



MERCURY SORBENT TRAP SAMPLING FOR COMPLIANCE IN THE US

The current US EPA mercury reference method is 30B. Prior to 2007, as part of the Clean Air Mercury Rule, EPA Method 324 was proposed along with PS-12A (68 FR 4652). During the field testing programs to demonstrate commercially available mercury CEMS at coal-fired utility boilers, the EMC (Emission Measurement Center) also evaluated procedures for long-term integrated mercury monitoring method using sorbent trap sampling. The results, along with comments received on proposed Method 324 were used to finalize procedures for sorbent trap mercury monitoring. These were published as Appendix K to 40 CFR Part 75 along with the Clean Air Mercury Rule on May 18, 2005.

Prior to this (ASTM) D6784-02, the Ontario Hydro (OH) method, and EPA Method 29 were the HG reference methods. Both are wet-chemistry-based methods that require a high level of quality assurance to obtain data that could meet CAMR (Clean Air Mercury Rule). The adoption of method 30B has simplified testing while providing more accurate mercury measurement results.

Now for the EU EN 13211 is the Standard Reference method for the measurement of mercury emissions. This method has been validated to measure total mercury levels from 1 to 500 $\mu\text{g}/\text{m}^3$. EN 13211 is also a wet chemistry approach that relies on absorption of mercury into impinger solutions like the Ontario Hydro Method. The sample is extracted from the stack using a heated probe and particulates are collected on a filter. After, the sample gas is passed through absorption bottles containing appropriate absorption solution to collect gaseous phase mercury.

Two absorption solutions can be used, either 2% $\text{KMnO}_4/10\% \text{H}_2\text{SO}_4$ (absorption solution 1) or 4% $\text{K}_2\text{Cr}_2\text{O}_7/20\% \text{HNO}_3$ (absorption solution 2). After sampling the filter and absorption, solutions are taken to the analytical laboratory and the result is given as the sum of the gaseous and particulate phases, i.e., as total mercury measurement.

In May 2005, the EPA finalized operational and quality assurance (QA) requirements for sorbent trap monitoring systems, in Appendix K of 40 CFR Part 75. Motivated by the regulatory flexibility allowing the use of sorbent traps, the industry committed resources to commercialize systems capable of meeting Appendix K requirements. By the following year, several vendors had developed field-worthy automated sorbent trap monitoring systems trap monitoring systems. Also, the development of a thermal desorption method 7473 for analyzing samples on-site had also significantly advanced. Appendix K was subsequently vacated as part of the vacatur of the May 2005 final rule. However, the basic requirements of Appendix K were later published in support of the cement industry MACT rule, as Performance Specification 12B (PS 12B) in 40 CFR Part 60.

On February 16, 2012, the EPA published the Mercury and Toxics



Standards (MATS) rule (40 CFR 63, Subpart UUUUU), establishing national emissions limitations and work practice standards for certain hazardous air pollutants (HAP) emitted from coal-fired and oil-fired electric utility steam generating units. The published MATS rule requires coal-fired units to monitor emissions using either mercury CEMS or sorbent trap monitoring systems, and the sorbent trap systems must be operated, maintained, and calibrated according to PS 12B.

Method Comparison

Method 30B is a procedure for measuring total vapor phase mercury (Hg) emissions from coal-fired combustion sources using sorbent trap sampling and an extractive or thermal analytical technique. This method is only intended for use only under relatively low particulate conditions (e.g., sampling after all pollution control devices). Quality assurance and quality control requirements are included to assure that you, the tester, collect the data of known and acceptable quality for each testing program. This method is designed to measure the mass concentration of total vapor phase Hg in flue gas, including elemental Hg (Hg^0) and oxidized forms of Hg (Hg^{+2}), in micrograms per dry standard cubic meter.

EN 13211 is a wet chemistry method approach that relies on isokinetic sampling stack gas passing through a filter to capture particulate then absorption of mercury into impinger solutions. This method is also not suited for low mercury concentration sources that are less than 1 $\mu\text{g}/\text{m}^3$. Field testing studies show that source mercury stack emissions after the ESP or bag house have indicated that the proportion of particulate bound mercury was extremely low. Testing data showed greater than 95% was vapor phase mercury both elemental & oxidized. EN 13211 sampling time is much longer than using EPA Method 30 B, and analysis of the solutions from the impingers is much more costly and time consuming.

Adopting EPA Method 30B as a HG reference method would increase accuracy of mercury measurement, reduce costs and simplify testing and this has been proven in the US with the adoption of Mats, Neshap & Industrial Boiler Mact rules for Coal & Oil fired power plants, Cement plants, Pulp & Paper and many other sources that use Method 30B to certify permanent sorbent trap systems or HG CEMS and use PS-12B for continuous HG monitoring using sorbent traps.

Ongoing Mercury Emissions Measurement

Referencing power plants' approach for continuous HG monitoring to comply with the release of the EPA Mats Rule in 2012 (Mercury

Air Toxic Standards) with an effective date of the rule is April 15th, 2015. Most of the power plants chose sorbent traps to comply with this new rule using Performance Specification 12B, the procedures for monitoring total vapor phase mercury emissions from stationary sources using a sorbent trap monitoring system.

The purpose of Performance Specification 12B (PS 12B) is to establish performance benchmarks for, and to evaluate the acceptability of, sorbent trap monitoring systems used to monitor total vapor-phase mercury (Hg) emissions in stationary source flue gas streams. These monitoring systems involve continuous repetitive in-stack sampling using paired sorbent media traps with periodic analysis of the time-integrated samples with typical sampling periods of 7 days between trap change outs. These procedures are only intended for use under relatively low particulate conditions (e.g., monitoring after all pollution control devices). This specification is for evaluating the acceptability of total vapor phase Hg sorbent trap monitoring systems installed at stationary sources at the time of, or soon after, installation and whenever specified in the regulations.

The Hg monitoring system must be capable of measuring the total concentration of vapor phase Hg (regardless of speciation), in units of $\mu\text{g}/\text{dscm}$. Comments have recently been made that sorbent traps can't report real time data. However, more continuous HG data is collected with a sorbent trap system using PS-12B traps than a HG CEMS because the trap runs continuously. The result being that more stack gas is sampled with a sorbent trap, thus giving a better total HG concentration average for the given period of sampling time.



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