

It shall be filled with 200 to 300 g of silica gel (6.11) to dry the sample gas prior to the suction unit, gas meter and flowmeter.

7.8 Suction unit

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.

7.9 Thermometer

It shall be fitted into the sampling train between the drying unit and the gas meter. The thermometer shall be capable of measuring absolute temperature to within 1 % of the absolute temperature.

7.10 Manometer

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

7.11 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 % at the volume determined from the sampling system flow rate.

7.12 Flowmeter

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

7.13 Barometer

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

8 Sampling

8.1 General

Sampling for particulate mercury is performed isokinetically and sampling for gaseous mercury is performed either isokinetically or non-isokinetically. When the flow rates or the total sampling volumes for the measurement of gaseous and particulate mercury is different, particle mercury and gaseous mercury are sampled separately by using either a side-stream sampling train or two sampling trains (7.1).

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.

8.2 Sampling position and sampling point

Sampling is carried out at a location which meets the requirements of ISO 9096 or ISO 12141. 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. When using two sampling trains, sampling of gaseous mercury shall be performed at a point adjacent to the particulate sampling point in which the physicochemical parameters such as mercury concentration and gas flow rate are considered to be equivalent.

8.3 Sampling duration and sample volume

The minimum sampling period and the number of samples taken depend on the nature of the process that is producing the emissions. If emissions from a cyclical process are to be measured, the total sampling period shall cover at least one cycle of the process operation.

The minimum sampling duration also needs to take into account the lower limit of determination of the analytical method. If the process is operated under a steady-state condition, the minimum sampling time and volume can be calculated prior to sampling by using the expected emitted concentration.

On the other hand, the maximum sampling duration depends on the upper limit of determination of the analytical method. The upper limit of determination in absolute mass of mercury is generally not less than 500 ng with the AAS and AFS. On this basis at 100 $\mu g/m^3$ of mercury, an upper sample volume of 0,005 m^3 would be required, which means sampling duration less than 25 min at the sampling flow rate of 0,2 l/min.

The maximum sampling duration also needs to take into account the lifetime of the stannous chloride reductant and gas-washing solution (phosphate buffer). Given this factor, this method is generally suitable for short-term sampling less than 200 min. For sources with a long-term variation of mercury concentration more than 200 min, repeated periodic sampling and analysis would be useful to know an average emission concentration. The stannous chloride and gas-washing solutions shall be replaced for each sample. It would be also useful to use an automated exchange system of $SnCl_2$ and gas-washing solutions and gold amalgamation traps parallelly arranged. Although the solid reductants have a long lifetime as compared with the $SnCl_2$ solution and can be reused for a certain number of times, users should consult with manufacturers about the lifetime before use and the maximum number of reuse shall not exceed 10 times to ensure the reduction capability in this standard.

8.4 Other measurements to be made prior to sampling

8.4.1 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 16911-1.

8.4.2 Moisture content of gas

The moisture content of flue gas is necessary to calculate the mercury concentration on wet basis and the isokinetical flow rate.

8.4.3 Oxygen content of gas

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

8.5 Assembly of sampling apparatus

Assemble the sampling equipment as illustrated in Figure 1, 2 or 3. Allow the sampling system equipment to reach operating temperature then check the system for leaks as described in 8.7.

8.6 Sampling

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°, open the shut-off valve, start the suction device 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 three impingers of the pretreatment unit but not so vigorous that the solution is carried over to the next impinger. A constant sampling flow rate shall be maintained within the range described in 8.8. 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 leak test of the equipment should then be carried out.

NOTE If the side-stream sampling is employed or particulate mercury and gaseous mercury are sampled separately, a sampling flow rate for gaseous mercury between 0,2 l/min and 1,0 l/min can be sufficient to allow efficient reduction of Hg^{2+} and collection of Hg^0. If the sampling durations of gaseous and particulate mercury are significantly different, the sampling of the shorter duration can be repeated during the longer sampling duration.

8.7 Checking for leaks

A pre-sample leak check should be carried out at the maximum vacuum expected during sampling and the post-sample leak check should be carried out at the maximum vacuum reached during sampling. The leakage flow rate, determined by pressure variation or a calibrated flowmeter 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 check 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, although this leak check is only useful for testing large leaks. The leak shall then be investigated and rectified.

8.8 Quality assurance

Prior to sampling, record the time and the current gas meter reading. During sampling, the flow rate of the sample gas shall be recorded periodically, together with the temperature and pressure at the gas meter to allow the calculation of the average temperature and pressure during the sampling period.

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, and

— the silica gel has not been exhausted.

  If the colour of the silica gel indicates that it is nearly exhausted, then the pump shall be switched off and the sampler withdrawn from the duct to be leak tested before a new bottle of silica gel is fitted into the system.

— the precipitates forming and colour change in the impingers.

  If the severe precipitates formation or colour change is observed in the impingers of stannous chloride solution or gas-washing solution (phosphate buffer), then the pump shall be switched off and the sampler withdrawn from the duct to be leak tested before a new impinger of stannous chloride solution or gas-washing solution is fitted into the system. Sampling a smaller volume or sampling at lower flow rate may minimize the problem.

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

The leak rate measured during any leak test shall not be greater than 2 % of the nominal flow rate. Otherwise the result is invalid.

8.9 Sample recovery

Turn off the pump and withdraw the probe from the duct and allow it to cool so that it can be handled.

Record the time and the current gas meter reading (V_f). Disconnect the first $SnCl_2$ impinger nozzle from the transfer line. Turn on the pump and introduce 5 ml of the rinse solution (6.10) through the inlet of the impinger nozzle to wash the adsorbed Hg^{2+} on the inner surface of this part. Washed Hg^{2+} is reduced to Hg^0 in the stannous chloride solution and purged to the gold amalgamation trap. Atmospheric air is used for purging Hg^0 from the stannous chloride solution. When a contamination of atmospheric air with mercury is suspected, place another gold amalgamation trap in front of the impinger nozzle after introducing the rinse solution to purify the atmospheric air. Repeat this washing process at least twice and then rinse with distilled water. Turn off the pump.

Remove each gold amalgamation trap from the sampling train and seal both ends. Wipe any deposited materials from the outside of the trap. Place the trap into a well-closed container and store/preserve it in a cool dark place.

Remove the filter and filter catch from the sampling train and place them into a well-closed container and store/preserve it in a cool dark place. Sample recovery for particulate mercury should only deal with the filter and filter catch. Then, wash nozzle, filter housing and transfer line with approximately 10 ml of the rinse solution (6.10). Repeat this washing process twice. If a long transfer line is used, increase the number of washing process. Then, transfer all the rinse solutions into a volumetric flask. Add water to a constant volume and record the volume of the solution in the volumetric flask. Transfer the solution into a fluoroplastic bottle made of PTFE, PFA or FEP.

Clearly label the sample storage containers for gold amalgamation trap, filter and filter catch, and rinse solution with the date and a unique identifier to enable the sample to be traced back to the measurement.

If a side-stream sampling is employed, the parts from nozzle to T-piece and the transfer line from T-piece to the first impinger nozzle of stannous chloride solution shall be rinsed with the rinse solution (6.10) separately. Then transfer each rinse solution in different volumetric flasks and add water to a constant volume. Record the volume of the solution in each volumetric flask. The recovered rinse solutions shall be kept in each sample storage container.

8.10 Reagent blank

A reagent blank shall be taken with each a different lot of reagent by passing purified air or nitrogen gas instead of drawing exhaust gas through the sampling equipment in the laboratory. Mercury existing as impurity, for example, in stannous chloride solution and gas-washing solution (phosphate buffer) is captured on the gold amalgamation trap and measured as described in 10.1. The results for the reagent blank shall be reported along with the samples. If the reagent blank value is equal to or greater than the minimum level of quantification, or greater than one-fifth the level in the associated samples, whichever is greater, results for the associated samples may be the result of contamination. If contamination of the reagent blank is suspected, the source of contamination should be identified, and corrective measures should be taken.

8.11 Field blank

A field blank shall be taken at each site at which measurements are carried out by performing all of the steps of the sampling gas procedure, but without drawing exhaust gas through the sampling equipment. The resulting filter, gold amalgamation trap and rinse solution shall be treated, labelled and handled in the same manner as the test samples. The results for the field blank shall be reported along with the samples from that site. If the field blank value is equal to or greater than the minimum level of quantification, or greater than one-fifth the level in the associated samples, whichever is greater, results for the associated samples may be the result of contamination. If contamination of the field blank is suspected, the source of contamination should be identified, and corrective measures should be taken.

9 Sample preparation

9.1 General

The methods given for particulate mercury analysis are valid for plane filters of approximately 100 mg per filter, and a maximum of 10 mg of particulate matter collected on the filter. If the actual figures differ significantly from these values, the amounts of HNO_3/HF or HNO_3/HCl solutions described in 9.2 respectively shall be changed proportionally.

9.2 Sample preparation for particulate mercury analysis

Desiccate the filter and filter catch without heating (do not heat the filters to speed the drying) and then weigh the desiccated sample.

Place the desiccated sample in a closed pressurized fluoroplastic vessel made of PTFE, PFA or FEP. Add 2 ml of concentrated HNO_3 (6.3) and 3 ml of concentrated HF (6.7) to the vessel. Heat the

closed pressurized vessel at 383 K for 1 h. Aqua regia of 1 ml of concentrated HNO_3 (6.3) and 3 ml of concentrated HCl (6.8) may be used as an alternative to the mixture of HNO_3 and HF.

Filter the solution using an acid-resistant filter paper (0,45 µm). Dilute to 25 ml (or the appropriate volume for the expected mercury concentration) with water. Record the volume of the sample.

When preparing and analysing samples containing hydrofluoric acid, glassware shall not be used for filtering apparatus and volumetric flask.

10 Analytical procedure

10.1 Analytical procedure for mercury collected with gold amalgamation trap

The standard method for the determination of mercury collected with gold amalgamation trap is thermal desorption followed by atomic absorption spectrometry (AAS) or atomic fluorescence spectrometry (AFS). A typical procedure with AAS is as follows:

Place the gold amalgamation trap for sample inside the heating furnace for vaporization shown in Figure 5, heat it at 873 K to 1 073 K for about 3 min while carrier gas is flowing at the flow rate of 0,2 l/min to 0,5 l/min, and collect the generated mercury using a re-trapping tube with mercury-trapping agent (6.12) operated at about 423 K. Switch the three-way stopcock to introduce carrier gas into an absorption cell. Heat the re-trapping tube at specified temperature from 773 K to 1 073 K, and introduce the generated mercury into the absorption cell. Measure the peak height or peak area given by absorption at 253,7 nm wavelength. Variation in the packing state of mercury-trapping agent (6.12) in the gold amalgamation trap causes the variation of desorption speed of mercury. The re-trapping tube with constant desorption performance shall be used for compensating the variation. Some organic compounds give absorption at the wavelength of mercury measurement. To eliminate these organic compounds, the re-trapping tube shall be heated at about 423 K while re-trapping mercury. The re-trapping tube can be generally used without change for more than 500 analyses. When a deterioration of peak shape for standard gas for calibration is detected, change it to a new re-trapping tube.

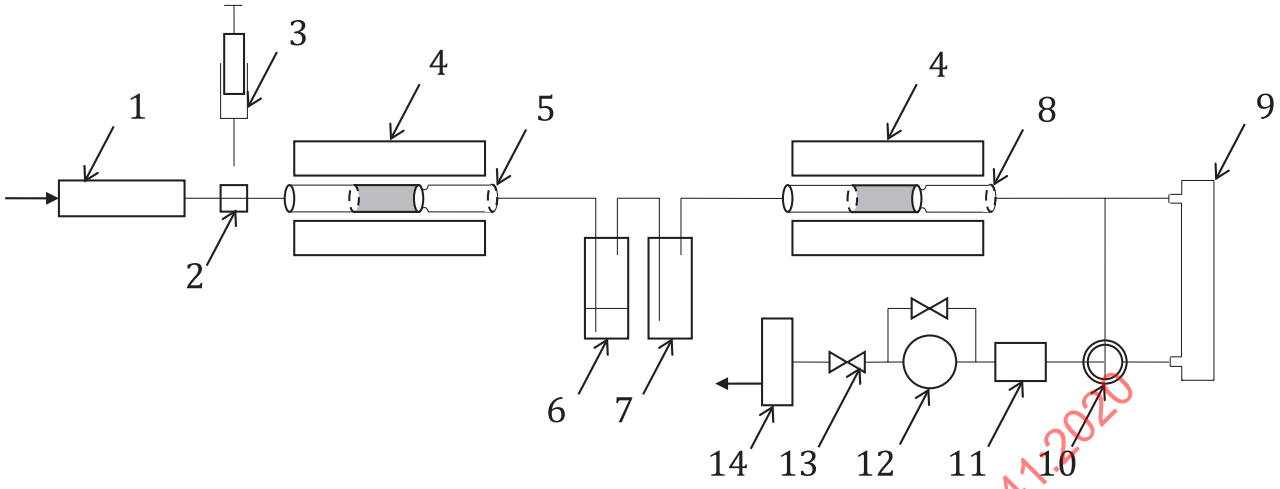
For measurement of reagent blank and field blank, place the gold amalgamation trap used for reagent blank test and field blank test, respectively, carry out the same procedures as the sample, and obtain the values of these blank tests.

Find the mass of mercury on the working curve and calculate the mass of mercury in the gold amalgamation trap.

Working curve for calibration shall be prepared as follows:

Take stepwise from 0,1 ml to 10 ml of mercury reference gas from an apparatus shown in Figure A.1 of Annex A using a gas tight syringe, and introduce them into the gold amalgamation trap through an injection port shown in Figure 5 while a suction pump is operated. Carry out the same procedures as the sample. Plot the relation curve between the mass of mercury and measured value and make it a working curve. Prepare the working curve when sample is determined.

NOTE Instead of the apparatus (shown in Figure A.1 of Annex A) for mercury reference gas, a mercury gas generation apparatus (shown in Figure A.2 of Annex A) can be used. It comprises of a gas flow pump and an impinger of stannous chloride solution to which mercury standard solution containing a known amount of mercury is added.



Key

1	mercury-removal unit	8	re-trapping tube of mercury
2	injection port of mercury reference gas	9	absorption cell
3	gas-tight syringe	10	three-way stopcock
4	heating furnace	11	mercury removal device
5	gold amalgamation trap	12	suction pump
6	gas-washing impinger	13	adjusting valve for flow rate
7	dehumidifying impinger (empty)	14	flowmeter

Figure 5 — Schematic diagram of thermal vaporization atomic absorption spectrometer

10.2 Analytical procedure for mercury in rinse solution and digested solution

The standard method for the determination of mercury in the rinse solution and digested solution is cold vapour AAS (CV AAS) and cold vapour AFS (CV AFS).

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 (9.2) they shall be analysed immediately.

— Atomic absorption spectrometry

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

— Atomic fluorescence spectrometry

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

11 Expression of results

11.1 Calculation of the volume of dry flue gas sampled at sampling conditions

The volume of dry flue gas sample (V_m) is calculated by subtracting the initial gas meter reading (V_i) from the final gas meter reading (V_f) correcting for any air drawn through the gas meter during leak checks (V_l) when equipment is replaced, or if carried out between sampling. The gas volume measured is on a dry basis.

$$V_m = V_f - V_i - V_l \quad (1)$$

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 tests (m^3).

11.2 Calculation of the volume of dry flue gas sample normalized to standard temperature and pressure

Calculate the volume of dry flue gas sample normalized to standard temperature and pressure, V_d, using Formula (2).

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

where

V_d is the volume of dry flue gas sample normalized to 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 the gas meter and the atmosphere (kPa);

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

11.3 Mass concentration of mercury expressed as elemental mercury in the flue gas on a dry basis at STP

The mass concentration of total mercury is calculated as the sum of gaseous and particulate mercury concentrations.

$$\rho_{Hg,dry} = \rho_{G,Hg,dry} + \rho_{S,Hg,dry} \quad (3)$$

For the main-stream arrangement,

$$\rho_{G,Hg,dry} = \frac{M_{A1,Hg} + M_{A2,Hg} + C_{R,Hg} \times v_R}{V_{G,d}} \quad (4)$$

$$\rho_{S,Hg,dry} = \frac{C_{S,Hg} \times v_S}{V_{S,d}} \quad (5)$$

where

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

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

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

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

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

$C_{R,Hg}$ is the concentration of mercury in a prepared sample of rinse solution that washed transfer line from the filter housing to the impinger nozzle of stannous chloride solution in main-stream sampling (see 8.9) (μg/ml);

$C_{S,Hg}$ is the concentration of mercury in a prepared sample solution for particulate mercury analysis (see 9.2) (μg/ml);

v_R is the volume of a recovered sample of rinse solution that washed transfer line from the filter housing to the impinger nozzle of stannous chloride solution in main-stream sampling (see 8.9) (ml);

v_S is the volume of a prepared sample solution for particulate mercury analysis (see 9.2) (ml);

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

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

For the side-stream arrangement,

$$\rho_{G,Hg,dry} = \frac{M_{A1,Hg} + M_{A2,Hg} + C_{R2,Hg} \times v_{R2}}{V_{side,d}} + \frac{C_{R1,Hg} \times v_{R1}}{V_{main,d} + V_{side,d}} \quad (6)$$

$$\rho_{S,Hg,dry} = \frac{C_{S,Hg} \times v_S}{V_{main,d} + V_{side,d}} \quad (7)$$

where

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

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

$C_{R1,Hg}$ is the 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);

$C_{R2,Hg}$ is the 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 in side-stream sampling (μg/ml);

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

v_{R1} is the volume of a recovered sample of rinse solution that washed transfer line from the filter housing to the T-piece (ml);

v_{R2} is the volume of a recovered sample of rinse solution that washed transfer line after the T- piece to the impinger nozzle of stannous chloride solution (ml);

v_S is the volume of a prepared sample solution for particulate mercury analysis (ml);

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

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

11.4 Mass concentration of mercury expressed as elemental mercury in the flue gas on a dry basis at STP and reference oxygen volume fraction

Calculate $\rho_{Hg,dry,O}$ using Formula (8):

$$\rho_{Hg,dry,O} = \rho_{Hg,dry} \times \left(\frac{20,9 - \varphi_{O,ref}}{20,9 - \varphi_{O,d}} \right) \quad (8)$$

where

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

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

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

11.5 Rate of mass discharge of mercury expressed as elemental mercury

The rate of discharge can be determined by finding the product of the concentration of mercury at reference conditions in micrograms per cubic meter by the average flow rate in the duct at reference conditions.

$$q_{m,Hg} = \frac{\rho_{Hg,i} \times q_{V,fg,i}}{1\,000} \quad (9)$$

where

$q_{m,Hg}$ is the rate of mass discharge of mercury expressed as elemental mercury (mg/s);

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

$q_{V,fg,i}$ is the volume flow rate of flue gas through the sampling plane at conditions *i* of temperature, pressure, moisture and oxygen content (m^3/s).

11.6 Mass concentration of mercury expressed as elemental mercury in the flue gas on a wet basis at STP

Calculate $\rho_{Hg,wet}$ using Formula (10):

$$\rho_{Hg,wet} = \rho_{Hg,dry} \times \frac{(100 - w_w)}{100} \quad (10)$$

where

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

w_w is the average moisture content of the flue gas at the sampling plane during the sampling period (%).

11.7 Mass concentration of mercury expressed as elemental mercury in the flue gas on a wet basis at STP and reference oxygen concentration

Calculate $\rho_{Hg,wet,O}$ using Formula (11):

$$\rho_{Hg,wet,O} = \rho_{Hg,wet} \times \left(\frac{20,9 - \varphi_{O,ref}}{20,9 - \varphi_{O,d}} \right) \quad (11)$$

where

$\rho_{Hg,wet,O}$ is the 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);

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

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

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

12 Performance characteristics

12.1 Detection limits

The instrumental detection limits for gaseous mercury by thermal desorption AAS and AFS are in the order of 0,01 ng and 0,001 ng, respectively, as absolute mass of mercury. The instrumental detection limits for particulate mercury by cold vapour AAS and AFS are in the order of 0,1 ng and 0,01 ng, respectively, as absolute mass of mercury. On the other hand, the method detection limits depend on not only the instrumental detection limits but also the reagent blank and the field blank, and they also depend on the sampled flue gas volume and the portion of prepared sample solution submitted to analysis. In view of these factors, the range of determination set in this method for gaseous mercury, from 0,01 μg/m^3 to 100 μg/m^3 (sampling volumes from 0,005 m^3 to 0,1 m^3) and that for particulate mercury, from 0,01 μg/m^3 to 100 μg/m^3 (sampling volume from 0,05 m^3 to 1 m^3) would be achievable without difficulty.

12.2 Evaluation of measurement uncertainty

Calculate the measurement uncertainty in accordance with ISO 20988 or ISO/IEC Guide 98-3 (see Annex B).

13 Test report

The test report shall refer to this document and shall include at least the following information:

a) identification of the sampling site, including:
   - the date,
   - time and duration of sampling,
   - the sampling and analytical personnel;

b) 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;

c) identification of the sampling location, including:
   - duct dimensions,
   - sampling position,
   - number and position of sampling points;

d) flue gas characteristics at the sampling location, including:
   - flue gas velocity,
   - flue gas static pressure,
   - temperature and oxygen profiles,
   - flue gas water vapour content;

e) measurement procedure:
   - whether sampling was carried out isokinetically, at sampling points according to ISO 9096 or ISO 12141 with justification or at a single point with justification,
   - entry nozzle diameter,
   - location of filter,
   - filtration temperature,
   - duration of each sampling;

f) 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,
   - the corrected concentration at standard conditions;

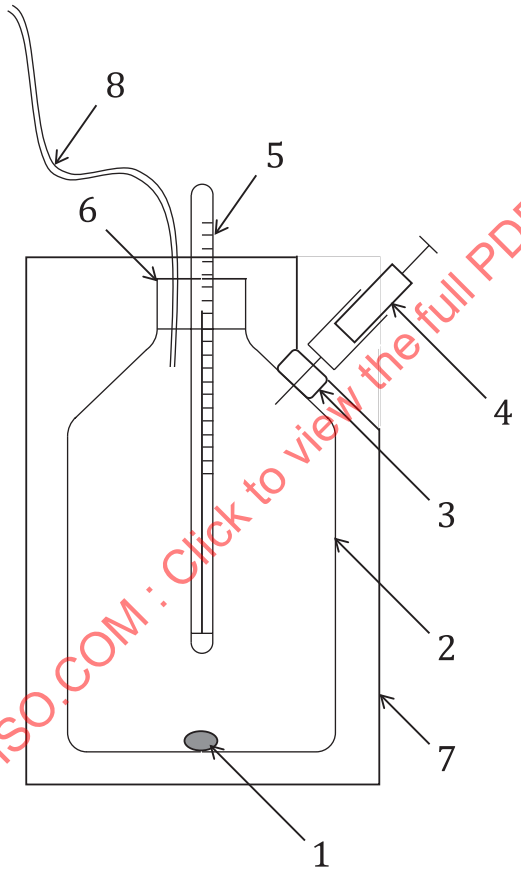
g) quality assurance:
   - leak test result,
   - reagent blank,
   - field blank,
   - information on measurement uncertainty,
   - collection efficiency;

h) comments:
   - any special circumstances that may have influenced the results,
   - report of any modification to the method.

Annex A
(informative)

Preparation of mercury reference gas

Figure A.1 shows an example of preparing apparatus for mercury reference gas. Place a little amount of mercury in a container and allow it to stand in a room at constant temperature for at least 1 hour. Read the temperature in the container with a thermometer and find the concentration of mercury in the container making use of Table A.1. Take a definite volume of this gas using a gas tight syringe, and make it a mercury reference gas.



Key

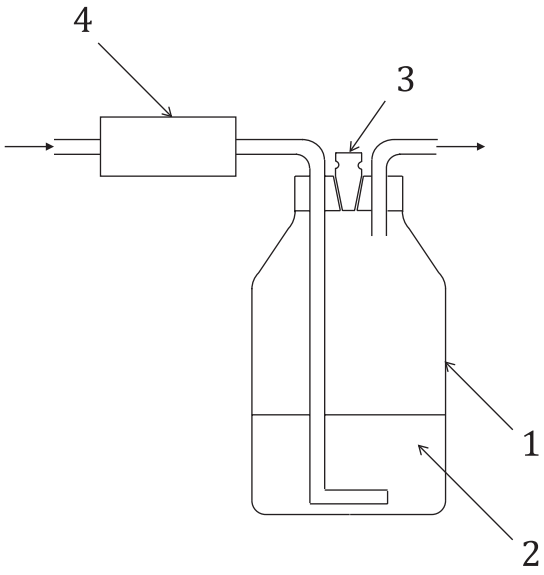
1 mercury
2 container (500 ml to 1 000 ml)
3 silicone stopper
4 gas-tight syringe
5 thermometer (with the least graduation of 0,1 °C)
6 silicone stopper
7 heat insulating material
8 pressure equalization capillary

Figure A.1 — Apparatus for preparing mercury reference gas (example)

Table A.1 — Concentration table of mercury vapor in the calibration apparatus

Temp. (°C)	Conc. of Hg (ng/ml)	Temp. (°C)	Conc. of Hg (ng/ml)	Temp. (°C)	Conc. of Hg (ng/ml)	Temp. (°C)	Conc. of Hg (ng/ml)	Temp. (°C)	Conc. of Hg (ng/ml)
0,0	2,179	0,2	2,225	0,4	2,271	0,6	2,319	0,8	2,368
1,0	2,417	1,2	2,465	1,4	2,514	1,6	2,564	1,8	2,614
2,0	2,666	2,2	2,716	2,4	2,766	2,6	2,818	2,8	2,871
3,0	2,924	3,2	2,978	3,4	3,033	3,6	3,089	3,8	3,146
4,0	3,204	4,2	3,264	4,4	3,325	4,6	3,388	4,8	3,451
5,0	3,516	5,2	3,583	5,4	3,650	5,6	3,719	5,8	3,789
6,0	3,861	6,2	3,933	6,4	4,007	6,6	4,083	6,8	4,159
7,0	4,237	7,2	4,316	7,4	4,396	7,6	4,478	7,8	4,561
8,0	4,645	8,2	4,731	8,4	4,817	8,6	4,905	8,8	4,994
9,0	5,085	9,2	5,178	9,4	5,273	9,6	5,369	9,8	5,467
10,0	5,567	10,2	5,666	10,4	5,767	10,6	5,870	10,8	5,974
11,0	6,079	11,2	6,187	11,4	6,296	11,6	6,407	11,8	6,519
12,0	6,633	12,2	6,751	12,4	6,870	12,6	6,992	12,8	7,115
13,0	7,240	13,2	7,369	13,4	7,501	13,6	7,635	13,8	7,771
14,0	7,909	14,2	8,049	14,4	8,191	14,6	8,335	14,8	8,481
15,0	8,630	15,2	8,781	15,4	8,935	15,6	9,092	15,8	9,251
16,0	9,412	16,2	9,575	16,4	9,742	16,6	9,910	16,8	10,081
17,0	10,255	17,2	10,429	17,4	10,604	17,6	10,783	17,8	10,964
18,0	11,148	18,2	11,337	18,4	11,529	18,6	11,724	18,8	11,922
19,0	12,123	19,2	12,328	19,4	12,536	19,6	12,747	19,8	12,961
20,0	13,179	20,2	13,400	20,4	13,623	20,6	13,851	20,8	14,081
21,0	14,315	21,2	14,553	21,4	14,795	21,6	15,040	21,8	15,289
22,0	15,542	22,2	15,800	22,4	16,061	22,6	16,326	22,8	16,569
23,0	16,869	23,2	17,148	23,4	17,431	23,6	17,718	23,8	18,010
24,0	18,306	24,2	18,606	24,4	18,911	24,6	19,220	24,8	19,534
25,0	19,852	25,2	20,174	25,4	20,500	25,6	20,830	25,8	21,166
26,0	21,506	26,2	21,853	26,4	22,204	26,6	22,560	26,8	22,922
27,0	23,289	27,2	23,660	27,4	24,036	27,6	24,418	27,8	24,805
28,0	25,198	28,2	25,598	28,4	26,003	28,6	26,415	28,8	26,832
29,0	27,255	29,2	27,685	29,4	28,121	29,6	28,564	29,8	29,012
30,0	29,467	30,2	29,928	30,4	30,395	30,6	30,868	30,8	31,348
31,0	31,835	31,2	32,329	31,4	32,830	31,6	33,339	31,8	33,854
32,0	34,376	32,2	34,908	32,4	35,448	32,6	35,995	32,8	36,549
33,0	37,111	33,2	37,681	33,4	38,258	33,6	38,843	33,8	39,437
34,0	40,038	34,2	40,647	34,4	41,264	34,6	41,889	34,8	42,523
35,0	43,165	35,2	43,819	35,4	44,481	35,6	45,152	35,8	45,832
Handbook of Chemistry and Physics, 53rd edition, p.150 (1972).									

Figure A.2 shows another example of preparing apparatus for introducing a definite amount of mercury into a gold amalgamation trap. Connect an outlet tube of an impinger containing an appropriate volume of stannous chloride solution to an injection port of mercury reference gas. Turn on a suction pump, and a mercury chloride solution with a known amount of mercury to the stannous chloride solution using a micropipette. Introduce the generated mercury vapour into the gold amalgamation trap.



Key

1 impinger
2 stannous chloride solution
3 injection port for mercury chloride solution
4 mercury-removing unit

Figure A.2 — Apparatus for generating mercury reference gas (example)

Annex B
(informative)

Results of evaluation of measurement uncertainties

The standard uncertainty and the expanded uncertainty of the measurement were calculated from the results of paired measurements for flue gases from three waste incinerators and one coal combustion plant using Formula (B.1) in accordance with ISO 20988:2007. Both sampling probes were placed at adjacent points in a sampling plane and the sampling were carried out simultaneously.

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

where

$u(y)$ is the standard uncertainty;

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

$y_{2,j}$ is the j th concentration value of the second measuring system;

n is the number of paired measured values.

The results of uncertainty analysis for gaseous mercury are described in Table B.1. The evaluated input data were obtained with two main-sampling trains and are given in Table B.2. As a reduction method stannous chloride solution unit was used in the measurements from 1 to 12, and heated solid catalytic reduction unit was used in the measurements from 13 to 15. All the concentrations for particulate mercury were below the lower measurement range (0,01 µg/m^3).

Table B.1 — Work steps and results for gaseous mercury analysis

Step	Element	Instruction	Result
1	**Problem specification**		
	Evaluated quantity	Result of measurement	y
	Required uncertainty parameters	Standard uncertainty of y Expanded 95 % uncertainty of y	$u(y)$ $U_{0,95}(y)$
	Input data	Series of observation $y_{1,j}$ and $y_{2,j}$ with j = 1 to n obtained in paired application of two identical mesuremering systems operated independently of each other.	See Table B.2
	Reference values	Mean values $y_{Rj} = (y_{1,j} + y_{2,j})/2$	See Table B.2
	Additional information	Standard uncertainty $u(y)$ Standard uncertainty of the unbiased reference values $u(y_R) = u(y) / \sqrt{2}$	constant constant
	Representativeness	The input data evaluated are considered representative for application of the considered method of measurement at two types of stationary sources	—