Dioxin Emission Monitoring Systems

The U.S. EPA Environmental Technology Verification (ETV) Program's Advanced Monitoring Systems (AMS) Center, operated by Battelle under a cooperative agreement with EPA, has verified the performance of four dioxin emission monitoring systems.[1] The verification test was conducted in collaboration with EPA's Office of Research and Development, Office of Solid Waste and Emergency Response, and Office of Air Quality Planning and Standards; the Chlorine Chemistry Council, and Battelle. The dioxin emission monitoring systems are designed to replace manual stack sampling techniques used to quantify dioxins in flue gas which are labor intensive and expensive. The verification reports and statements can be found at: **http://www.epa.gov/nrmrl/std/etv/vt-ams.html** under dioxin emission monitoring systems.

Technology Description and Verification Testing

ETV verified the technologies using a 2.94 million British thermal unit (860 kilowatts) per hour, 3-Pass Wetback Scotch Marine Package Boiler, manufactured by Superior Boiler Works, Inc., and located at the EPA Research Triangle Park (NC) facility. The four verified technologies (**Table 1**) fall under one of two categories: automated isokinetic sampling systems of flue gas with laboratory analysis, or semi-continuous laser-based systems that produce ions which are typically detected using a time-of-flight mass spectrometer (TOFMS). Long-term continuous samplers collect samples over time periods up to several weeks to obtain a cumulative record of source emissions and provide evidence of emission levels. Real or semi-real-

Verification test site for dioxin emission monitoring systems

Dioxin at a Glance

Dioxins refers to a group of chemical compounds that are members of three closely related families: the polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and certain polychlorinated biphenyls (PCBs).

Health Effects

Short-term exposure of humans to high levels of dioxins may result in skin lesions, such as chloracne and patchy darkening of the skin, and altered liver function. Long-term exposure is linked to impairment of the immune system, the developing nervous system, the endocrine system, and reproductive functions. Chronic exposure of animals to dioxins has resulted in several types of cancer.

Sources

Dioxins are mostly formed as a result of combustion processes such as commercial or municipal waste incineration and from burning fuels (like wood, coal or oil). EPA's Draft Dioxin Reassessment Report[1] makes the finding that anthropogenic emissions dominate current releases in the United States, but acknowledges the need for more data on natural sources.

[1] Draft has been provided to The National Academy of Sciences for review.

Table 1. Verified Dioxin Emission Monitors

Technology Name	Description
BM Becker Messtechnik Gmbh AMESA (Adsorption Method for Sampling Dioxins and Furans)	A long-term sampling apparatus which is based on the isokinetic sampling of flue gas and the adsorption of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and other persistent organic pollutants on an exchangeable adsorption-resin-filled cartridge.
Monitoring Systems GmbH Dioxin Monitoring System	A long-term sampling device using an automatic isokinetic sampler for measurement of PCDDs, PCDFs, and other persistent organic pollutants. Samples are collected using a filter cartridge.
IDX Technologies, LTD. RIMMPA-TOFMS (Resonance Ionization with Multi-Mirror System Photon Accumulation Time-of-Flight Mass Spectrometer)	A laser-based mass spectrometry system that has been developed for the real-time detection and quantification of PCDD and PCDFs.
SRI International Jet-REMPI (Resonance Enhanced Multi-photon Ionization)	A laser-based system that produces ions which are typically detected using a TOFMS that takes advantage of the pulsed nature and well-defined temporal character of laser ionization.

[1] The ETV Program operates largely as a public-private partnership through competitive cooperative agreements with non-profit research institutes. The program provides objective quality-assured data on the performance of commercial-ready technologies. Verification does not imply product approval or effectiveness. ETV does not endorse the purchase or sale of any products and services mentioned in this document.

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time continuous monitors, with a frequency of measurement at real time or up to an hour, provide quick feed back to the plant operator by measuring dioxin emission levels on-site.

ETV evaluated the performance of the dioxin monitoring systems in terms of relative accuracy (RA), range, data completeness, and operational factors (ease of use, maintenance, and consumables/waste generated). RA and range were determined by comparing the dioxin monitoring systems results to those from EPA Method 23 reference samples collected simultaneously. Range was determined from measurements of a variety of defined operating conditions that produced different levels of dioxins. **Table 2** contains some of the test parameter results. Because the ETV Program does not compare technologies, the performance results shown in **Table 2** do not identify the vendor associated with each result and are *not* in the same order as the list of technologies in **Table 1**.

Table 2. Selected Performance Results for Verified Dioxin Monitoring Systems				
Measurement Systems				
	A	**B**	**C**	**D**
RA[a] (%)	22.6	48.2	78.2	Analysis of the collected samples could not positively quantify PCDD/PCDFs
RSD[b,c] (%)	9.7	21.9	61.5	No quantifiable results
Operational Factors				
Instrument Installation Time	<48 hrs	<48 hrs	N/A[d]	Could not be evaluated
Time for Operation Training	1 - 2 hrs in basic operation	2 hrs in basic operation	Extensive training/ experience for operation of system	Extensive training/ experience for operation of system
Down Time	<1%	3%	7%	Could not be evaluated

[a] Relative Accuracy for PCDDs and PCDFs. A 0% value means perfect accuracy.
[b] Relative Standard Deviation: The intermethod relative standard deviation (RSD) was calculated using the standard deviation of the paired dioxin monitor and reference method results for the test run.
[c] Relative Standard Deviation of Reference Method 23 was found to be 8.4
[d] Installation time was not part of the verification test for this monitor. Instrument was installed before verification testing.

Potential Outcomes of Dioxin Emission Monitoring Systems

Demonstrated effectiveness of dioxin emission monitoring systems promotes:

- More continuous monitoring of dioxin emissions

- Improved emission inventories

- Better estimates of human exposures

- Opportunities for process control to reduce dioxin emissions.

Verified dioxin monitoring systems

References

U.S. EPA, ETV, http://www.epa.gov/etv/.

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