Mercury CEM for Stack Gas Monitoring

Mercury is a naturally occurring heavy metal. At ambient temperature and pressure, it is a silvery-white liquid that readily vaporizes and may stay in the atmosphere for up to a year. When released to air, mercury is transported and deposited globally. Mercury enters the food chain primarily through atmospheric deposition.

Mercury is highly toxic, especially when metabolised into methyl mercury. It may be fatal if inhaled and harmful if absorbed through the skin. Around 80% of the inhaled mercury vapour is absorbed in the blood through the lungs. It may cause harmful effects to the nervous, digestive, respiratory, immune systems and to the kidneys, besides causing lung damage. Recent studies suggest that mercury may have no threshold below which some adverse effects do not occur.

The World Health Organization (WHO) lists Mercury as one of the toxic substances of greatest concern.

Mercury is emitted to the atmosphere by natural degassing of the earth's surface and by re-evaporation of mercury vapour previously deposited on the earth's surface. Naturally occurring Mercury(II) sulphide (HgS) Has no vapour pressure and is not soluble in water but decomposes under the presence of Oxygen to elemental Mercury (Hg^0) and Sulfur-dioxide (SO_2) when exposed to temperatures higher than 600°C. That means in particular a large natural source of elemental Mercury is volcanism. Annual natural emissions are estimated to be between 2700 and 6000 tonnes

Anthropogenic sources of mercury are numerous and worldwide. Mercury is produced by the mining and smelting of cinnabar ore. It is used in chloralkali plants (producing chlorine and sodium hydroxide), in paints as preservatives or pigments, in electrical switching equipment and batteries, in measuring and control equipment (thermometers, medical equipment), in mercury vacuum apparatus, as a catalyst in chemical processes in the production and use of high explosives using mercury fulminate, in copper and silver amalgams in tooth-filling materials, and as fungicides in agriculture (especially as seed dressings), in mercury quartz and luminescent lamps, a point of particular concern with the rise in use of low energy lamps,

Mercury is a commonly found trace element, found in coal (0.1 – 0.5ppm), crude oil and natural gas (up to 28 mg/m^3) the burning of coal and natural gas or refining of crude oil releases Mercury to the atmosphere.

In total, human activities have been estimated to add 2000–3000 tonnes to the total annual release of mercury to the global environment. However, it should be stressed that there are considerable uncertainties in the estimated fluxes of mercury in the environment and in its speciation

Mercury exists in three oxidation states: Hg^0 (metallic), Hg+ (mercurous) and Hg^{++} (mercuric) mercury. The latter forms a variety of inorganic as well as organometallic compounds.

Elemental Mercury (Hg^0) is less toxic. But if released to the atmosphere it undergoes a metamorphosis. At the end of this cycle, nature stores the Mercury as HgS in the soil again. But in the process it will be oxidised, form inorganic compounds and under oxygen free conditions organic compounds like Dimethylmercury $Hg(CH_3)_2$. This compound is fat soluble and the most toxic version of Mercury. The LD 50 ratio (rat) is 463 ppm! LD 50 means the ratio that kills 50 % of all test animals by given the substance at once.

In response to the risks posed by Mercury emissions, The US introduced the Clean Air act amendments in 1990; Germany introduced a regulation requiring Continuous Emission Monitoring (CEM) for Mercury in 1992. The Netherlands, France, Belgium, Spain, Austria, Portugal and Italy followed on a voluntary basis.

With European wide regulations governing mercury emissions from combustion processes likely to go into effect soon, there is a pressing need to ensure that flue gas mercury measurements can be made accurately and reliably

CEM setup

CEMs for Mercury, under the German regulations, is required for most plants under the Waste Incineration and Large Combustion Plant Directives (WID/LCPD). The emission limit is 50 µg/Nm³ (half hourly average) and 30 µg/Nm³ (daily average). Typical measuring ranges are 0 – 45 µg/Nm³ and/or 0 – 75 µg/Nm³. The instrument has to monitor and report total Mercury (Hg_{TOT}). The reason for this is Mercury appears as elemental (Hg^0) and oxidized form (Hg) in the flue gas. Total Mercury is the sum of the elemental and the oxidized form. Reasonable concentrations on particulate bonded Mercury are negligible provided the sample probe is properly heated at temperatures above 140°C

The typical requirements of a CEM system to produce a standardised dry Mercury measurement are a heated sample probe and line (≥180°C), a catalyst to convert the oxidized Mercury into elemental Mercury, a sample cooler to remove moisture, a sample cell, a UV detector and a method for deriving sample volume (Figure 1). A heated probe and line is necessary to transport the oxidized Mercury to the thermo-reactor catalyst which consists of a solid catalyst material at a constant temperature.

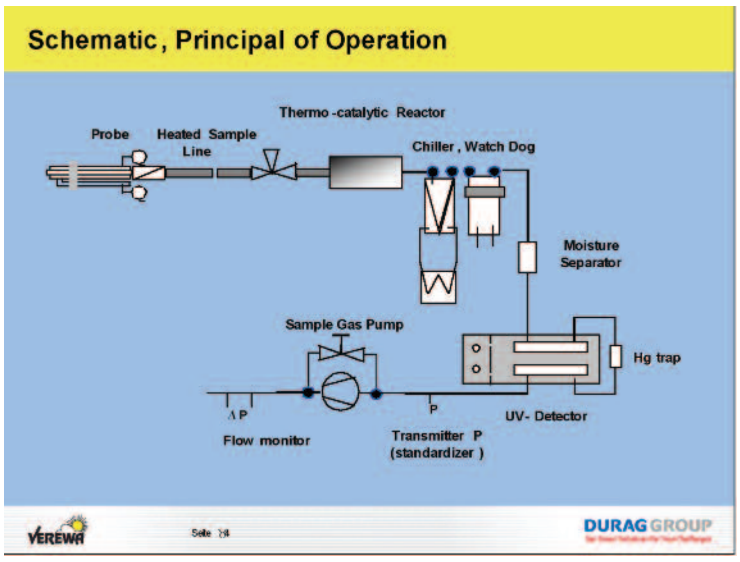

Figure 1: Principal schematic of a Mercury CEM

The advantage of using a thermo-reactor at constant temperature, rather than the temperature cycled gold trap is a true continuous measurement. The temperature cycling required for amalgamation and subsequent release of Hg^0 results in a sample time of around 5 minutes. Use of a dual beam cell and UV detector with a Mercury trap suppresses the interference from SO_2 (figure 2).

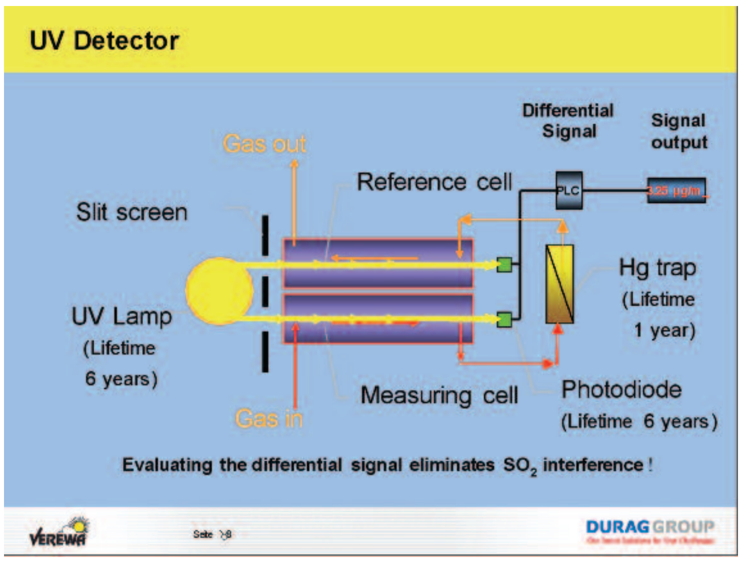

Figure 2: Dual beam UV detector

Reference method and certification

For Applications in Europe Mercury CEM's must be certified according to EN 14181 and EN 14884. Part of this certification is a comparison using the standard reference method and the records of the CEM (figure 3). A typical method is the Ontario Hydro Method using a method 5 extraction to a sorbent capture device; the concentration is then derived in a laboratory using traditional wet chemistry. The Initial certification is divided into a laboratory test which covers interferences (e.g. SO_2, aromatics, etc…), climatic chamber checks and a field test where two instruments are connected to one stack standing side by side. The requirement is a deviation between the records of both instruments less than 0.5 µg/Nm³ for a period twice that of the maintenance cycle. To comply with EN14181 (QAL3) a linearity check of standards graded in approximately 0, 20, 40, 60, 80 and 100% steps of full scale are provided to the CEM. This can be realised using a mercury reference solution and a vaporiser, the rate of solution supply can be controlled to vary the required concentration. The CEM has to respond with 97.5 % accuracy in less than 200 seconds.

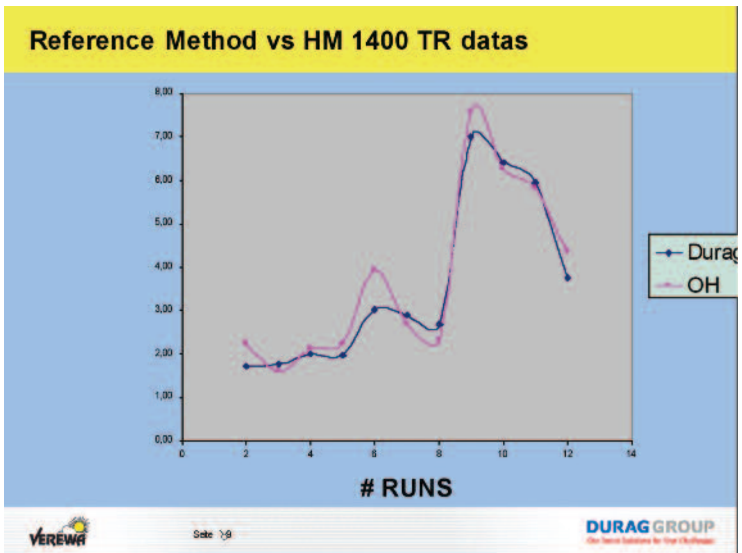

Figure 3: CEM vs reference method

Zero Check

As an internal check the Mercury CEM should carry out an automatic zero control regularly. One method is to pass ambient air over iodine charcoal (mercury trap) for a period sufficient for the checks to be completed. Due to reporting requirements (a minimum of 20 minutes valid readings are needed to get a valid half hour average). Therefore 10 minutes for the complete self check cycle would be a maximum to ensure no valid averages are lost.

Span Check

An internal span check would use the same apparatus as the Linearity check. Working on a regular basis depending on the requirements of the local authorities. The principal is vaporising a defined amount of a certified Mercury solution ($HgCl_2$) in a vaporiser (180°C). This vapour ($HgCl_2$) is diluted in a defined amount of carrier gas. and introduced to the sample probe (prior to the Thermo-catalyst). The overflow of vapour should then be returned to the process stack (figure 4 and figure 5).

Mercury oddities

Mercury sometimes shows a behaviour that is different to other gases.

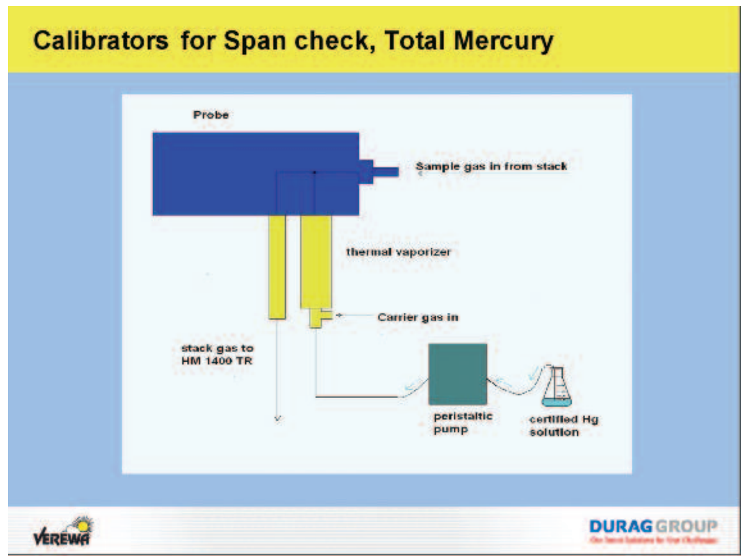

Figure 4: span check, setup

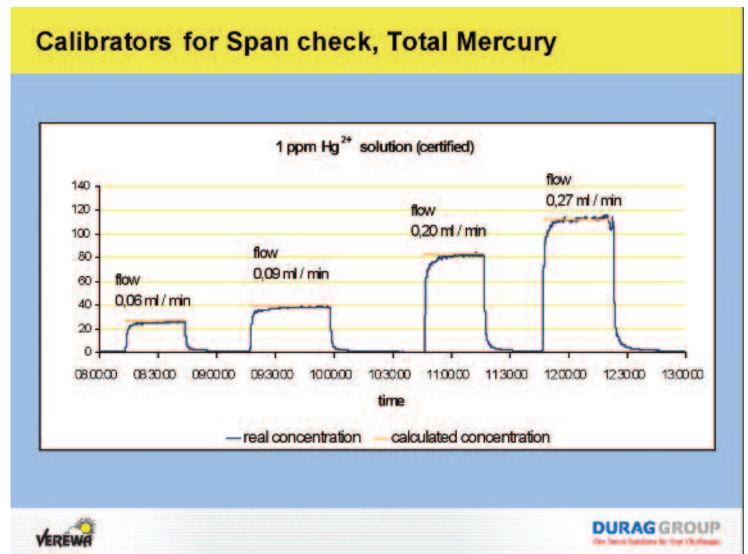

Figure 5: span check, response on several set points

This is caused by the different physicochemical properties of the Mercury forms. Elemental Mercury (Hg^0) is not water soluble and even at 0°C has a vapour pressure to keep around 2 mg/Nm³ in the vapour phase. A typical behaviour of elemental Mercury is to form an amalgamation, a cold alloy with metals. This could cause a memory effect in the process itself. When a unit is shut down and process gas is going through the system, Mercury concentration can start rising by vaporising out of surfaces.

Oxidised Mercury, mostly discussed as $HgCl_2$, is soluble in water (70 g/l) and needs minimum temperatures around 120°C to start developing a vapour pressure. Due to this any cold spots between the sample probe and the catalyst will capture oxidised Mercury. If this cold spot is cold enough to form condensates from the process gas, the solubility of $HgCl_2$ will cause spiking or a noisy signal. If there is no condensation possible at the cold spot Carbon Monoxide (CO) can also release Mercury because of its red ox potential. Sometimes a CO peak during the process is often also related to a Mercury peak.

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