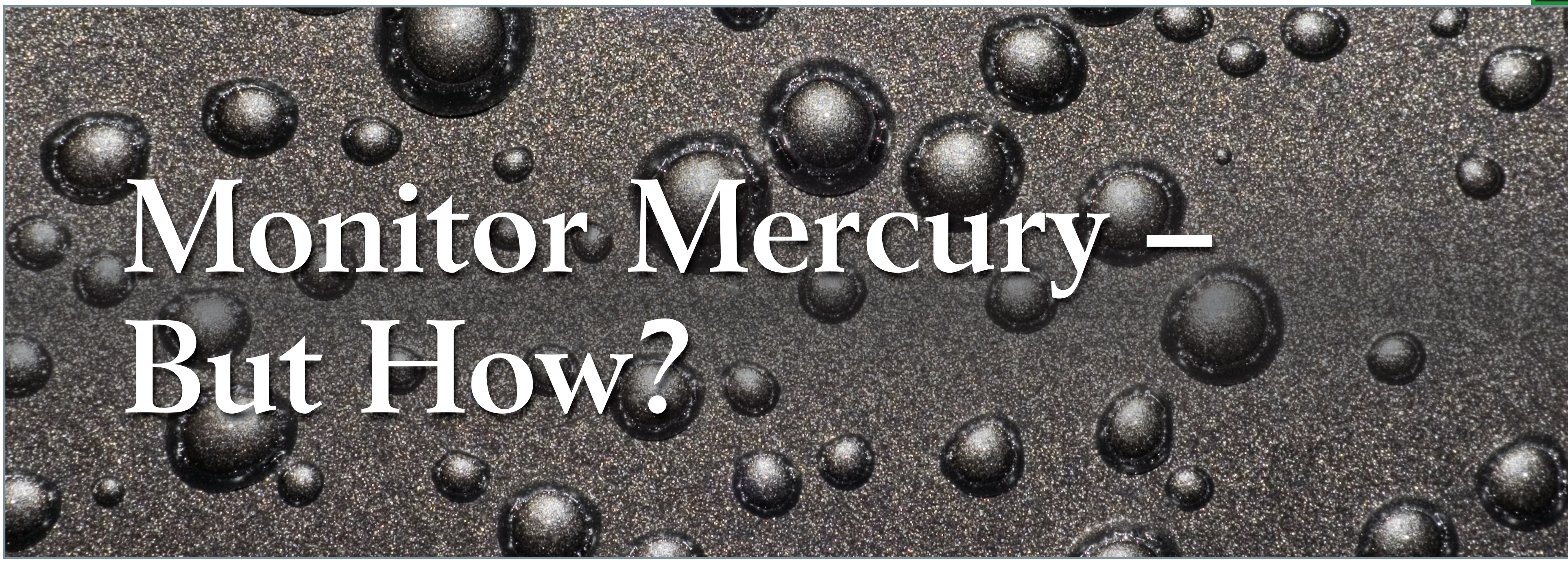

Monitor Mercury – But How?

Due to its high toxicity mercury has to be closely monitored in flue gases from coal fired power plants, waste incinerators and cement plants all around the world. Limit values must be maintained in the lower µg-range. For this reason, measuring devices need to be extremely sensitive, highly accurate as well as being able to withstand the harsh industrial environment. Meanwhile different types of mercury monitoring systems are available. But how should the ideal system perform in terms of performance and acceptable low maintenance for the plant operator?

"In order to ensure accurate measurements, the detection of the mercury should directly take place within the conversion process."

Sample gas conditioning, reduction and existing measurement technology

Existing measurement technology is based on extractive gas sampling, conversion, possibly amalgamation and UV measurement. Sample gas conditioning plays a special role in mercury monitoring. All mercury analysers have one thing in common: They can only detect metallic mercury (Hg^{0}). The flue gas does however not only contain metallic mercury but also oxidised mercury compounds, mainly mercury chloride ($HgCl$, $HgCl_2$). These compounds cannot be detected directly and must be reduced to metallic mercury by appropriate measures in sample gas conditioning.

Various methods are used for reduction of oxidised mercury. 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 which is more often used over the past years is the so-called dry reduction. Dry reduction uses converters in gas sampling which convert the oxidised mercury compounds to metallic mercury either at low temperatures (approximately 250°C) or high temperatures (approximately 450 – 700°C). Both methods have advantages and disadvantages, and are rated by operators very differently regarding operating, efficiency and reliability. One major disadvantage here is the risk of contamination as a result of sulphur and chlorine compounds, which may be present in the flue gas. This leads to increased operating costs as a result of the shortened operational lifetime of the converter.

Mercury measurement with MERCEM300Z

A new approach dispenses of any consumables – dry converters and chemical solutions. At very high temperatures (above 900°C), mercury only exists in its elemental form. This allows for so-called thermal conversion. The big advantage of this approach is the increase of the total availability of the measurement without being poisoned by any other flue gas component.

In order to ensure accurate measurements, the detection of the mercury should directly take place within the conversion process. This prevents any losses of mercury detection by recombination effects during the transportation of the mercury sample to the analyser.

The heated sample gas line, heated at least to 180°C, should be kept as short as possible, to prevent any absorption during transportation.

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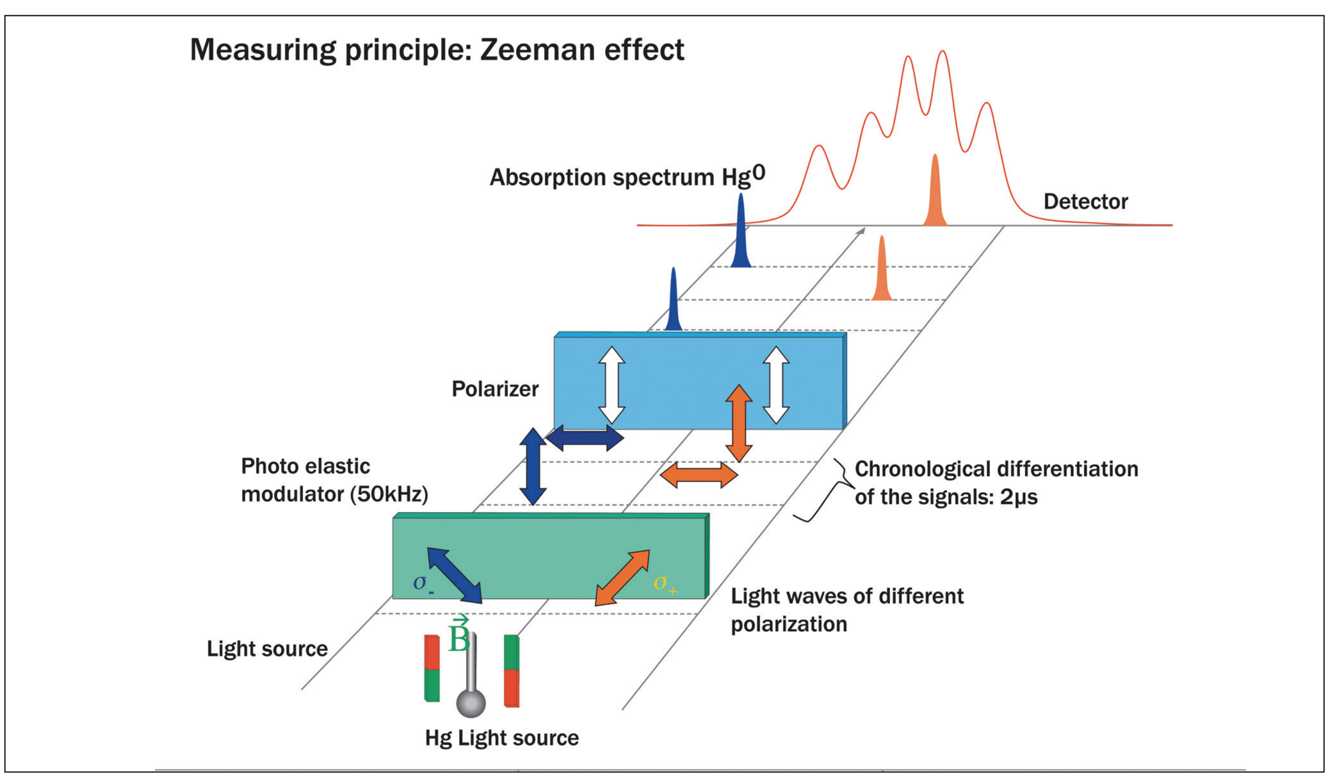
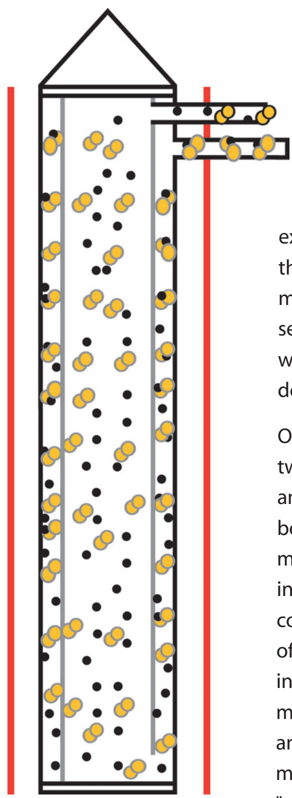


Best possible interference compensation due to the Zeeman atomic absorption spectroscopy



High temperature conversion

Some manufacturers also offer dilution probes for gas sampling. Sample gas dilution however requires even more sensitive measuring methods, for example atomic fluorescence. On the downside, fluorescence methods are also known to be sensitive to quenching effects, which leads to wrong mercury detection signals.

Other mercury systems use single or twin beam UV photometers. An amalgamation step is carried out before measurement (e.g. in some measuring systems to prevent cross-interference from other gas constituents). Due to the separation of the sample and the flue gas, cross interference effects are minimised. A major disadvantage of this amalgamation process is that mercury values can only be output "semi-continuously" (approximately 180 - 400 seconds per measurement).

In order to prevent from the influence of cross interferences together with the advantage of a continuous and direct measurement of mercury, a new device using the Zeeman AAS principle has been introduced. Due to the Zeeman effect all interferences are directly compensated for during measurement without the need of any amalgamation step or any separation of mercury from the flue gas. With this approach a fast, reliable and cost effective mercury monitoring was established.

Validating the measuring device

As previously described, various points must be taken into account due to the complexity involved with checking analysers. Some devices use a mercury permeation chamber to create a mercury test gas. With this approach it is only possible to check the analyser with elemental mercury test gas. There are also some gas suppliers on the market, who can deliver such metallic mercury test gases.

However, complete and sustainable conversion of oxidised mercury to metallic mercury is becoming the focal point for measuring systems. Test gases with oxidised mercury are not commercially available. Gaseous mercury compounds can only be created through vaporisation of a $HgCl_2$ solution. Such vaporisers are already available on the market and normally have suitable mass flow controllers for accurate dilution with instrument air to create different mercury calibration gas concentrations. The conversion of the mercury compounds to metallic mercury can now be checked in measuring systems by feeding those mercury test gases to the sampling probe. Some mercury monitoring devices have as an option, an integrated test gas generator, which is the only reliable check of the entire CEMS.

A new measuring method for continuous mercury measurement MERCEM300Z

Measuring gas transportation, secure and reliable conversion to metallic mercury and cross sensitivity compensations are difficult in mercury monitoring. But how should an ideal mercury measuring system be designed?

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 lowest possible maintenance effort and should not have any cooling stages or converters 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 with shortest T-90 reaction time. 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. 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. All mercury compounds in the sample gas are reduced to metallic mercury at this temperature. The fact that no gas cooling is done, means that recombination of Hg° to oxidised mercury compounds (oxide or chloride) cannot occur. The TÜV type approval tests have also shown a faster running-in behavior (T-90 time) than ever seen before as well as excellent linearity. Typical cross-sensitivities such as those known for SO_2 and other gas components do not occur when using the Zeeman AAS method. Comparative measurements on plants with existing mercury CEMS show excellent conformity, also compared to reference measurements of a certified Test Institute according to German stack testing institute "Messstelle § 26".

For quality control of measurements, known $HgCl_2$ concentrations can be fed to the measuring system automatically via a vaporiser. A swiveled-in integrated calibration filter is also available for simple drift checks. Due to this major advantages, the MERCEM300Z is the first device which is certified according to EN15267 with a lowest measuring range of 0 – 10 $\mu g/m^3$. A unique maintenance interval of 6 months has been reached during 12 months field test for the standard range of 0 – 45 $\mu g/m^3$.

Features and Benefits

The decisive advantages over mercury CEMS available on the market up to now are:

- Smallest certified measuring range 0 -10 $\mu g/m^3$
- Maintenance interval of 6 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
- No additional amalgamation step, continuous real-time measurement instead
- Drift check of analysers without test gas with internal filter control
- No cross-sensitivities determined for typical accompanying components in exhaust gases
- Optional automated driven $HgCl_2$ test gas evaporation unit inside the analyser cabinet