

Continuous measurement of mercury emissions in combustion plants

(Overview and new measuring method)

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Introduction

Continuous measuring devices have been used for continuous recording of Hg emissions in waste incineration plants since the early Nineties. Operators of combustion plants must maintain a 24-hour measured value of $30 \mu\text{g}/\text{m}^3$ mercury and a half-hourly average value of $50 \mu\text{g}/\text{m}^3$ in accordance with the 13th and 17th BImSchV.

In order to meet these requirements, measuring devices used for the measuring ranges $0 - 45 \mu\text{g}/\text{m}^3$ and $0 - 75 \mu\text{g}/\text{m}^3$ must be suitability tested and certified. Apart from waste incineration plants, more and more cement plants and power plants that use substitute fuels for example, fall within the scope of this Directive.

1. Sample gas conditioning, reduction and existing measurement technology

Existing measurement technology is based on extractive gas sampling, conversion, possibly amalgamation and UV measurement (Fig. 1). Sample gas conditioning plays a special role for mercury measurement. The reason for this is that UV analyzers with atomic absorption spectroscopy usually used can only detect metallic mercury. The flue gas does however not only contain metallic mercury but also oxidized mercury compounds, mainly mercury chloride (HgCl , HgCl_2). These compounds cannot be detected directly and must be reduced to metallic mercury through appropriate measures in sample gas conditioning. The total mercury in the flue gas can first be recorded after this reduction.

Various methods are used for mercury chloride reduction (Fig. 2). One method uses the classic wet chemical reduction, for example, with a tin chloride solution, as also used in laboratories for reference measurements.

Another method being used more and more over the past years is the so-called dry reduction. Dry reduction uses converters in gas sampling which convert the oxidized mercury compounds to metallic mercury either at low temperatures (approximately 250°C) or high temperatures (approximately 700°C). The methods used each have advantages and disadvantages, and are rated by operators very differently regarding operating, efficiency and reliability.

Also very important for gas sampling is a probe with filter which is heated continuously to at least 180°C as well as a heated sample gas line which is kept as short as possible to prevent thermal bridges during gas sampling. Mercury losses during measurement and memory effects are preprogrammed as soon as condensate forms in unheated

connection pieces.

Some manufacturers, mainly in the USA, also offer dilution probes for gas sampling. Sample gas dilution means even more sensitive measuring methods must be used for mercury measurement, for example atomic fluorescence. Single or twin beam UV photometers are normally used in measuring systems in Germany and Europe. An amalgamation step is carried out before measurement in some measuring systems to prevent cross-sensitivities (Fig. 3). The metallic mercury property to amalgamate completely on gold/platinum alloys is utilized here. After amalgamation, the gold/platinum net is heated to over 700° C in a quartz tube and the condensing mercury transferred to the actual measuring cell of the analyzer using nitrogen (Fig. 4). Apart from the advantage of mercury measurement free from cross-sensitivity, this Hg separation also has the advantage of being able to record even smaller quantities or concentrations (for example < 10 µg/m³) due to mercury enrichment possible through longer load times. A disadvantage of this amalgamation process is that mercury values can only be output "quasi-continuously" (approximately 180 seconds per measurement).

Another method of measuring mercury is using a twin beam UV photometer. Here, the sample gas is led from the gas matrix to the analyzer without separation and then transferred sequentially to a sample gas cell and a span gas cell. The sample gas is fed through an iodized carbon filter on the reference cell inlet so that the reference cell only contains gas free from mercury. Absorption and mercury concentration are then determined from the energy consumption of light absorbed by the mercury between the sample gas and reference cells.

2. Measuring device validation

Various points must be taken into account due to the complexity of checking analyzers. Only a metallic Hg⁰ gas is available as mercury test gas. Apart from that, a mercury permeation chamber can also be used to create a mercury test gas. One drop of mercury is enclosed in a thermostatic-controlled chamber. The exact amount of mercury in the chamber is determined from the mercury vapor pressure curve depending on the temperature set. A stream of nitrogen transports the amount of mercury determined from the vapor pressure curve to the analyzer either manually or in a specified interval to check the analyzer. This also allows checking the gold trap function for amalgamation because experience has shown that the load efficiency deteriorates over a time frame of one to two years.

However, complete and sustainable conversion of oxidized mercury to metallic mercury is becoming the focal point for measuring systems. Test gases are not available here. Gaseous mercury compounds can only be created through vaporization of an HgCl₂ solution. Such vaporizers are already available on the market and normally have suitable mass flow controllers for exact dilution with nitrogen to create differing calibration gas concentrations (Fig. 5). The conversion of these mercury compounds to metallic mercury can now be checked in measuring systems by feeding oxidized mercury compounds as calibration gas to the sampling probe, as already carried out in the USA. Some operators

have reported that the conversion to metallic mercury was not satisfactory after just a few weeks when using dry catalysts. Even though the reduction solution for conversion using wet chemical reference methods has to be replaced every three months, these methods deliver reliable conversion rates independent of the plants.

3. Summary of existing measuring methods

To summarize, one can say that all continuous mercury measuring systems demand much more extensive maintenance than known gas measuring systems. The main reason is that the mercury measuring range is three times as small. For example, the HCl limit value is 10 mg/m³ whereas the limit value for mercury is 30 µg/m³ and therefore must be recorded reliably in the lower ppb (parts per billion).

Apart from that, secure and reliable conversion to metallic mercury is difficult in gas conditioning. Erroneous functions lead to low quality for total mercury and no mandatory regulations exist for checking the conversion level and therefore can only be proven using reference measurements by approved laboratories. The obligation for weekly test gas feeding of oxidized mercury compounds over the probe already exists in the USA.

How should an ideal mercury measuring system be designed?

4. A new measuring method for continuous mercury measurement MERCEM300Z

Existing physical and chemical conditions are such that extractive gas sampling is always necessary for an ideal mercury measuring system. It should allow reliable conversion with the smallest possible maintenance effort and should not have any cooling stages when possible. The measuring method should be free from cross-sensitivity or at least with reliable correction of cross-sensitivity and be able to measure the total mercury in the flue gas and have short reaction times. An automatic check of measuring precision to ensure the reliability of the measuring system should also be available.

The newly developed mercury measuring system MERCEM300Z fulfills these criteria (Fig. 6). The so-called Zeeman AAS method is used here for continuous mercury measurement for the first time, coupled with a high temperature gas cell at 1,000° C (Figs. 7 and 8). All mercury compounds in the sample gas are reduced to metallic mercury at this temperature. The fact that no cooling is done means low quality through the recombination of Hg⁰ to oxidized mercury compound (oxide or chloride) is excluded. The first TÜV laboratory tests have also shown a faster running-in behavior (T-90 time) than ever known before and excellent linearity. Comparative field measurements in waste incineration plants and cement production could also be completed successfully in the meantime. Typical cross-sensitivities such as those known for SO₂ and other gas components do not occur when using this method (Fig. 9). Comparative measurements on plants with existing mercury CEMS show excellent conformity, also compared to reference measurements of a certified Test Institute according to "Messstelle" § 26.

For quality control of measurements, known HgCl_2 concentrations can be fed to the measuring system automatically via a vaporizer. A swiveled-in integrated calibration filter can also be used for simple drift control. This can also be used for drift control at the reference point as required for QAL-3 for example. A patent for this measuring method has already been applied for.

5. Summary and Outlook

The decisive advantages over mercury measurement systems available on the market up until now are:

- Smallest checked measuring range 0 -10 $\mu\text{g}/\text{m}^3$
- Targeted maintenance interval of minimum 3 months
- Measuring system suitability tested with a heating hose length of 35 m
- Direct conversion with simultaneous measurement in a sample gas cell at 1,000° C
- Certification according to EN 15267
- Gas sampling with ejector instead of heated diaphragm vacuum pump (quasi maintenance free)
- No consumables such as conversion substances or solutions for conversion
- No additional amalgamation but continuous real-time measurement instead
- Drift check of analyzers without test gas with internal filter control
- No cross-sensitivities determined for typical accompanying components in exhaust gas
- Optional automated HgCl_2 test gas feed to the probe in freely programmable intervals

The TÜV laboratory test was completed successfully in the first Quarter of 2011. The field test for suitability test is running at this time and will probably be completed in the Autumn of 2011.

Sources of information

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Fig. 1: Existing measuring methods for total mercury

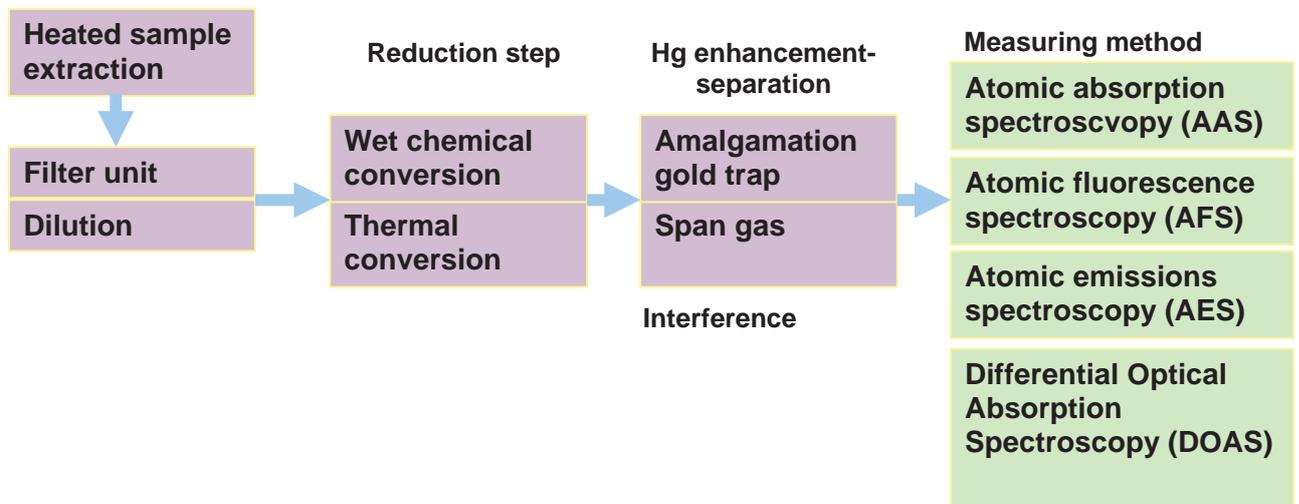
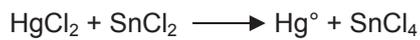


Fig. 2: Conversion to metallic Hg (wet chemical and dry)



Dry conversion

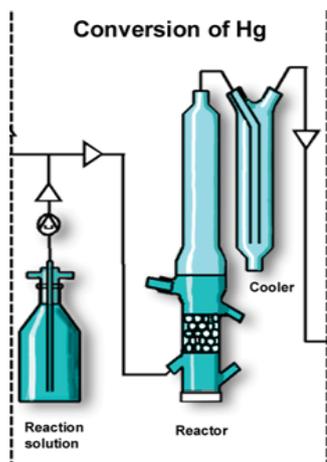


Fig. 3: Amalgamation of mercury on a gold trap

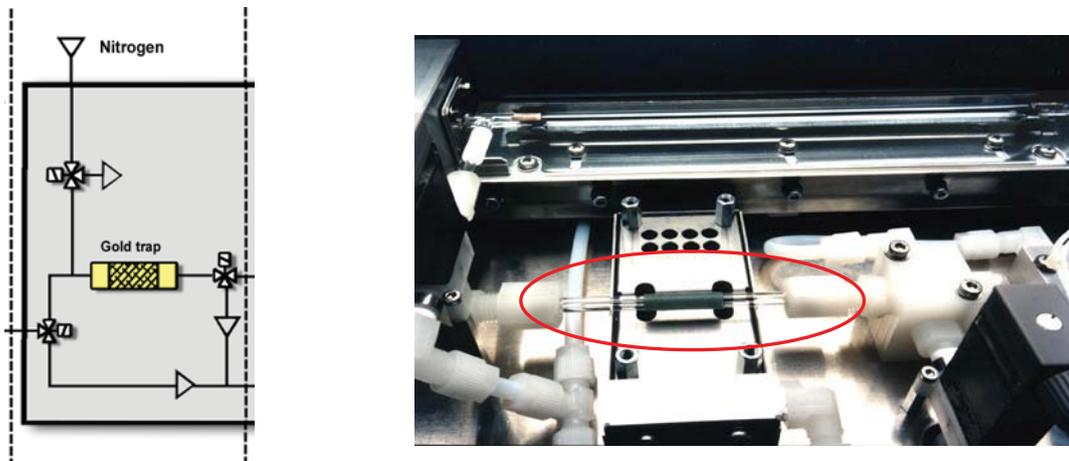


Fig. 4: Measuring principle (Cold Vapour Atomic Absorption Spectroscopy, CVAAS)

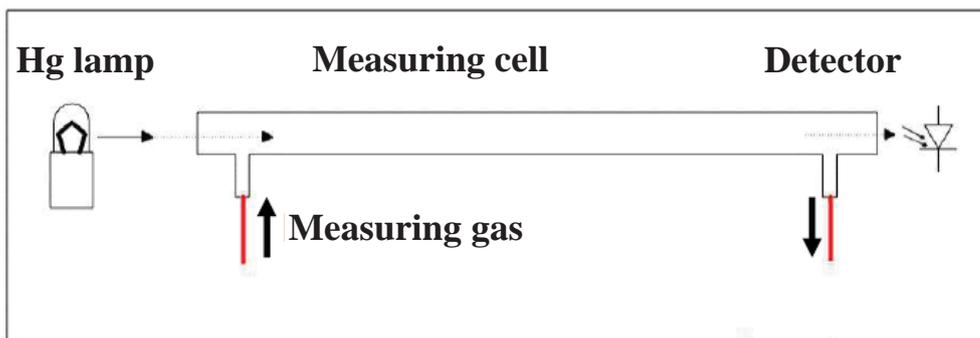


Fig 5: HgCl_2 - Test gas generator with vaporizer

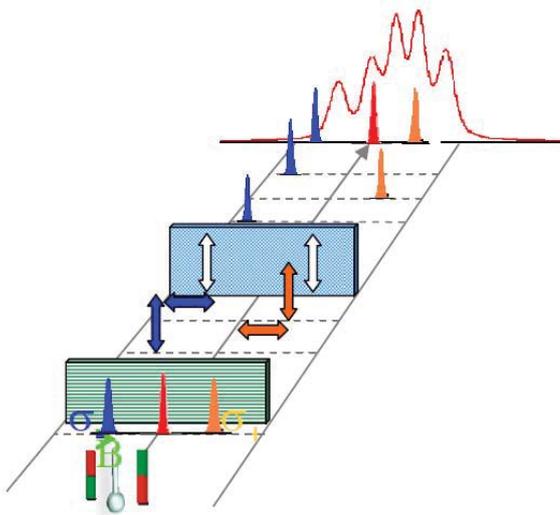


Fig. 6: Cabinet inner view MERCEM300Z (new development)



Fig. 7: Zeeman measuring principle

Blue = background measurement; Orange = Hg absorption measurement



Hg line splitting through magnetic field at the light source

Fig. 8: Quartz sample gas cell at 1,000° C for conversion and simultaneous real-time measurement (patented)

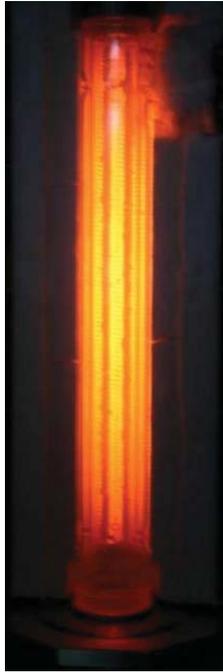


Fig. 9: Cross-sensitivity Table for typical interfering components

Component	Concentration	Cross sensitivity on Hg
SO ₂	1000 mg	0,00 µg/m ³
H ₂ O	30 Vol%	0,02 µg/m ³
CO	300 mg/m ³	0,09 µg/m ³
NO	300 mg/m ³	0,05 µg/m ³
CO ₂	15 Vol%	0,00 µg/m ³