

Monitoring Mercury Emissions

WHITE PAPER

Background

Mercury is recognized as a chemical of global concern (UNEP, 2006) due to its long-range transport in the atmosphere, persistence in the environment, toxicity, ability to bio-accumulate in ecosystems and its harmful effects on human health.

Some types of bacteria and fungi can change mercury into its most toxic form, methyl mercury, which accumulates in fish, but especially in predatory species such as shark, swordfish, and tuna.

Mercury comes from a range of natural sources such as volcanoes, soils, undersea vents, mercury-rich geological zones and forest fires, as well as from fresh water lakes, rivers and oceans.

However, human activity has increased the amount of mercury in the environment in several ways, including through a variety of combustion and industrial processes such as coal-fired power generation, metal mining and smelting, cement production and waste incineration. Products such as batteries, thermostats, barometers and dental fillings may also contain mercury.

Hg



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Global efforts to reduce mercury emissions

In 2011 the United States Environmental Protection Agency (US EPA) issued the Mercury and Air Toxics Standards (MATS) which were designed to reduce emissions by relying on pollution controls already in use at many coal-fired power plants.

In 2013 a UNEP global treaty on mercury, the Minamata Convention, was signed by almost 140 countries. The objective of the Minamata Convention was to protect human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds. The treaty contains provisions including controls and reductions across a range of products, processes and industries where mercury is used, released or emitted.

In Europe, members of the European Union (EU) approved new air pollution limits for large combustion plants in April 2017 that will require utilities to invest in new pollution abatement technology. This strengthens the requirements of the Industrial Emissions Directive (IED) (**DIRECTIVE 2010/75/EU**) for both abatement and monitoring requirements, both of which are addressed in the "**Best Available Techniques Conclusions for Large Combustion Plants**" (**BREF LCP**). The BREF LCP includes new emission limits values (ELVs) for sulphur dioxide, nitrogen oxides, mercury, and particulate matter, and requires large thermal power plants in Europe to comply with those limits by 2021.

The emissions of heavy metals are generally reduced by the application of high performance dust removal technologies such as electrostatic precipitators or fabric filters. However, mercury is also present in the vapor phase, and with a high vapor pressure at the typical control device operating temperatures, its collection by particulate matter control devices is highly variable.



Best available techniques & current emission limits

In July 2017, the Commission Implementing Decision (EU) 2017/1442 established best available techniques (BAT) conclusions, under **Directive 2010/75/EU** for large combustion plants (with a total rated thermal input of 50 MW or more). This included new requirements for mercury abatement and monitoring.

BAT-associated emission levels (BAT-AELs) for mercury emissions to air are specified for coal and lignite burning power plants. For example, a new coal-fired power plant with a thermal input over 300MW has a BAT-AEL of <1-2 µg/Nm³ mercury (yearly average), and an existing lignite-fired power station with a thermal input under 300MW has a BAT-AEL of <1-10 µg/Nm³ mercury. Permits will have to be updated to take these into account within four years.

BAT-AELs are set as a range and based on evidence from plants that are in operation all over the world. The concept of BAT covers not only the environmental performance of the technique but also that it is currently used and economically viable.

National competent authorities shall set ELVs in permits for polluting substances listed in **Annex II of Directive 2010/75/EU**, and for other polluting substances, which are likely to be emitted from the installation concerned in significant quantities. The BAT AEL-ranges shall be the reference for setting these emission limit values, taking into account fuel type, combustion technology and other relevant conditions.

The cement industry is a significant contributor to global mercury emissions to air (>10%) because mercury is present at trace levels in both the raw materials (e.g. limestone) and fuel. The mercury content of raw materials varies between individual deposits and even within the same deposit. In fuels, the mercury content can vary in a similar way, depending on the fuel type and the fuel source. Monitoring is therefore an essential component of emissions control. In the BREF guidance for Cement kilns (**CLM BREF**), mercury has a BAT-associated emission level of 0.05 mg/Nm³ (50 µg/Nm³) for the half-hour average.

Frequency of monitoring mercury emissions

As a minimum, the frequency of emission monitoring will be determined by the type and size of plant. For example, solid biomass plants will be required to take measurements at least once per year; waste co-incinerators with biomass will measure at least once every 3 months; and large coal and lignite including waste co-incineration plants (≥ 300MW) will be required to monitor continuously.

It is believed that most coal-fired power plants emit up to 20 µg/Nm³ mercury, so these new regulations will have major implications for the power sector, and abatement technologies will have to be monitored carefully to determine which are the most effective and commercially viable.

Future legislation for mercury measurements

A new EU Directive (Directive (EU) 2015/2193) for Medium Combustion Plant (MCP) will come into force in December 2017, with similar requirements to those in the IED for large combustion plant. At the time of writing, mercury is not included in the emission limit values for MCP, however, many believe that mercury will be included in a future update. The monitoring requirements of the MCP Directive are specified within Annex IV with the first measurements taken within 3 months following registration/permitting. As a minimum, emissions must be monitored every 3 years for plants with a thermal rating from 1MW to 20MW and annually for those between 20MW and 50MW. Importantly, for plant using secondary abatement equipment to meet ELVs monitoring should be continuous.

CEN TC 264 Working group 8 is creating technical specifications of measuring total mercury emissions, including prEN14884 for the determination of total mercury with automated measuring systems.



Mercury Emissions Monitoring

The three principal methods for the measurement of mercury emissions are: wet chemistry, the sorbent trap method, and continuous emissions monitoring systems (CEMs). However, this document will focus on continuous monitoring methods, because, whilst generally lower in cost, non-continuous methods do not provide sufficient insight for process control. In addition, by measuring process emissions over a short period of time, non-continuous methods risk failing to provide sufficient information on the variability of mercury emissions over time and between differing feedstocks.

Continuous monitoring is a particular advantage where abatement systems can be adjusted according to the mercury levels in the plant emissions. Where flue gas treatment is used to achieve lower mercury emissions, continuous monitoring data can be used to optimize sorbent injection rates, for example.

The analytical methods used to determine mercury concentration include cold vapor atomic absorption (CVAA), cold vapor atomic fluorescence (CVAF) and inductively coupled plasma mass spectrometry (ICP-MS).

In general, the key requirements of a continuous mercury monitoring system are as follows:

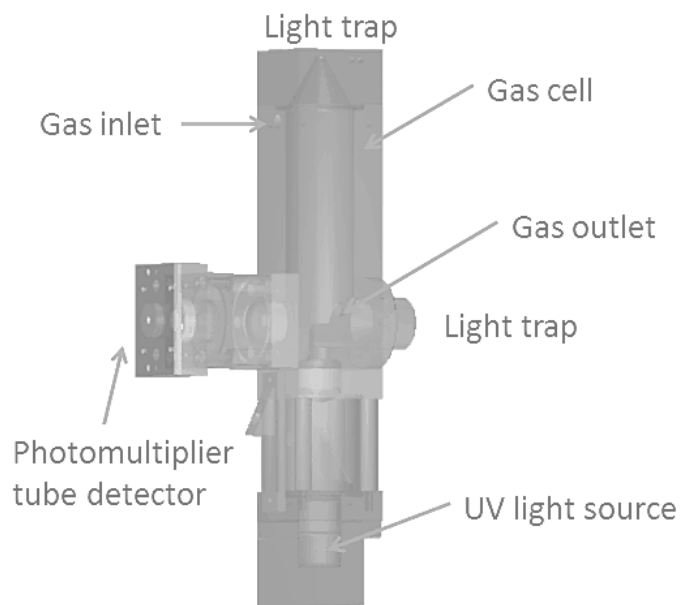
- > measures all forms of mercury
- > measures at low levels with high sensitivity during all process conditions
- > measures excursions to higher concentrations
- > low cross-interference from gases such as sulphur dioxide
- > no analyte loss or other sampling issues in high dust loading
- > stable calibration and simplified calibration check routine

These requirements have been met through the development of CEMs that employ CVAF, and the remainder of this paper will describe the main features of the continuous mercury emissions monitor (known as the CMM), employing CVAF technology, that has been developed by Gasmeter Technologies (Finland).



Continuous Mercury Monitor

The Gasmeter CMM analyzer is integrated in an air-conditioned cabinet together with a vacuum pump, an automatic calibrator and a nitrogen gas generator. The sample gas is extracted from the process duct with a dilution probe and a heated sample line specially designed for sampling mercury from harsh process conditions.



The analyzer has a detection limit of 0.025 $\mu\text{g}/\text{Nm}^3$ and the lowest measuring range for total mercury concentration is 0 – 5 $\mu\text{g}/\text{Nm}^3$ when a dilution rate of 1:50 is used in the sample extraction probe.

The CVAF spectrometer provides excellent sensitivity. Measurement uncertainty in traditional analyzers is increased by the presence of moisture and oxygen which reduce the fluorescence signal from mercury in the sample. Gasmeter has avoided this 'quenching effect' in the CMM by developing a dilution sampling approach, with synthetic nitrogen as the dilution gas, formed in a nitrogen generator inside the analyzer cabinet. By lowering the concentration of interfering gases by a factor of 50, the quenching effect is avoided, but with the CMM's extremely low detection limit, the

sensitivity of the mercury measurement is unaffected. Importantly, the measurement of mercury in a gas consisting of 98% nitrogen guarantees consistent results regardless of the fuel or emission abatement techniques used in the plant.

The CVAF spectrometer measures atomic mercury vapor (Hg^0) and in order to measure total mercury including oxidized forms, a thermal catalytic converter is used to convert all forms of mercury such as mercury chloride into atomic mercury. The converter is directly connected to the fluorescence cell to prevent recombination reactions, where atomic mercury converts back to oxidized forms.

To characterize the suitability and long-term stability of the sample probe and dilution system in various processes, the system has been field tested in a variety of industrial applications such as coal-fired power plant, hazardous waste incinerator, sulphuric acid plant and cement plant.

Given the reactive nature of mercury, special care has been taken to ensure that mercury in the flue gas is not absorbed into dust accumulating in the sample probe filters. Mercury reacts readily with limestone dust, resulting in analyte loss and increased response time of the analyzer. The Gasmeter CMM therefore includes a smaller filter element, which minimizes the amount of dust deposition on the filter, and a two-stage blowback mechanism which first removes dust from the filter element and then in the second stage expels the dust from the probe tube back into the process.

CVAF FAQ

The most frequently asked questions about Cold Atomic Fluorescence (CVAF) spectroscopy and mercury emission measurements are introduced and answered below

1. What does CVAF mean? How does it work?

CVAF stands for Cold Vapor Atomic Fluorescence. It is an extremely sensitive and selective measurement principle for the measurement of trace mercury levels. In a CVAF mercury analyzer the main parts are:

- > Mercury vapor lamp emitting UV light at the precise wavelength specific for mercury (253.7nm)
- > Sample flow-through cell where the gas stream crosses the UV beam coming from the lamp
- > Photomultiplier tube UV detector capable of detecting single photons, mounted at 90° to the UV lamp
- > Light traps, polarizer plates, and other features used to eliminate stray light

The UV detector does not see the light from the lamp, because of the 90° measurement geometry and light traps for stray light. The only signal picked up by the detector is the fluorescent light coming from the mercury atoms in the sample gas.

2. What is UV fluorescence?

Fluorescence is an effect seen with many substances that absorb ultraviolet or visible light. In the case of a mercury atom (Hg) the sequence of interactions with light can be summarized as follows:

$\text{Hg (ground state)} + h\nu \rightarrow \text{Hg (excited state)}$
(step 1)

$\text{Hg (excited state)} \rightarrow \text{Hg (ground state)} + h\nu$
(step 2)

The fluorescence photons ($h\nu$) produced in step 2 have the same wavelength as the photons from the UV lamp in step 1. However, they can be distinguished from each other by the fact that fluorescence photons (2) are emitted in all directions from the mercury atoms, whereas the UV light from the lamp in step 1 is in a parallel beam directed at a light trap at the end of the sample cell. By the use of light traps and 90° measurement geometry the photons produced in step 2 can be detected without interference from the photons in step 1.

3. CVAF or CVAA?

In comparison with the atomic absorption measurement technique, the atomic fluorescence used in the Gasmeter CMM offers superior sensitivity and reduced cross-interference effects thanks to the very specific nature of the fluorescence effect. This is a particular advantage in applications where the concentration of mercury is low and the concentration of other UV absorbing gases such as SO₂ is high. CVAF is therefore the best technology for example for coal-fired power plants and cement kilns.

When compared with other atomic fluorescence analyzers, the Gasmeter CMM is a more compact and cost-effective solution with several accuracy and reliability advantages:

- > no recombination of mercury compounds after converter
- > sample probe has a unique two-stage blowback mechanism for removing dust from filter surfaces

- > clean filters prevent analyte loss in the probe and minimize memory effects
- > ensures low maintenance

4. Is there any interference from SO₂?

Other UV absorbing gases such as SO₂ do not interfere with this measurement as the light source is selective to mercury and only the fluorescent light from the sample is detected. The CMM has been used to measure mercury in a sulphuric acid production process with 5–10 vol-% SO₂ present, and even in this extreme gas matrix the SO₂ interference is not an issue.

5. What is quenching and how it is minimized?

Quenching is an effect where collisions between mercury atoms and molecules such as O₂ take place in the tiny timeframe between absorption of UV light from the lamp and emission of fluorescent light from the mercury atoms. A collision at this time may remove the energy stored in the mercury atom and transfer it to the quenching molecule (O₂). Quenching lowers the amount of light falling on the UV detector and makes the instrument read low unless measures are taken to prevent it.

Quenching gases include O₂, CO₂, and H₂O. N₂ is not a strong quencher and other gases in a stack sample matrix have typically sub-% concentrations and can be ignored. Diluting sample gas in a 1:50 ratio lowers the concentrations of quenching gases considerably and the excellent sensitivity of CVAF means that a fairly high dilution ratio can be used. If the diluent is air, the O₂ content of the air still causes considerable quenching of the fluorescence signal and for this reason, the CMM system uses nitrogen for dilution. The

nitrogen diluent gas is made in a nitrogen generator inside the CMM system from compressed air. By replacing air with N₂ as the diluent the sensitivity of the system increases by a factor of 10.

6. What is the detection limit of the Gasmeter CMM?

The detection limit is 0.5 nanograms per cubic meter in sample gas diluted with synthetic nitrogen. Taking the dilution ratio into account the detection limit is 25 ng/m³ (0.025 µg/m³) in an undiluted stack gas.

7. How are all mercury compounds measured?

CVAF instruments only detect atomic mercury vapor (Hg⁰) whereas stack gas contains also oxidized mercury compounds such as HgCl₂. In the CMM system, the gas passes through a thermal converter just before the fluorescence measurement cell. Mercury compounds break and atomic mercury vapor is released in the converter, enabling a measurement of total gaseous mercury emissions. As the measurement is made immediately after conversion, no recombination reactions take place between conversion and measurement.

8. What are the typical applications for the Gasmeter CMM?

As outlined above, continuous mercury monitoring is either advantageous or a regulatory requirement for waste incineration plants, power plants, and cement kilns. Thanks to high sensitivity (low measuring ranges) and reduced cross-sensitivity, the Gasmeter CMM is well suited to all of these emission monitoring applications. The CMM can also be used for

process control in sulphuric acid manufacturing. The raw sulphur used in this process frequently has mercury impurities from mineral sources and the CMM is used to monitor trace levels of mercury in a process stream containing 5 to 10 vol-% SO₂ to ensure that the end product has acceptably low levels of mercury.

9. How is calibration performed?

The CMM is calibrated for zero and span using synthetic nitrogen zero gas generated in the cabinet and Hg⁰ vapor span gas generated in the mercury calibrator which is an important part of the CMM system. The calibration is performed automatically at user-defined intervals. The factory set calibration interval is one day. The system can also perform automatic zero and span drift tests, and optionally converter efficiency and system integrity tests using HgCl₂ test gas generated in the calibrator.

10. How sensitive is the CMM to reactive gases?

The CMM withstands high concentrations of SO₂ for example, and the cross-interference effects are virtually eliminated by the use of the Atomic Fluorescence measurement principle, (see question 1).

11. What are the special features of the CMM software?

The Mercury Analyzer User Interface (MAUI) is easy to use, touch panel oriented software for controlling the analyzer, calibrator and sampling probe blowback mechanism. MAUI visualizes mercury measurement values in

trend (60 min/24 hrs) and the latest measured concentration displays. The software shows status and warning messages sorted into four categories (system alarm, service request, maintenance, result valid) and allows the user to define calibration settings and probe blowback routines.

12. How is sample contamination avoided?

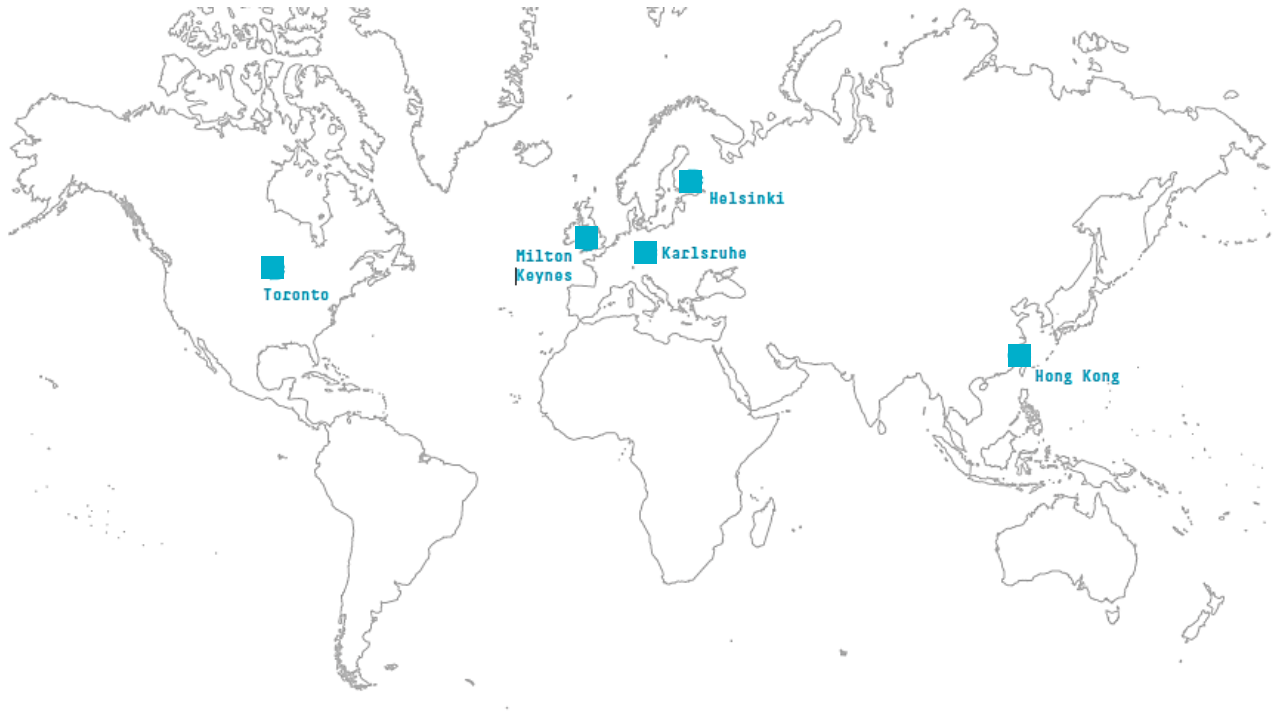
The metal parts of the CMM probe and filters have special coatings to ensure that mercury does not react with the metals, and the flexible tubing parts are made from a perfluoropolymer with excellent chemical resistance.

In addition to the material choices explained above, the following precautions ensure minimal analyte loss or memory effects:

- > Trace heating of the entire sampling train beginning at the probe tube
- > Reduced size filter element with frequent, two-stage blowback to prevent dust from accumulating in large amounts on the filter element
- > Sample lines are only in contact with diluted sample gas
- > Sample cell is maintained at low pressure (below 100 mbar)

13. Why and how is sample gas dilution performed?

Sample gas is diluted with nitrogen to eliminate quenching (see question 5) and to reduce the reactions between mercury in the sample gas and sample line surfaces. Dilution is achieved by using an eductor pump with an orifice that limits the flow of undiluted sample gas into the pump. Dilution gas (nitrogen) enters the eductor and provides the flow which pulls sample gas from the probe into the analyzer.



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