Monitoring Mercury Emissions – Standards Under Development

In 2013, the United Nations Environment Programme (UNEP) finalised the global legally binding instrument (LBI) on mercury. This LBI includes targets for mercury reduction and requirements for best available technologies for reduction. In order for the LBI to function, there must be valid monitoring methods available to monitor emissions. The current European methods for mercury monitoring – wet chemical methods and AMS/CEMs – are both expensive and challenging, especially for emerging economies who have never monitored such a challenging pollutant before. The sorbent tube system is very simple to use, as has been demonstrated during UNEP Coal Partnership studies in Russia and South Africa. The LBI will result in significantly increased use of this methodology in developing countries and economies in transition. Further, the EU Industrial Emissions Directive (IED) will call for annual monitoring of mercury beyond 2016 and, as set down in the new BREF documents requirements this will require more frequent mercury monitoring and control on some plants.

Since the sorbent tube method is likely to become the method of choice for mercury monitoring globally within the next 5-10 years, it is important that the methodology is standardised as soon as possible and CEN TC264 has recognised this challenge and has commissioned Working Group 8 to develop the new method based on sorbent tube system and also to revisit and revise the existing European mercury and metals standards.

Principle of Sorbent Trap Sampling

Known volumes of flue gas are extracted from a stack or duct through paired, in stack sorbent media traps at an appropriate flow rate. Collection of mercury on the sorbent media in the stack mitigates potential loss of mercury during transport through a probe/sample line. For each test run, paired train sampling is required to determine measurement precision and verify acceptability of the measured emissions data. The sorbent traps are recovered from the sampling system, prepared for analysis as needed, and analysed by any suitable determinative technique that can meet the performance criteria.

Ease of Operation

The simplicity of sorbent trap monitoring over other technologies is significant. With budgets constantly being reduced, sorbent trap monitoring often only required 30 minutes a week of a field technicians time compared with over 30 minutes a day for other technologies. With environmental departments being asked to do more with less, sorbent trap sampling is often received as a welcomed alternative to the complicated, labour intensive operation of other environmental sampling equipment.

Ease of Installation

The sorbent trap system is easy to install and much more robust than other options available for mercury emissions monitoring. The simple, proven technology used to perform sorbent trap sampling tends to handle the unforgiving conditions these systems often find themselves installed, more so than other technologies that use much more sensitive componentry.

Cost

With sorbent trap monitoring systems often costing less than half the price of other monitoring options, sorbent trap monitoring is a cost effective way to monitor mercury emissions. Cost savings are also seen in the reduced labour needed to run the system as well as operating and repair costs.

Multiple Configuration Options

Mercury Sorbent trap systems can be configured in several ways to accommodate any site specific challenges with little or no costly changes to existing infrastructure. Configurations can be designed from having all of the sampling equipment located at the sampling location to extracting the sample and bringing it down to an existing shelter for moisture knock-out and volumetric gas reading.

Reliability

With regulatory agencies requiring a steady supply of sample reporting data, reliability in any sampling system is essential as down-time can often result in penalties or fines. The simple sampling principles of sorbent trap sampling lend themselves to be more easily troubleshot and repaired in the field by operators who can be trained within only a few days. The modular design of the sorbent trap sampling system also allows for components to be replaced in the field, minimising down-time.

Ease of Maintenance

Sorbent trap sampling technology is based on simple proven technology that in-turn requires simple auditing and calibration procedures to keep the system in valid working condition. Unlike complex real-time mercury monitoring systems that require daily maintenance and costly calibrations/carrier gases, sorbent trap technology requires simple leak checks when traps are changed and quarter audits using reference devices that most operators are already familiar with.

When monitoring technology is inexpensive and simple to use,

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not only does it motivate the operators of this equipment to become more proficient at operating and troubleshooting the equipment, it also provides more reliable sample data due to the fact that there is more trust the equipment is operating correctly and any operating issues can be resolved with more confidence that the equipment is back to the operating standard.

Emission Limits

In the draft of the LCP-BREF document BAT associated emission levels for mercury emissions to air from the combustion of anthracite and bituminous coal (> 300 MWth) are referred to as 0.2 - 2 µg/m³ for new plants and as 0.2 - 6 µg/m³ for existing plants.

In Europe there are meanwhile a couple of legally binding operating permits for new and recently modified coal fired power plants in place where limits of mercury emissions to air have been fixed to values in the range of 1 – 3 µg/m³.

In the context of the above described implementation or tightening of mercury emission limits on a European level the question may be raised how mercury emissions can be measured reliably in very low concentrations. Furthermore, especially upstream of a wet scrubber for flue gas desulphurisation, the oxidation stage of mercury in the flue gas is of specific importance to achieve further reduction of mercury emissions. For the European standard reference method for determination of total mercury in flue gases EN 13211 [4] 2.6 µg/m³ is mentioned as the detection limit and repeatability is described as 1.7 µg/m³. This is not sufficient to control emission limits in the range of 1 - 3 µg/m³, as they are already effective in individual permits of coal fired power plants in Europe. In addition, the standard reference method delivers only numbers for total mercury but does not allow differentiation between elemental (metallic) mercury and oxidised mercury which can be removed in a wet scrubber much more easily.

Benefits of Alternative Measuring Methods to Standard Reference Method

The European standard reference method EN 13211 for measuring mercury emissions to air was released already in 2001. At that time ELVs were in place only in the range of 30 – 50 µg/m³ and the lower application limit of EN 13211 was appropriate for monitoring mercury emissions within that context. Nowadays, when ELVs are in the range of 1 – 3 µg/m³, alternative methods with lower application limits are necessary to demonstrate reliably compliance with such low emission limits.

EN 13211 is a wet chemical measuring method with limited flue gas throughput and limited sampling time. Furthermore it requires a lot of manual operations. Therefore reducing the lower application limit is not so easy. Many of the existing alternative methods are based on the adsorption of mercury on solid adsorbent traps, consisting of activated charcoal or iodised activated charcoal. Other solid adsorbents like potassium chloride (KCl) or the ion exchange resin Dowex® retain selectively oxidised mercury. Handling of the traps is usually very easy and the sampling can easily be automated which allows extension of the sampling time from hours to days and weeks. In particular, the combination of KCl or ion exchange traps with activated charcoal traps allows furthermore the differentiation of oxidised and elemental mercury in the flue gas duct.

The aforementioned benefits make adsorbent trap measuring methods a valuable alternative to the standard reference method as they allow easy and cost effective verification of mercury mitigation measures as part of permit obligations, differentiation of mercury oxidation state and thus reduction of costs for base line and performance tests required by authorities and finally verification of performance guarantees from catalyst suppliers regarding mercury oxidation activity of SCR catalysts.

European and International Studies

Various studies have been made in Europe and internationally which include;

Measurement of low Mercury Concentrations in Flue Gases of Combustion Plants funded by VGB and the participating power companies GDF SUEZ, Enel and E.ON.

Evaluation and comparison of US and EU reference methods for the measurement of mercy, heavy metals, PM2.5 and PM10 emission from fossil-fired power plants (The Armstrong Project) by Energy Research Center, Lehigh University, USA in collaboration with various manufacturers, suppliers and test houses from USA and Europe.

EU CEN Standards - Development of technical specification by CEN TC264 working group 8

The purpose of this Technical Specification is to establish performance benchmarks for, and to evaluate the acceptability of, sorbent trap monitoring systems used to monitor total vapour- phase mercury (Hg) emissions in stationary source flue gas streams. These monitoring systems involve continuous repetitive in-stack sampling using paired sorbent traps with subsequent analysis of the time-integrated samples.

This Technical Specification is suitable for both short term (periodic) measurements and long term (continuous) monitoring using sorbent traps.

The substance measured according to this specification is the total vapour phase Hg in the flue gas, which represents the sum of the elemental Hg (Hg0, CAS Number 7439-97-6) and gaseous forms of oxidised Hg (i.e., Hg^{2+}) in mass concentration units of micrograms (µg) per dry meter cubed (m³).

The sorbent tube approach is intended for use under relatively low particulate conditions when monitoring downstream of all pollution control devices, e.g., at coal fired power plant and cement plant. In this case, the contribution of mercury in the particulate fraction is considered to be negligible (typically less than 5 % of total Hg). However, it should be noted that the sorbent trap does take account of the finest particle fraction that is sampled with the flue gas, in addition to capturing the vapour phase mercury. Under these circumstances, the sorbent trap approach is considered to provide a representative measure of the total mercury content.

This specification also contains routine procedures and specifications that are designed to evaluate the ongoing performance of an installed sorbent trap monitoring system. The source owner or operator is responsible for the correct calibration, maintenance and operation of the monitoring system. Additional quality assurance requirements for continuous monitoring systems are defined in EN 14884 and EN 14181.

The European standard specifies a manual reference method for the determination of the mass concentration of mercury in exhaust gases from ducts or chimneys. The standard was validated for the determination of the mass concentration of total mercury in exhaust gases from the incineration of waste for the concentration range of total mercury from 0,001 mg/m³ to 0,5 mg/m31). The method may be applicable for exhaust gases from other sources with the following typical composition:

Total suspended matter	from 0 mg/m³ to 20 mg/m³
CxHy	from 0 mg/m³ to 10 mg/m³
HCl	from 0 mg/m³ to 50 mg/m³
HF	from 0 mg/m³ to 10 mg/m³
SO_2	from 0 mg/m³ to 250 mg/m³
CO	from 0 mg/m³ to 250 mg/m³
NO_x	from 0 mg/m³ to 500 mg/m³
CO_2	from 0% (volume fraction) to 15% (volume fraction)
H_2O	from 2% (volume fraction) to 25% (volume fraction) (actual)
O_2	from 8% (volume fraction) to 15% (volume fraction) (dry, actual)
Temperature	from 60°C to 140°C

CEN TC 264 working group 8 are tasked with updating and revising the standard.

The Source Testing Association

The Source Testing Association (STA) was established in 1995 the membership comprises representation from process operators, regulators, equipment suppliers and test laboratories. The STA is a non-profit making organisation.

The STA is committed to the advancement of the science and practice of emission monitoring and to develop and maintain a high quality of service to customers.

Its aims and objectives are to:

(i) contribute to the development of industry standards, codes, safety procedures and operating principles;

(ii) encourage the personal and professional development of practicing source testers and students;

(iii) maintain a body of current sampling knowledge;

(iv) assist in maintenance of a high level of ethical conduct;

(v) seek co-operative endeavours with other professional organisations, institutions and regulatory bodies, nationally and internationally, that are engaged in source emissions testing.

The Associations headquarters are based in Hitchin, Hertfordshire with meeting rooms, library and administration offices.

The Association offers a package of benefits to its members which include:

- Technical advice relating to emission monitoring
- Conference and exhibition opportunities
- Seminars and training on a variety of related activities
- Representation on National, European and International standards organisations
- Training in relation to many aspects of emission monitoring
- Liaison with regulators, UK and International, many of whom are members.

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