

Guidance document on BAT/BEP

[Note: Table of contents for the whole document (in harmonized format) will be inserted during later editing of the document.]

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BAT guidance

BEP guidance

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1.7.1 Considerations in selecting and implementing BAT

The definition of best available techniques in Article 2 of the Convention is the basis for determining BAT for a Party, or for a facility within the territory of a Party. The definition states that:

¹ NOTE : text will be added in each section currently left blank at the fourth meeting of the group of technical experts

(i) “Best” means most effective in achieving a high general level of protection of the environment as a whole;

(ii) “Available” techniques means, in respect of a given Party and a given facility within the territory of that Party, those techniques developed on a scale that allows implementation in a relevant industrial sector under economically and technically viable conditions, taking into consideration the costs and benefits, whether or not those techniques are used or developed within the territory of that Party, provided that they are accessible to the operator of the facility as determined by that Party; and

(iii) “Techniques” means technologies used, operational practices and the ways in which installations are designed, built, maintained, operated and decommissioned;

The use of BAT to control, and where feasible to reduce emissions, is required for new sources as defined in paragraph 2(c) of Article 8 and is one of several measures which a Party may use for existing sources as defined in paragraph 2(e) of Article 8. This guidance is intended to support Parties in selecting and implementing BAT.

The guidance may be used when selecting and implementing BAT for individual sources or for source categories.

The process for selecting and implementing BAT could be expected to include the following general steps.

Step 1: establish information about the source, or source category. This may include, but not be limited to, information on the processes, input materials, feedstocks or fuels, and on the actual or expected activity levels including throughput. Other relevant information could include the expected life of the facility, which is likely to be particularly relevant when an existing facility is being considered, and any requirements or plans for controlling other pollutants.

Step 2: identify the full range of options of emission control techniques and combinations thereof, which are relevant for the source under consideration, including the techniques described in section 1.7.2 of this introduction, and in the chapters on specific source categories of this guidance.

Step 3: amongst these, identify technically viable control options, giving consideration to techniques applicable to the type of plant within the sector as well as any physical limitations which may influence the choice of certain techniques.

Step 4: from these, select the control technique options which are the most effective to control and where feasible reduce emissions of mercury and to achieve a high general level of protection of the environment as a whole.

Step 5: determine which of these options can be implemented under economically and technically viable conditions taking into consideration costs and benefits and that they are accessible to the operator of the facility as determined by the Party concerned. The need for good maintenance and good operational control of the techniques to maintain achieved performance over time should be taken into account.

BEP reference *(to be completed)*

1.7.2 Common techniques for emission reduction

While each of the sectors listed in Annex D has specific techniques to reduce mercury emissions, there are a number of common techniques for pollution reduction applicable to all sectors. These are described in this introductory section, while the sector specific sections include descriptions of more specific techniques. In order to consider all possible options relevant to the sector of interest, it is necessary to consider both the common techniques described in this sector and the specific techniques described for each sector.

Particle-bound emissions of mercury can be captured to a varying extent by dust-cleaning devices. Most of the dust-cleaning techniques are generally applied in all sectors. The degree of mercury control depends on the chemical state and form of the mercury, e.g. oxidized or elemental. Elemental mercury is gaseous and is mostly not captured in dust-cleaning devices. The removal efficiency of mercury in the dust-cleaning device can be enhanced by oxidizing the gaseous mercury. The most commonly used techniques for dust abatement are bag filters, electrostatic precipitators (ESP) and dust scrubbers.

A common technique across sectors for specific mercury removal is to use activated carbon (AC) either injected into the flue-gas stream or in a filter bed. To improve the removal efficiency of the activated carbon oxidizing agents can be used (e.g. injected in the flue-gas stream or adsorbed on the AC).

Fabric filters

Bag filters (fabric filters, textile filters) use filtration to separate dust particulates from dusty gases. They are one of the most efficient and cost effective types of dust collectors available and can achieve a collection efficiency of more than 99.99 per cent for very fine particulates. Gases enter the filter device and pass through fabric bags. The bags can be made of different materials (e.g. woven or felted cotton, synthetic or glass fiber material) depending on the properties of the flue-gas.

To improve the ability to filter dust and enhance the life the filter material is often coated. The most common material is chemically inert limestone (calcium carbonate). It increases the efficiency of dust collection via formation of a so called filter cake. A filter cake improves trapping fine particulates and provides protection of the filter material itself from moisture or abrasive particles. Without a pre-coat the filter material allows fine particulates to bleed through the bag filter system, especially during start-up, as the bag can only do part of the filtration leaving the finer parts to the filter enhancer filter cake.

Gaseous mercury will mainly pass through a bag filter. Therefore to improve the efficiency, gaseous mercury should be converted as far as possible into its oxidized form which can bind to particles. The efficiency of the bag filter can be increased with different measures, e.g. coupling with dry or semi-dry sorbent injection (spray drying), providing additional filtration and reactive surface on the filter cake.

Electrostatic Precipitators

Electrostatic precipitators use electrostatic forces to separate dust particles from exhaust gases. The dust laden gases flow through the passage formed by the discharge and collecting electrodes. The airborne particles receive a negative charge as they pass through the ionized field between the electrodes. These charged particles are attracted to a grounded or positively charged electrode and adhere to it. The material collected on the electrodes is removed by rapping or vibrating the collecting elec-

trodes either continuously or at predetermined intervals. Precipitators can usually be cleaned without interrupting the airflow.

The main factors affecting the collection efficiency of electrostatic precipitators are electrical resistivity and particle size distribution. Other influencing factors are temperature, flow rate of the flue-gas, moisture content, conditioning agents in the gas stream or an increased collection surface.

A wet electrostatic precipitator (WESP or wet ESP) operates with water vapor saturated air streams (100 per cent relative humidity). WESPs are commonly used to remove liquid droplets such as sulfuric acid mist from industrial process gas streams. A WESP is also commonly used where the gases are high in moisture content, contain combustible particulate, or have particles that are sticky in nature.

Wet Scrubbers

Dust scrubbers that use liquid are known as wet scrubbers. In these systems, the scrubbing liquid (usually water) comes into contact with a gas stream containing dust particles. Greater contact of the gas and liquid streams yields higher dust removal efficiency.

There is a large variety of wet scrubbers. Humidification leads to agglomeration of fine particles making their collection easier. Other scrubbers place droplets of liquid in the gas stream. As the agglomerates grow larger, they settle into a collector.

The "cleaned" gases are normally passed through a mist eliminator to remove water droplets from the gas stream. The dirty water from the scrubber system is either cleaned and discharged or recycled to the scrubber. Dust is removed from the scrubber in a clarification unit or a tank. The solid material settles on the bottom of the tank. In these systems sludge is formed and has to be removed and deposited.

Up to 95 per cent of oxidized mercury can be removed in wet scrubbers whereas the removal rate of elemental mercury is only 0-10 per cent (European Commission, 2005). Elemental mercury adsorption can be improved by addition of sulfur compounds or activated carbon to the scrubber liquor (Miller et al., 2014).

Precipitation is another measure often used to remove oxidized mercury in scrubbing waters. Sulfur compounds can serve as a flocculation agent, added to the scrubbing water to convert soluble mercury into an insoluble compound efficiently. To bind the mercury directly after the conversion in the liquid phase, another possibility is to add activated carbon to the scrubbing water (Bittig, 2014).

With the measures to enhance the elemental mercury adsorption 20-30 per cent removal is possible. The overall mercury removal (both elemental and oxidized) efficiency is around 85 per cent.

A re-emission of mercury can occur when reducing compounds such as sulfite are present in the scrubbing water. Then mercury can be converted back to elemental mercury and re-emitted. (Keiser, et. al, 2014) This can be avoided by presence of ions with which mercury can react to form a complex, such as fluoride, chloride, bromide or iodide.

Summary of dust cleaning devices

Table 1 provides information on the performances of dust-cleaning devices

Table 1. Performance of dust-cleaning devices expressed as hourly average dust concentrations

	Dust concentrations after cleaning (mg/m ³)
Fabric filters	< 1 - 5
Fabric filters, membrane type	< 1
Dry electrostatic precipitators	< 5 – 15
Wet electrostatic precipitators	< 1- 5
High-efficiency scrubbers	< 20

Source: extracted from the Guidance document on best available techniques for controlling emissions of heavy metals and their compounds from the source categories listed in annex II to the Protocol on Heavy Metals (ECE/EB.AIR/116, 2013)²

Activated Carbon and Oxidizing agents

Activated carbon is an effective sorbent for mercury capture from flue gas. The activated carbon can be injected into the flue gas upstream of dust-cleaning devices, bag filters or ESP, or else the flue gas can be distributed throughout a carbon filter bed. The effectiveness of activated carbon for mercury control is temperature dependent. Specifically, the mercury capture or removal capacity of a particular sorbent typically increases as the flue gas temperature decreases. The flue gas temperature is primarily determined by plant design and operating factors. Depending on plant specifics such as flue gas constituents and operation of the dust control device, mercury removal is relatively effective at temperatures below 175 °C with standard activated carbon. Special high temperature activated carbon sorbents exist for capture of mercury above 175 °C and generally up to 350 °C.

All activated carbons are combustible and, under certain conditions, auto-ignitable, and explosive. The fire and explosion risk is dependent on the combustion and explosion characteristics of the pulverized product, as well as the process and plant conditions. Quality activated carbon is highly processed and poses a lower risk of fire and explosion than low quality carbon. However partially activated carbons can pose a high risk and may require special handling. The adsorbent should be selected carefully and used with proper handling guidance, including fire and explosion preventing equipment, (e.g. avoidance of low-velocity air flows through beds, avoidance of large-volume deposits in the process by continuous and monitored discharge from the hoppers to avoid fire risks, and good housekeeping for spill cleanup). Dilution of carbon with inert material can suppress the potential for explosion. In applications where activated carbon is added to gas streams which have little process dust it may be advantageous to blend carbon with non-combustible sorbents. (Licata et al 2007; Derenne et al., 2008)

The mercury capture can be enhanced by adding oxidizing agents (i.e. halogens) to the flue gas or by using impregnated activated carbon with halogens.

Activated carbon waste should be handled as hazardous waste.

In the following table (Table 2) mercury removal performances of activated carbon techniques are given.

² Note there is an issue with oxygen levels used as a proxy for the amount of dilution occurring, and the expert group is investigating this.

Table 2. Minimum expected mercury removal performances of activated carbon techniques expressed as hourly average mercury concentrations

	Mercury content after cleaning (mg/m ³)
Carbon filter	< 0.01
Sulfur impregnated carbon filter	< 0.01
Carbon injection + dust separator	< 0.05
Injection of brominated activated Carbon+ dust separator	0.001

Source: extracted from the Guidance document on best available techniques for controlling emissions of heavy metals and their compounds from the source categories listed in annex II to the Protocol on Heavy Metals (ECE/EB.AIR/116, 2013)

1.7.3 Cross-cutting considerations (case studies, as available)

- **Waste management considerations**
- **Management of flue gas and other residue**
- **Training of decision makers and technical personnel**
- **Testing, monitoring and reporting**

1.8 Mercury Emissions Monitoring

1.8.1 Overview

Monitoring of mercury emissions is an essential part of overall BAT and BEP implementation for controlling mercury emissions to the environment and for maintaining high operating efficiency of the abatement techniques used. Monitoring of mercury emissions should be conducted according to overall best practices using approved/accepted methods. Representative, reliable and timely data obtained from mercury emissions monitoring is needed to evaluate and ensure the effectiveness of the mercury emission control techniques in use at a facility.

All relevant sources of mercury emissions should undertake mercury emissions monitoring. While the techniques are listed in this introduction, each relevant source may have particularly applicable monitoring techniques and practices, which are referenced in the individual chapters of this guidance. The first step in conducting mercury emissions monitoring is to take direct measurements of the mercury concentrations in the applicable gas streams to establish a performance baseline. Subsequently, more measurements are taken at specific time intervals (e.g. daily, weekly, monthly) to characterize the mercury concentration in the gas at that point in time. Monitoring is then conducted by compiling and analyzing the emissions measurement data to observe trends on emissions and operating performance. Should the measurement data indicate any areas of concern, such as increasing mercury concentrations over time or peaks of mercury emissions associated with certain plant operations, swift action should be taken by the facility to rectify the situation.

The selection of a measurement or monitoring approach should begin with consideration of the intended outcomes. Short term measurements may be needed to provide quick feedback for process optimization, or long term monitoring may be desirable for emissions inventory reporting. Continuous emissions monitoring may be needed to control the process if mercury emissions are highly variable, for example due to rapidly changing mercury contents in the feed materials.

In addition, site-specific characteristics may need to be taken into account when selecting the most appropriate monitoring method and planning for the sampling campaign. Depending on the process, mercury may be present to a variable extent as particulate-bound mercury, gaseous elemental mercury (Hg^0) and/or in the ionized gaseous forms, $\text{Hg}(\text{I})$ or $\text{Hg}(\text{II})$. The partitioning may even vary significantly among facilities conducting similar processes. For some processes, it may be useful to measure these different mercury species individually, for example, to inform decisions on effective control technologies or to conduct risk assessments.

The sampling point should be easily accessible, meet occupational health and safety requirements, meet regulatory requirements, and allow for the retrieval of representative samples. Ideally, the same sampling points should be used for subsequent sampling campaigns to provide comparability between results. To prevent dilution of the samples and avoid false low results, ambient air should not infiltrate the sampling points. Preferably, the gas velocity flow profile should be considered when identifying the sample location to avoid areas of flow disturbance, which would affect the representativeness of the sample. Detailed information on the design and installation of measurement points are available in the European guideline EN 15259:2007³ “Air Quality-Measurement of stationary source emissions – Requirements for measurement sections and sites and for the measurement objective, plan and report”. The guideline is applicable for continuous as well as discontinuous measurements.

To provide representative data, the sample timing, duration and frequency should be determined by considering various parameters, including the measurement and monitoring method used, the facility operating conditions and site-specific process variations and requirements to show compliance under the applicable regulatory process. Samples should be taken at steady-state conditions representative of normal facility operations. If the emissions are highly variable, or emissions are from a batch process, longer sample duration should be used or more samples collected (e.g. samples taken across the entire batch) to provide a reliable average measurement. Also, low concentrations of mercury in the sample stream may necessitate longer duration to provide a total sample mass above the method detection limit. Furthermore, periodic composite samples (e.g. over ½ hour, 12 hours, 24 hours) provide more representative results compared to random grab samples.

Mercury emissions can vary significantly within a single facility over time or among facilities conducting similar processes due to variable mercury content in the materials entering the process. Mercury concentrations can change rapidly in the fuel, raw materials or other inputs, such as waste. During the emissions measurement procedure, the mercury content in the process inputs should also be documented to assist with quality assurance. When conducting sampling, care must be taken, as far as possible, to ensure that the process is operating at normal steady state, mercury concentrations in

³ European Committee for Standardization, “EN 15259:2007: Air quality - Measurement of stationary source emissions - Requirements for measurement sections and sites and for the measurement objective, plan and report”, August 18, 2007. http://standards.cen.eu/dyn/www/f?p=204:110:0:::FSP_PROJECT:22623&cs=106F3444821A456A90F21590F3BFF8582

the input streams are representative of normal feeds, and that fugitive emissions are minimized. If the operating conditions are not typical, extrapolation of the sampling data may provide results with a large margin of error.

Operating conditions should be documented before, during and after the sampling campaign. Specific parameters, such as the volumetric gas flow rate, gas temperature, water vapor content of the gas, static pressure of the gas duct, and atmospheric pressure⁴, should be accurately recorded to allow for conversion of the measured mercury concentrations to standard reference conditions (0 °C, 1 atm, measured or reference oxygen content and on a dry gas basis). The quantity of mercury emitted over time can be determined by multiplying the mercury concentration in the exhaust gas by the stack volumetric gas flow rate, as follows:

For example:

$$E_{\text{Hg}} = C_{\text{Hg}} \times F \times T$$

Where:

E_{Hg} = Annual emissions of mercury (kg/y)

C_{Hg} = Mercury concentration in the gas stream (kg/m³)

F = volumetric flow rate of the gas stream (m³/h)

T = operating time per year (h/y)

Most direct emissions monitoring methods rely on sampling at a point source, such as a stack. Measurement of diffuse emissions, including fugitive emissions, is normally not practiced and methodologies that do exist for measuring diffuse emissions typically produce results with high uncertainty. Thus, it should be noted that emissions monitoring results from point sources may not provide complete data on the total mercury emissions from a facility.

Monitoring method selection should be based on various criteria, such as: site characteristics; process specifics; measurement certainty; cost considerations; regulatory requirements; and, maintenance requirements. To compare the facility's mercury emissions over time, consistent sampling methods should be used in subsequent years.

1.8.2 Direct Measurement Methods

Direct measurement methods are generally considered as the most reliable techniques for mercury emissions monitoring. When correctly conducted, these methods can provide representative, reliable data to allow for more precise estimation of a facility's actual mercury emissions.

⁴ EU IPPCB, NFM BREF Draft, February 2013, p. 67

1.8.2.1 Short Term Measurements

1.8.2.1.1 Impinger Sampling

Impinger sampling of mercury emissions from a stationary source is conducted by manually collecting a sample of exhaust gas from an outlet such as a stack or duct with an isokinetic sampling system, whereby the sample gas stream that is extracted is of the same velocity as the main stream. The isokinetic sampling accounts for changes in gas flow rate and for some particulate loading in the gas. However, this method is not suitable for gases with heavy particulate loading.

This method requires the use of an intricate sampling train to recover mercury from the gas stream into a solution that is then sent for laboratory analysis. While this method allows for good accuracy in mercury concentration measurement, it requires continuous attendance during the sampling period. An advantage of this method is that recovery is possible for both mercury in gaseous form and mercury bound to particulate matter. Because of the complexity of this procedure, source testing tends to be performed only periodically (e.g. once or twice per year). In general, facilities engage specialized source testing consultants to conduct the sampling and analysis.

A probe is inserted into the outlet gas stream to extract a representative sample over a set time period. Since impinger sampling is typically done only a few times per year at most, sampling should be conducted when the process is operating at steady state to allow for extrapolation of the data over an operating year. Operating conditions should be documented before, during and after the sampling campaign. In the US, the general practice is to take three impinger samples, each several hours in length under typical operating conditions, and to calculate the average of the results for the final concentration value. Careful impinger preparation and post handling of solutions is critical for the success of impinger methods. Measurement errors are often related to the loss of mercury from the solutions.

As this is not a continuous emission monitoring method, the results obtained would not provide data on mercury emissions during irregular events, such as wide production swings, process startups, shutdowns or upsets. It should be noted that mercury emissions generated during such events could be significantly higher or lower than during normal operating circumstances.

However, even under normal, steady-state conditions, there could be significant variability in the mercury volumes being emitted when the mercury content in fuels or feedstocks fluctuate over short periods. In particular, for waste incineration and cement facilities using waste fuels, the mercury content entering the system or facility may be unpredictable. Similarly, in the non-ferrous metals sector, mercury in furnace feeds can change rapidly depending on the concentrates being processed. Therefore, results from intermittent impinger sampling may not provide representative data when extrapolated over a long period of time (e.g. annual averages).

To obtain maximum value for investment, mercury emissions source testing should be conducted during broader sampling campaigns for air pollutants such as particulate matter, NO_x, SO₂, and VOC. The addition of mercury testing when conducting these broader air pollutant sampling campaigns may increase operating costs of a facility. Actual costs will depend on various factors, such as sample method, sampling frequency, support services, analytical methods and site preparation.

Existing reference methods:

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- **Method EN 13211:2001/AC: 2005⁵** - Air quality - Stationary source emissions - Manual method of determination of the concentration of total mercury

This is the reference method in Europe for the measurement of total mercury. The method is applicable for the concentration range of total mercury from 0.001 to 0.5 mg/m³ in exhaust gases. The procedure is a manual method of determining the concentration of total mercury using an acid aqueous solution of potassium permanganate or potassium dichromate for the sampling of vapor-phase mercury, as well as a filter paper for the collection of particle bound mercury. The sampling time should be 30 minutes up to 2 hours.

- **Method EN 14385:2004⁶** - Air quality - Stationary source emissions - Determination of the total emission of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl and V.

This is a manual reference method in Europe for the determination of the mass concentration of specific elements in exhaust gases from hazardous waste incinerators. The method is applicable for the concentration range of each of the specific elements of 0.005 mg/m³ to 0.5 mg/m³ (gas volumes are expressed at dry conditions, normalized to 273 K and oxygen content 101.3 kPa, and normalized to a dry oxygen content of 11 per cent on the volume/volume basis). Mercury may be determined as well, by using a side stream arrangement of the sampling train according to Method EN 13211.

- **US EPA Method 29⁷** - Metals Emissions from Stationary Sources.

In this method, particulate emissions are isokinetically collected in the probe and on a heated filter, and gaseous emissions are then collected in an aqueous acidic solution of hydrogen peroxide (analyzed for all metals including mercury) and an aqueous acidic solution of potassium permanganate (analyzed only for mercury). The recovered samples are digested, and appropriate fractions are analyzed for mercury by cold vapor atomic absorption spectroscopy (CVAAS) and for various other metals using inductively coupled argon plasma emission spectroscopy (ICP-MS). This method is suitable for measurement of mercury concentrations ranging from approximately 0.2 to 100 µg/m³. Since this method collects oxidized mercury in the hydrogen peroxide solution, it is appropriate for determination of mercury speciation.

⁵ European Committee for Standardization, “EN 13211:2001/AC:2005: Air quality - Stationary source emissions - Manual method of determination of the concentration of total mercury”, February 15, 2005.
http://standards.cen.eu/dyn/www/f?p=204:110:0:::FSP_PROJECT,FSP_ORG_ID:25042,6245&cs=19B884B499893080A731C45504F6F2FB2

⁶ European Committee for Standardization, “EN 14385:2004: Stationary source emissions - Determination of the total emission of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl and V”, February 25, 2004.
http://standards.cen.eu/dyn/www/f?p=204:110:0:::FSP_PROJECT,FSP_ORG_ID:13553,6245&cs=184B6D42F6F6A95AC76948B4F30C61F0F

⁷ US EPA, “Method 29 - Metals Emissions from Stationary Sources”.
<http://www.epa.gov/ttn/emc/methods/method29.html>

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- **Method ASTM D6784- 02 (Reapproved 2008)**⁸ - Standard test method for elemental, oxidized, particle-bound and total mercury in flue gas generated from coal-fired stationary sources (Ontario Hydro Method)

In this method a sample is withdrawn from the flue gas stream isokinetically through probe/filter system, maintained at 120 °C (~~250°F~~) or the flue gas temperature (whichever is greater), followed by a series of impingers in an ice bath. Particle-bound mercury is collected in the front half of the sampling train. Oxidized mercury is collected in impingers containing a chilled aqueous potassium chloride solution.

Elemental mercury is collected in subsequent impingers (one impinger containing chilled aqueous acidic solution of hydrogen peroxide and three impingers containing chilled aqueous solutions of potassium permanganate). Samples are recovered, digested, and then analyzed for mercury using cold-vapor atomic absorption (CVAAS) or fluorescence spectroscopy (CVAFS). The scope of the method applies to determination of elemental, oxidized, particle-bound and total mercury emissions from coal-fired stationary sources with concentrations ranging from approximately 0.2 to 100 µg/m³.

- **JIS K0222**⁹ (**Article 4(1)**) – Methods for determination of mercury in stack gas (wet absorption and cold vapor atomic absorption method)

This reference method from Japan measures total vapor phase mercury in the sample gas. In this method, vapor phase mercury is collected in an aqueous acidic solution of potassium permanganate (non-limiting isokinetic sampling). The dust containing the particle-bound mercury in the stack gas is isokinetically collected on the filter in accordance with reference method JIS Z8808:2013¹⁰ “Methods of measuring dust concentration in flue gas”. The recovered samples are digested, and appropriate fractions are analyzed for mercury by cold vapor atomic absorption spectrometry.

1.8.2.1.2 Sorbent Trap Sampling

Sorbent traps provide an average mercury concentration measurement over a sampling period, similar to the impinger methods. In addition, sorbent traps provide more stable mercury retention and a simpler sampling protocol which allows for unattended operation of the sampling over extended periods.

Sorbent traps are used to measure mercury emissions from point sources with low particulate matter concentrations.

Typically, duplicate samples are extracted in parallel using probes inserted into the gas stream. The probes contain sorbent traps which accumulate mercury from the gas. The sorbent material used is

⁸ American Society for Testing and Materials (ASTM), “*Standard Test Method for Elemental, Oxidized, Particle-Bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method)*”, 2008.
<http://www.astm.org/Standards/D6784.htm>

⁹ Japanese Standards Association, “*JIS K0222;1997; Methods for determination of mercury in stack gas*”, August 20, 1997.

¹⁰ Japanese Standards Association, “*JIS Z8808:2013: Methods of measuring dust concentration in flue gas*”, August 20, 2013.

mainly halogenated carbon. Standard sorbent traps are intended to measure gaseous mercury but due to the operation of the sampling method, particulates containing mercury can be drawn into the sorbent traps. This particulate is analyzed and the measured amount is added to the carbon bed amounts to form the total mercury value. However, the sorbent trap method does not collect particulates isokinetically so it is not an accurate method for measuring particulate bound mercury. Nevertheless, because the facilities concerned would be expected to run efficient particulate matter control devices, there should be minimal amounts of particle-bound mercury in the gas stream.

At the end of the sampling period, the sorbent traps are manually replaced, and the used traps are analyzed for mercury content. If results of the sorbent tube analyses agree within a specified range, then the two results are averaged for the final value. Analytical methods for mercury content include traditional wet chemical methods or small thermal desorption systems, which can provide immediate results. A distinct advantage of this method is that operating personnel can be quickly trained to conduct the sampling.

Sorbent traps provide good sensitivity and accuracy for mercury across a wide range of concentrations. However, it is necessary to know the expected minimum and maximum concentrations in the flue gas so that the correct sorbent trap and sampling time can be selected. For instance, if the concentration is too large or the sampling time too long, the mercury absorption capacity of the sorbent trap could be exceeded. This event would cause an under-reporting of the actual mercury concentration. On the other hand, a short sampling time of flue gas with very low concentrations of mercury can result in too little mercury captured in the traps, which would negatively impact trap analysis accuracy.

Existing reference methods:

- **US EPA Method 30B¹¹** – Determination of Total Vapor Phase Mercury Emissions from Coal-Fired Combustion Sources Using Carbon Sorbent Traps

This method is a procedure for measuring total vapor phase mercury emissions from coal-fired combustion sources using sorbent trap sampling and an extractive or thermal analytical technique. This method is only intended for use only under relatively low particulate conditions (e.g., sampling after all pollution control devices). Method 30B is a reference method for relative accuracy test audits (RATAs) of vapor phase mercury CEMS and sorbent trap monitoring systems installed at coal fired boilers and is also appropriate for mercury emissions testing at such boilers. In cases where significant amounts of particle bound mercury may be present, an isokinetic sampling method for mercury should be used.

- **JIS K0222 (Article 4(2))** – Methods for determination of mercury in stack gas (Gold amalgamation and cold vapor atomic absorption method)

¹¹ US EPA Method 30B, <http://www.epa.gov/ttn/emc/promgate/Meth30B.pdf>

This reference method from Japan uses a sorbent containing gold and measures vapor phase elemental mercury (Hg^0) concentration in stack gas. After the sample gas is washed by water and vapor phase oxidized mercury (Hg^{2+}) in the sample gas is removed, vapor phase mercury in the sample gas is trapped by the sorbent as gold amalgam. The sorbent is heated and vaporized mercury is measured by cold vapor atomic absorption spectrometry.

1.8.2.1.3 Instrumental Testing

Instrumental testing can be used for short term measurements of vapor phase mercury concentrations in gas. In this method, a gas sample is continuously extracted and conveyed to a mobile analyzer which measures elemental and oxidized mercury (Hg^0 and Hg^{2+}), either separately or simultaneously. The mobile analyzer uses a measurement technique similar to that used in continuous emissions monitoring (see Section 1.8.3.1).

- **US EPA Method 30A¹²** - Determination of Total Vapor Phase Mercury Emissions From Stationary Sources (Instrumental Analyzer Procedure)

Method 30A is a procedure for measuring total vapor phase mercury emissions from stationary sources using an instrumental analyzer. This method is particularly appropriate for performing emissions testing and for conducting relative accuracy test audits (RATAs) of mercury continuous emissions monitoring systems and sorbent trap monitoring systems at coal-fired combustion sources. Quality assurance and quality control requirements are included.

1.8.2.2 Long Term Measurements

1.8.2.2.1 Sorbent Trap Monitoring Systems

Sorbent trap monitoring systems are used to monitor mercury emissions from point sources with low particulate matter concentrations. These systems are permanently installed at a suitable sampling point to provide consistent, representative samples and operated on a continuous basis over a set time period, such as 24 hours up to 168 hours¹³, or even 14 days for samples of low mercury concentration. As with other extractive methods, the location of the sample point should be carefully chosen to provide representative and useful data.

¹² US EPA Method 30A, <http://www.epa.gov/ttnemc01/promgate/Meth30A.pdf>

¹³ US EPA Performance Specification 12B, p.13. <http://www.epa.gov/ttn/emc/perfspec.html>

Cost for installing a sorbent trap monitoring system is estimated at about US\$ 150,000. Using US data from 2010, annual operating costs for the sorbent trap monitoring system for coal-fired power plants are US\$ 26,000 to \$ 36,000 and annual labor costs for operation are US\$ 21,000 to \$ 36,000¹⁴.

Existing reference methods:

- **US EPA Method PS-12b¹⁵ (Performance Specification 12b)** – Specifications And Test Procedures For Monitoring Total Vapor Phase Mercury Emissions From Stationary Sources Using A Sorbent Trap Monitoring System

This method is used to establish performance benchmarks for, and to evaluate the acceptability of, sorbent trap monitoring systems used to monitor total vapor-phase mercury emissions in stationary source flue gas streams. This method is appropriate for long-term mercury measurements up to a sampling time of 14 days in order to monitor low levels of mercury emissions.

1.8.3 Continuous Measurements

1.8.3.1 Continuous Emissions Monitoring Systems (CEMS)

Continuous emissions monitoring systems (CEMS) are used to monitor gaseous emissions from point sources over long durations. This monitoring method does not measure particulate mercury. With this automated method, representative samples are taken continuously or at set time intervals using a probe inserted into the gas stream. CEMS are therefore useful for uninterrupted monitoring of mercury emissions, which can be variable over short time intervals due to changing mercury concentrations in raw materials, fuels or reagents. For example, CEMS would be useful during the co-incineration of waste material as fuel because of the rapidly changing mercury content in the waste. Due to regulatory monitoring and reporting requirements, there has been a growing use of this method in the US and the EU among certain sources over the last 10 years. While the cost of installation and operation may be high compared to other methods, CEMS provide the greatest data quantity, generating real-time information over various types of operations and process fluctuations.

The location of the sample point should be carefully chosen to provide representative and useful data. In a complex facility with multiple outlets potentially emitting mercury, the cost of installing CEMS on each outlet may be very high. Using US data from 2010, the general cost of installing a new mercury CEMS in a coal-fired power plant is estimated at about US\$ 500,000, with \$ 200,000 for the system, including startup and training, and \$ 200,000 to \$ 300,000 for site preparation¹⁶. At facilities

¹⁴ Amar, P, Senior, C, Afonso, R, and Staudt, J (2010). NESCAUM Report “*Technologies for Control and Measurement of Mercury Emissions from Coal-Fired Power Plants in the United States: A 2010 Status Report.*”, July, 2010, p.2-22. <http://www.nescaum.org/activities/major-reports>

¹⁵ US EPA Performance Specification 12B. <http://www.epa.gov/ttn/emc/perfspec.html>

¹⁶ Amar, P, Senior, C, Afonso, R, and Staudt, J (2010). NESCAUM Report “*Technologies for Control and Measurement of Mercury Emissions from Coal-Fired Power Plants in the United States: A 2010 Status Report.*”, July 2010, p.2-7. <http://www.nescaum.org/activities/major-reports>

with multiple stacks and where CEMS would be technically and economically viable, as well as informative, the CEMS should be located on the outlet emitting the bulk or largest mass of mercury emissions at the facility. While the CEMS in such a case would not provide information from all gas outlets, the resulting data may provide a useful real-time indication of process performance trends and mercury control efficiency.

For mercury CEMS, the extracted sample is filtered to remove particulate matter and the resulting vaporous sample is routed to a mercury analyzer. In general, CEMS analyzers should be kept under steady temperature control to avoid instrument errors and drift in the results. Note that these analyzers detect mercury only in the vapor phase (Hg^0 and Hg^{2+}), and any particle-bound mercury in the sample would be trapped by the filter. However, as the facilities concerned should be operating with efficient particulate matter control devices, there should not be significant concentrations of particulate matter in the final stack emissions, and consequently, little particle-bound mercury in the final gas stream. CEMS can be used for sampling of dry flue gas or water saturated flue gas, such as after a wet scrubber. However, CEMS monitoring water saturated gas require a special fixed filter probe to avoid blockage from condensation of water. It should be noted that some CEMs could also experience interference from other substances in the gas stream.

Mercury CEMS directly measure elemental mercury (Hg^0) gas using either cold vapor atomic adsorption (CVAA) or cold vapor atomic fluorescence (CVAF). Therefore, gaseous oxidized mercury (Hg^{2+}) in the sample gas must be reduced to Hg^0 before it can be measured. This process is referred to as sample gas conversion. The reduction occurs when passing the sample gas either through a high temperature, thermal reduction cell or through an impinger containing a reducing chemical, such as tin chloride.

CEMS can be used to provide mercury emissions data continuously, or over set time periods, such as ½ hourly, or hourly. Notably, data from the CEMS can be relayed on a continuous basis to the process control system through a feedback loop to indicate real-time operating trends and assist in maintaining peak operating efficiency.

The CEMS should be correctly calibrated to ensure data accuracy. This is done by comparing readings with samples taken simultaneously from the same sampling point that are then analyzed by relevant manual source testing methods. Some calibration gas standards may be available and, if so, may be used to calibrate the instrument directly. Regular maintenance and quality control procedures should be conducted, as per the relevant authority or manufacturer specifications, to minimize data drift.

Existing reference methods:

- **US EPA Method PS-12a¹⁷ (Performance Specification 12a)** – Specifications And Test Procedures For Total Vapor Phase Mercury Continuous Emission Monitoring Systems In Stationary Sources

This method is used for evaluating the acceptability of total vapor phase mercury CEMS installed at stationary sources at the time of, or soon after, installation and whenever specified as per regulatory requirements. The CEMS measures total mercury concentration in $\mu\text{g}/\text{m}^3$ of vapor phase mercury,

¹⁷ US EPA Performance Specification 12A. <http://www.epa.gov/ttn/emc/perfspec.html>

regardless of speciation, and records the results at standard conditions on a wet or dry basis. This method does not measure mercury bound to particulate matter.

- **EN 14181:2014¹⁸** – Stationary source emissions - Quality assurance of automated measuring systems

This European standard is designed to be used after the CEMS has passed a suitability test (QAL1) and describes the quality assurance procedures needed to ensure that a CEMS is capable of meeting the uncertainty requirements on measured values. The uncertainty requirements are given by legislation such as EU Directives or national legislation. Three quality levels are defined to achieve this objective: suitability test (QAL 1), calibration (QAL 2) and ongoing quality assurance during operation (QAL3). QAL1 is a procedure defined in EN 15267¹⁹ to demonstrate that an automated measuring system is suitable for the intended purpose before installation on site. QAL2, QAL3 and also a procedure for annual surveillance test (AST) are included in EN 14181

- **EN 14884:2005²⁰** – Air quality - Stationary source emissions - Determination of total mercury: Automated measuring systems

This European standard describes the quality assurance procedures related to CEMS for the determination of total mercury in flue gas, in order to meet the uncertainty requirements on measured values given by regulations, national legislation or other requirements. The standard is in line with the general document on quality assurance on CEMS described in EN 14181.

- **Method EN 13211:2001/AC: 2005²¹** - Air quality - Stationary source emissions - Manual method of determination of the concentration of total mercury

¹⁸ European Committee for Standardization, “*EN 14181:2014: Stationary source emissions - Quality assurance of automated measuring systems*”, October 11, 2014.

http://standards.cen.eu/dyn/www/?p=204:110:0::: FSP_PROJECT:33416&cs=1D563C09742AECB59945D4E1D645A5DCB

¹⁹ EN 15267-1 Air quality - Certification of automated measuring systems - Part 1: General principles, EN 15267-2: Air quality – Certification of automate measuring systems – Part 2: Initial assessment of the AMS manufacturer’s quality management system and post certification surveillance for the manufacturing process, EN 15267-3: Air quality - Certification of automated measuring systems - Part 3: Performance criteria and test procedures for automated measuring systems for monitoring emissions from stationary source

²⁰ European Committee for Standardization, “*EN 14884:2005: Air quality - Stationary source emissions - Determination of total mercury: automated measuring systems*”, November 28, 2005.

http://standards.cen.eu/dyn/www/?p=204:110:0::: FSP_PROJECT:22225&cs=1D527AD08718E6354287EA554A53ADF26

²¹ European Committee for Standardization, “*EN 13211:2001/AC:2005: Air quality - Stationary source emissions - Manual method of determination of the concentration of total mercury*”, February 15, 2005.

http://standards.cen.eu/dyn/www/?p=204:110:0::: FSP_PROJECT, FSP_ORG_ID:25042,6245&cs=19B884B499893080A731C45504F6F2FB2

This European standard specifies a manual reference method for the determination of the mass concentration of mercury in exhaust gases from ducts and stacks. This is the reference method for comparative measurements for calibrating mercury CEMS. The method is applicable for the concentration range of total mercury from 0.001 to 0.5 mg/m³ in exhaust gases. The procedure is a manual method of determining the concentration of total mercury using an acid aqueous solution of potassium permanganate or potassium dichromate for the sampling of vapor-phase mercury, as well as a filter paper for the collection of particle bound mercury. The sampling time should be 30 minutes up to 2 hours.

- **JIS K0222 (Article 4(3))** – Methods for determination of mercury in stack gas (Continuous monitoring method)

This reference method from Japan directly measures total vapor phase mercury from stationary sources on a continuous basis using cold vapor atomic absorption spectrometry. In this method, vapor phase oxidized mercury (Hg²⁺) in the sample gas is reduced to elemental mercury (Hg⁰) by passing the sample gas through tin chloride.

1.8.4 Indirect Measurement Methods

The indirect measurement methods described below are helpful in estimating mercury emissions from a process or facility. However, they are not usually considered as reliable and accurate techniques for mercury emissions monitoring. In contrast to direct measurement methods, indirect measurement methods do not provide information on mercury concentrations in stack gases or total emission rates. When conducted according to proper test procedures, the direct measurement methods previously listed would provide more representative mercury emissions data than indirect measurement methods. Nevertheless, these non-measurement engineering methods are useful as investigative and screening tools to monitor general process performance and in estimating mercury abatement efficiency. For reporting purposes, these indirect measurement methods may be used to provide a general estimate of facility-level emissions if direct measurement methods are not available or applicable.

1.8.4.1 Mass balance

Mass balance is conducted by applying the law of mass conservation to a system (e.g. facility, process or piece of equipment). In such a system, any mercury entering in the feedstock, additives, or fuel must exit via the products, by-products, waste or emissions and releases. Mercury emissions and releases are therefore determined from the differences in input, output, accumulation and depletion. The general equation for a mass balance is²²:

²² Environment Canada, “*Guide for Reporting to the National Pollutant Release Inventory (NPRI) 2012 and 2013, Canadian Environmental Protection Act, 1999 (CEPA 1999)*”, 2013, p. 18. . <https://www.ec.gc.ca/inrp-npri/default.asp?lang=En&n=28C24172-1>

$$M_{in} = M_{out} + M_{accumulated/depleted}$$

Where:

M_{in} = mass of mercury entering the facility in the feedstock, fuel, additives, etc.

M_{out} = mass of mercury leaving the facility in finished products, byproducts, wastes and emissions and releases

$$(M_{out} = M_{product} + M_{by-product} + M_{waste} + M_{emissions} + M_{releases})$$

$M_{accumulated/depleted}$ = mass of mercury accumulated or depleted within the facility

To calculate mercury emissions in a system using a mass balance, the mercury concentrations and mass flowrates of all other streams (e.g. products, by-products, effluents, sludges) should be tracked and recorded over a specified period. Mercury mass data would be calculated by multiplying the mercury concentration by the stream mass flowrate and the time period (e.g. one year). An advantage of using the mass balance method is that mercury emissions can be estimated for all point and diffuse sources (including fugitive emissions).

In a system with multiple emission sources and limited data from outlet stacks or ducts, the mass balance approach may provide more useful and representative information on mercury flows over a long duration, such as a year. In some cases, results from a complete annual mass balance may provide more representative emissions data than an annual stack test. However, obtaining accurate, representative measurements of mercury content in variable fuels or feed materials may be challenging. Additionally, in cases where internal mercury loads are recycled in the process (e.g. in stockpiles, intermediate products, sludges), care should be taken to account for mercury in these streams. In complex processes with multiple input and output flows, or where data is estimated, it may be challenging to reach closure on a mass balance.

1.8.4.2 Predictive emissions monitoring systems (PEMS)

Predictive emissions monitoring systems (PEMS), also referred to as parametric monitoring, operate by developing correlations between process operating parameters and mercury emissions rates using continuous monitoring of surrogate parameters, emission factors and source testing. No ongoing mercury sampling is actually conducted in this method. In modern facilities, parameters such as fuel usage, furnace temperature, gas pressure and flowrate are typically monitored on a continuous basis using process control systems to ensure operational efficiency.

In certain types of processes where there is little variability in the mercury content of the feedstock, fuel and other input streams, PEMS may be a useful method to provide an indication of mercury emission trends.

However, PEMS may not be a reliable method of mercury emissions monitoring in applications where mercury content in fuels or feedstocks can vary significantly over short periods. For example, in waste incineration and cement facilities using waste fuels, the mercury content entering the system or facility is generally unpredictable. In coal-fired power plants, mercury emissions can vary due to changes in mercury content of the coal. Similarly, in the non-ferrous metals sector, mercury in furnace feeds can change rapidly depending on the concentrates being processed. In addition, mercury emissions can

vary in many processes due to temperature fluctuations and changes in mercury speciation. As a result, the establishment of correlations between surrogate parameters and mercury emissions may not produce representative results. If PEMS are considered, thorough analysis should first be done to determine the uncertainty of the method on a case by case basis and they should be regularly compared to a reference test method. When a sufficient, comprehensive pool of reference data can be collected to provide a substantial base to develop the PEMS algorithm, the data quality provided by the PEMS would be expected to improve.

1.8.4.3 Emission factors

While the use of emission factors is not a monitoring method *per se*, this engineering technique can be used to provide a useful general estimate of mercury emissions from a system or facility.

Emission factors are used to provide an estimate of the quantity of emissions released from a source based on typical levels of emissions from that activity. For mercury, emission factors could be expressed as the mass of mercury emitted divided by: the mass or volume of input material consumed; or the mass or volume of output material generated.

Site-specific emission factors, developed by facilities based on actual emissions testing data and source activity information, are expected to provide more accurate estimates than the use of general, published emission factors. Site-specific emission factors would need to be established by testing during periods of normal operation to better represent the average mercury emissions rate from the particular process or facility. If site specific measurement data becomes available, calculations based on those measured values would be preferred to the use of general published factors.

Where site-specific emission factors are unavailable, published emission factors may be used to provide a rough emissions estimate. Published emission factors may be available for the overall process or for the particular mercury control device. However, it should be noted that such general emission factors provide highly uncertain emission estimates.

However, in processes where there may be variability in the mercury content of fuels and /or feedstocks, emission factors may not provide reliable estimates of mercury emissions. For example, in waste incineration or cement manufacturing using waste fuels, mercury content in the fuel can vary significantly within short periods.

The general equation for estimating mercury emissions using an emissions factor is:

$$E_{\text{Hg}} = \text{BQ} \times \text{CEF}_{\text{Hg}} \text{ or}$$

$$E_{\text{Hg}} = \text{BQ} \times \text{EF}_{\text{Hg}} \times (100 - \text{CE}_{\text{Hg}})/100$$

Where:

E_{Hg} = Emission of mercury (kg or other unit of mass)

BQ = Activity rate or base quantity (base quantity unit)

CEF_{Hg} = Controlled emission factors of mercury (kg/BQ) [dependent on any emission control devices installed]

EF_{Hg} = Uncontrolled emission factors of mercury (kg/BQ)

CE_{Hg} = Overall emission control efficiency of mercury (per cent)

1.8.4.4 Engineering estimates

General estimates of mercury emissions can also be obtained using engineering principles, knowledge of the relevant chemical and physical processes, application of related chemical and physical laws, and familiarity with site-specific characteristics.

For example, annual mercury emissions from fuel use can be estimated as follows:

$$E_{\text{Hg}} = Q_{\text{F}} \times \% \text{ Hg} \times T$$

Where:

E_{Hg} = Annual emissions of mercury (kg/y)

Q_{F} = Rate of fuel use (kg/h)

% Hg = per cent of mercury in fuel, by weight

T = operating time (h/y)

Engineering estimates should only be considered as rapid general approximations with a high level of uncertainty. Results from engineering estimates should be compared periodically against data obtained from direct measurement methods to increase accuracy. Where site specific information becomes available, those data are expected to provide more useful information and would be preferred in terms of understanding actual source emission rates. Engineering estimates are the last resort where no emissions data or emission factors are available.

1.8.5 Emissions reporting

Emissions reporting is an essential part of the emissions monitoring cycle at a facility level.

Where compliance with a legal or regulatory measure must be demonstrated, the operator is generally responsible for reporting monitoring results to the competent authority. In addition, facility level data is an essential component of national emissions inventories that are compiled using a bottom-up approach. Even where emissions reporting is not explicitly required, it is considered a best practice to share data voluntarily with authorities and the public concerned.

Reporting of emissions monitoring involves summarizing and presenting the monitoring results and related information, such as quality assurance and quality control methods, in an effective way, according to the needs of the intended audience. The report should be clear, transparent and accurate. Results should be presented in a useful, informative format.

Mercury emissions should be expressed in one or more of the following ways: mercury concentration in the outlet gas; mass of mercury emitted per amount of product produced (emission factor); mass of mercury emissions over a given time period (e.g. per day or per year).

Quality considerations regarding sampling, analysis and the results should be discussed in the report. In addition, the measurement results should be provided in a format that would enable the correlation of mercury emissions with process operating parameters.

Clarity should be provided on the method used (e.g. standards used for sampling and analysis) and conditions encountered during data collection, such as: process conditions; production rate during sampling; occurrences or malfunctions during sampling in the production process or the abatement systems; and variations in the input material.