Guidance on best available techniques and best environmental practices

Monitoring

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Monitoring

Mercury emissions monitoring

Introduction

Emissions monitoring is a key component in enabling a party to evaluate the performance of the measures that it has applied. This chapter therefore describes general emissions monitoring techniques that a party may consider. In addition, emissions monitoring techniques specific to the point source categories listed in Annex D are addressed in the relevant chapters of this guidance. Article 8 does not include specific obligations on emissions monitoring. In its paragraph 6, however, the Article does require that the measures applied by a party achieve reasonable progress in reducing emissions over time. In addition, paragraph 11 requires that each party report (pursuant to Article 21) on the effectiveness of the measures that it has taken in controlling and, where feasible, reducing emissions of mercury and mercury compounds from the point sources falling within the source categories listed in Annex D.

The preparation of the guidance has drawn on relevant experience at national and regional levels. Some of this experience has been referenced for information. The referencing of such information in no way prejudices the autonomy of the Conference of the Parties, or a Party's autonomy in accordance with Article 8. Any references to costs are based on information at the time of preparation of the guidance document. It is noted that costs are expected to change over time.

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 or accepted methods. Representative, reliable and timely data obtained from mercury emissions monitoring are 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 emission 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.

1.1   General steps in conducting mercury emissions monitoring

The first step in conducting mercury emissions monitoring is to establish a performance baseline, either by taking direct measurements of the mercury concentrations in the gas streams or using indirect measurements to estimate facility emissions. Subsequently, more measurements are taken at specific time intervals (e.g., daily, weekly, monthly) to characterize the mercury concentration in the gas or the mercury emissions at that point in time. Monitoring is then conducted by compiling and analysing the emissions measurement data to observe trends in 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.

1.2   Considerations in selecting a measurement or monitoring approach

The selection of a measurement or monitoring approach should begin with consideration of the intended outcomes. Periodic short-term measurements, conducted over a brief time period, such as one hour or one day, may be conducted to provide quick feedback for process optimization. Long-term measurements, such as over several months or a year, using permanently installed equipment on a semi-continuous basis, may be desirable for emission inventory reporting. Continuous emission monitoring which is currently being implemented in some countries may be used to control the process if mercury emissions are highly variable, for example owing to rapidly changing mercury contents in the feed materials.
In addition, site-specific characteristics 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 as particle-bound mercury, gaseous elemental mercury (Hg^0) or in the ionized gaseous forms, Hg(I) or Hg(II) or in combinations of these forms. 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 is available in the European guideline EN 15259:2007[1] "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 to 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, measurement location, the facility operating conditions, site-specific process variations, and requirements to show compliance under the applicable regulatory process. Samples should be taken at conditions representative of normal facility operations. If the

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[1] 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"*, 18 August 2007.
http://standards.cen.eu/dyn/www/f?p=204:110:0::::FSP_PROJECT:22623&cs=106F3444821A456A9 0F21590F3BFF8582.

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. In, addition 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 – for example, over half an hour, 12 hours or 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, because of 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 representative conditions, mercury concentrations in 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 throughout the sampling campaign. Specific parameters, such as the volumetric gas flow-rate, gas temperature, water vapour content of the gas, static pressure of the gas duct, and atmospheric pressure,[2] 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:

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

Where:

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

C_{Hg} = Mercury concentration in the gas stream (kg/m^3)

F = volumetric flow-rate of the gas stream (m^3/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 practised 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.

1.3   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 conducive to the more precise measurement of a facility's actual mercury emissions.

1.3.1   Short-term measurements

1.3.1.1   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. This method is not suitable, however, for gases with heavy particulate loading.

The 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

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[2] EU IPPCB, NFM BREF Draft, February 2013, p. 67.

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 and sample nozzle are 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 United States, 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. It is therefore essential to avoid any loss of the sample as this will cause the test results to be misleadingly low.

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 start-ups, 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.

Even under normal, steady-state conditions, however, there could be significant variability in the mercury volumes being emitted when the mercury content in fuels or feedstocks fluctuates 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 may change rapidly depending on the concentrates being processed. In such cases, results from intermittent impinger sampling may not provide representative data when extrapolated over a long period of time (e.g., annual averages). Thus, increasing the sampling frequency (e.g., to three measurements per year over many years) can provide a better understanding of actual source emissions over time.

To obtain maximum value for investment, mercury emissions source testing should be conducted during broader sampling campaigns for air pollutants such as particulate matter, NOx, SO_2, and VOC. The addition of mercury testing when conducting these broader air pollutant sampling campaigns may increase the 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:

- *Method EN 13211:2001/AC: 2005 – Air quality – Stationary source emissions – Manual method of determination of the concentration of total mercury*[3]

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/m^3 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 vapour-phase mercury, together with a filter paper for the collection of particle-bound mercury. The sampling time should be between 30 minutes and two hours.

US EPA Method 29 – Metals Emissions from Stationary Sources [4]

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 (analysed for all metals including mercury) and an aqueous acidic solution of potassium permanganate (analysed only for mercury). The recovered samples are digested, and appropriate fractions are analysed for mercury by cold vapour atomic absorption spectroscopy (also referred to as CVAAS) and for various other metals using inductively coupled plasma-mass spectroscopy (also referred to as ICP-MS). This method is suitable for measurement of mercury concentrations ranging from approximately 0.2 to 100 μg/m^3. Since this method collects oxidized mercury in the hydrogen peroxide solution, it is appropriate for the determination of mercury speciation.

US EPA SW-846 Method 0060 – Determination of Metals in Stack Emissions[5]

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

[4] US EPA, *"Method 29 – Metals Emissions from Stationary Sources"*. http://www.epa.gov/ttn/emc/methods/method29.html.

[5] US EPA, *"Method 0060 – Determination of Metals from Stack Emissions"*. http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/0060.pdf.

This method is used to determine the concentration of metals in stack emissions from hazardous waste incinerators and similar combustion processes. In this method, a sample is withdrawn from the flue gas stream isokinetically through a probe and filter system. Particulate emissions are collected in the probe and on a heated filter and gaseous emissions are collected in a series of chilled impingers. Two impingers are empty, two impingers contain an aqueous solution of dilute nitric acid combined with dilute hydrogen peroxide, two other impingers contain acidic potassium permanganate solution, and the last impinger contains a desiccant.

The recovered samples are digested, and appropriate fractions are analysed for mercury by CVAAS. Remaining fractions may be analysed for various other metals by inductively coupled plasma-atomic emission spectrometry (ICP-AES), flame atomic absorption spectrometry (FLAA), or ICP-MS.

Method ASTM D6784- 02 (Reapproved 2008) – Standard Test Method for Elemental, Oxidized, Particle-Bound and Total Mercury in Flue Gas Generated from Coal-fired Stationary Sources (Ontario Hydro Method)[6]

In this method a sample is withdrawn from the flue gas stream isokinetically through a probe and filter system, maintained at 120 °C 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 analysed for mercury using CVAAS or cold vapour atomic 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 $\mu g/m^3$.

- *JIS K0222 (Article 4(1) – Methods for determination of mercury in stack gas (wet absorption and cold vapour atomic absorption method)*[7]

This reference method from Japan measures total vapour phase mercury in the sample gas. In this method, vapour 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 Z8808:2013[8] "Methods of measuring dust concentration in flue gas". The recovered samples are digested, and appropriate fractions are analysed for mercury by cold vapour atomic absorption spectrometry.

1.3.1.2   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. In general, samples are taken at a location following a particulate control device.

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 mainly halogenated carbon. Standard sorbent traps are intended to measure gaseous mercury but, because of the operation of the sampling method, particulates containing mercury can be drawn into the sorbent traps. This particulate is analysed 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 particle-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 analysed 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. Another advantage is that the results from thermal

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[6] 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.

[7] Japanese Standards Association, *"JIS K0222;1997; Methods for determination of mercury in stack gas"*, 20 August 1997.

[8] Japanese Standards Association, *"JIS Z8808:2013: Methods of measuring dust concentration in flue gas"*, 20 August 2013.

desorption analysis may be known while the tester is still in the field. This is useful for engineering tests with varying conditions, or for mercury monitor relative accuracy test audits.

Sorbent traps provide good sensitivity and accuracy for mercury across a wide range of concentrations. It is necessary, however, 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 affect trap analysis accuracy.

Existing reference methods:

- *US EPA Method 30B – Determination of Total Vapor Phase Mercury Emissions from Coal-Fired Combustion Sources Using Carbon Sorbent Traps*[9]

This method is a procedure for measuring total vapour phase mercury emissions from coal-fired combustion sources using sorbent trap sampling and an extractive or thermal analytical technique. This method is 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 vapour 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 vapour atomic absorption method)*[10]

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

1.3.1.3   Instrumental testing

Instrumental testing can be used for short-term measurements of vapour phase mercury concentrations in gas. In this method, a gas sample is continuously extracted and conveyed to a mobile analyser which measures elemental and oxidized mercury (Hg^0 and Hg^{2+}), either separately or simultaneously. The mobile analyser uses a measurement technique similar to that used in continuous emissions monitoring (see section 2.4 below).

- *US EPA Method 30A – Determination of Total Vapour Phase Mercury Emissions from Stationary Sources (Instrumental Analyser Procedure)*[11]

Method 30A is a procedure for measuring total vapour phase mercury emissions from stationary sources using an instrumental analyser. This method is particularly appropriate for performing emissions testing and for conducting 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.

1.3.2   Long-term measurements

1.3.2.1   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, using sorbent traps to provide consistent, representative samples. In contrast to the use of sorbent traps for short-term measurements over brief periods, sorbent trap monitoring systems are operated on a continuous basis over set time periods, which may range between 24 and 168 hours,[12] 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.

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[9] US EPA Method 30B, http://www.epa.gov/ttn/emc/promgate/Meth30B.pdf.

[10] Japanese Standards Association, *"JIS K0222;1997; Methods for determination of mercury in stack gas"*, 20 August 1997.

[11] US EPA Method 30A, http://www.epa.gov/ttnemc01/promgate/Meth30A.pdf.

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

The cost of installing a sorbent trap monitoring system is estimated at about $150,000. Using United States data from 2010, annual operating costs for the sorbent trap monitoring system for coal-fired power plants range between $26,000 and $36,000 and annual labour costs for operation between $21,000 and $36,000.[13]

Existing reference methods:

- *US EPA PS-12b (Performance Specification 12b) – Specifications and Test Procedures for Monitoring Total Vapour Phase Mercury Emissions from Stationary Sources Using a Sorbent Trap Monitoring System*[14]

This performance specification is used to establish performance benchmarks for, and to evaluate the acceptability of, sorbent trap monitoring systems used to monitor total vapour-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.

1.4   Continuous measurements

1.4.1   Continuous emission monitoring systems (CEMS)

Continuous emission 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 because of 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. Regulatory monitoring and reporting requirements have led to the growing use of this method in the United States and the European Union 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 United States data from 2010, the general cost of installing a new mercury CEMS in a coal-fired power plant is estimated at about $500,000, of which $200,000 is for the system, including start-up, training and calibration systems, and between $200,000 and $300,000 for site preparation[15] in newer systems, where daily calibrations are not required costs are much lower. Recent information from a provider of mercury measurement equipment in the European Union indicates a cost of approximately €150,000 ($170,000), which includes the system itself, necessary infrastructure and installation, servicing, calibration and validation.[16]

At facilities with multiple stacks and where CEMS would be technically and economically viable, and also informative, the CEMS should be located on the outlet emitting the bulk or largest mass of mercury emissions at the facility. While in such cases the CEMS 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 analyser. In general, CEMS analysers should be kept under steady temperature control to avoid instrument errors and drift in the results. It should be noted that these analysers detect mercury only in the vapour phase (Hg^0 and Hg^{2+}), and any particle-bound mercury in the sample would be trapped by the filter. As, however, 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. CEMS used to monitor water-saturated gas require a special fixed filter probe, however, 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.

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[13] Amar, P., C. Senior, R. Afonso and J. Staudt (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, pp. 2–22. http://www.nescaum.org/activities/major-reports.

[14] US EPA Performance Specification 12B. http://www.epa.gov/ttn/emc/perfspec.html.

[15] Amar, P., C. Senior, R. Afonso and J. Staudt (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, pp. 2–7. http://www.nescaum.org/activities/major-reports.

[16] Gerter, F., and A.G. Sick, Germany, personal communication. September 2015.

Mercury CEMS directly measure elemental mercury (Hg^0) gas using either cold vapour atomic adsorption (CVAA) or cold vapour atomic fluorescence (CVAF). Accordingly, 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 half-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 for process control and assist in maintaining peak operating efficiency.

The CEMS must be correctly calibrated to ensure data accuracy. This is achieved by comparing readings with samples taken simultaneously from the same sampling point that are then analysed 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 PS-12a (Performance Specification 12a) – Specifications and Test Procedures for Total Vapour Phase Mercury Continuous Emission Monitoring Systems in Stationary Sources*[17]

This performance specification is used for evaluating the acceptability of total vapour 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 $\mu g/m^3$ of vapour phase mercury, 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 14884:2005 – Air quality – Stationary source emissions – Determination of total mercury: Automated measuring systems*[18]

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 specified by regulations, national legislation or other requirements. The standard is in line with the general standard on quality assurance on CEMS (EN 14181:2014 – Stationary source emissions – Quality assurance of automated measuring systems[19]).

Standard EN 14181:2014 is designed to be used after the CEMS has passed a suitability test (QAL1, as defined in EN 15267[20]) demonstrating that it is suitable for the intended purpose before installation on site. EN14181:2014 describes the quality assurance procedures needed to ensure that a CEMS is capable of meeting the uncertainty requirements on measured values, which are specified in European Union or national legislation.

- *Method EN 13211:2001/AC: 2005 – Air quality – Stationary source emissions – Manual method of determination of the concentration of total mercury*[21]

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. This method has been previously listed in section 1.1.2.1.1 on impinger sampling.

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

[18] European Committee for Standardization, *"EN 14884:2005: Air quality – Stationary source emissions – Determination of total mercury: automated measuring systems"*, 28 November 2005. http://standards.cen.eu/dyn/www/f?p=204:110:0::::FSP_PROJECT:22225&cs=1D527AD08718E6354287EA554A53ADF26.

[19] European Committee for Standardization, *"EN 14181:2014: Stationary source emissions - Quality assurance of automated measuring systems"*, 11 October 2014. http://standards.cen.eu/dyn/www/f?p=204:110:0::::FSP_PROJECT:33416&cs=1D563C09742AECB59945D4E1D645A5DCB.

[20] 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 sources.

[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/f?p=204:110:0::::FSP_PROJECT,FSP_ORG_ID:25042,6245&cs=19B884B499893080A731C45504F6F2FB2.

• JIS K0222 (Article 4(3) – Methods for determination of mercury in stack gas (Continuous monitoring method)[22]

This reference method from Japan directly measures total vapour phase mercury from stationary sources on a continuous basis using cold vapour atomic absorption spectrometry. In this method, vapour phase oxidized mercury (Hg^{2+}) in the sample gas is reduced to elemental mercury (Hg^0) by passing the sample gas through tin chloride.

1.5   Indirect measurement methods

The indirect measurement methods described below are helpful in estimating mercury emissions from a process or facility. In general, most indirect measurement methods are not usually considered to be as reliable and accurate as direct measurement techniques for mercury emissions monitoring. In contrast to direct measurement methods, indirect measurement methods provide no 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 most indirect measurement methods. Nevertheless, these non-measurement engineering methods are useful as investigative and screening tools for the monitoring of general process performance and estimation of 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.

1.5.1   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 the process 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 is:[23]

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

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 flow-rates 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 flow-rate and the time period (e.g., one year). An advantage of using the mass balance method is that mercury emissions can be estimated for both point and diffuse sources (including fugitive emissions), if a party wishes to estimate emissions from non-point sources as well.

In a system with multiple emission sources and limited data from outlet stacks or ducts, the mass balance approach may provide useful and representative information on mercury flows over a long period, such as a year. In processes where the emissions could vary greatly over time, results from a complete annual mass balance may provide more representative emissions data than punctual direct measurements, such as an annual stack test. For example, cement facilities in the European Union have come up against uncertain readings using direct measurement methods due to high uncertainty in emissions volume measurement at the stack. For these facilities, use of the mass balance method has reduced the relative uncertainty in the estimation of mercury emissions, by comparison with direct measurement methods.

Accurate, representative measurements of mercury content in variable fuels or feed materials may, however, be difficult to achieve. In addition, 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

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[22] Japanese Standards Association, *"JIS K0222;1997; Methods for determination of mercury in stack gas"*, 20 August 1997.

[23] 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.

with multiple input and output flows, or where data are estimated, it may be difficult to come up with definitive figures for the mass balance.

1.5.2   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 the continuous monitoring of surrogate parameters, emission factors and source testing. This method can be useful in providing an indication of mercury control efficiency on a real-time basis. No ongoing mercury sampling is actually conducted in this method. In modern facilities, parameters such as fuel usage, furnace temperature, gas pressure and flow-rate are typically monitored on a continuous basis using process control systems to ensure operational efficiency. While these types of indicators may be a useful starting point, the selection of relevant parameters and their corresponding correlations to mercury emission rates would likely be unique to the process or facility.

In certain types of processes where there is little variability in the mercury content of the feedstock, fuel and other input streams, PEMS may offer a useful means of providing an indication of mercury emission trends. For example, some facilities in the industrial gold sector in the United States monitor the operating efficiency of their mercury chloride scrubbers, tracking the scrubber inlet solution pressure, inlet gas temperature and mercury(II) chloride concentration in the solution exiting the scrubber.

PEMS may not, however, 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 in response to changes in the 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 because of 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 carried out 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.

1.5.3   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 on the basis of actual emissions testing data and source activity information, are expected to provide more accurate estimates than general, published emission factors. Site-specific emission factors would need to be established by testing during periods of normal operation, with a view to providing a better representation of the average mercury emissions rate from the particular process or facility. If site-specific measurement data become 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. It should be noted, however, that such general emission factors provide highly uncertain emission estimates.

That said, in processes where there may be variability in the mercury content of fuels 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:

$E_{Hg} = BQ \times CEF_{Hg}$ or

$E_{Hg} = BQ \times EF_{Hg} \times (100 - CE_{Hg})/100$

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)

1.5.4 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:

$E_{Hg} = Q_F \times \% \, Hg \times T$

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. In order to improve accuracy, results from engineering estimates should be compared periodically with data obtained from direct measurement methods. 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.

1.5.5 Emissions reporting

Emissions reporting is an essential part of the emissions monitoring cycle at the 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 constitute 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); and 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.