

*Presented at the 17th Annual Waste Testing and Quality Assurance Symposium
August 15, 2001, Arlington, Virginia*

Development and Evaluation of Mercury CEMS for Combustion Emissions Monitoring

Jeffrey V. Ryan

U.S. Environmental Protection Agency
National Risk Management Research Laboratory
Air Pollution Prevention and Control Division
Research Triangle Park, North Carolina 27711

ABSTRACT

Continuous emission monitoring systems (CEMS) for mercury (Hg) are receiving increased attention and focus. Their potential use as a compliance assurance tool is of particular interest. While Hg CEMs are currently used in Europe for compliance purposes, use of Hg CEMS in the United States (U.S.) has focused on combustion research and Hg control technology evaluation applications. Hg CEMS are now receiving increased attention as compliance assurance tools. Several programs exist to evaluate Hg CEM measurement performance. It is through these efforts that application-specific measurement issues are investigated. Collectively, these efforts have served to advance the state-of-the-art of the technology as evidenced by the number and types of CEMS now available and the various applications in use.

INTRODUCTION AND BACKGROUND

Anthropogenic releases of Hg to the environment have become a serious global and national concern due to the toxicity of Hg in its organic form. Combustion of fossil fuels, municipal and medical waste, as well as hazardous waste collectively represents a significant contribution to the Hg released in the U.S. These combustion processes emit Hg in a number of inorganic forms that can be converted, by naturally occurring biological processes, into the highly toxic methyl Hg species. Understanding combustion source emissions is a necessary step in understanding the fate and transport of Hg, and ultimately the risk to human health and the environment. Hg CEMS are valuable tools that can aid in understanding the contributions from these sources as well as potentially provide assurance of compliance with established emission limits. In addition, Hg CEMS can provide a number of other potential benefits, including:

- Real-time emission data
- Greater understanding of process variability and operation
- Operational data for system optimization and process control
- Evaluation of Hg control strategies

- Potentially less reliance on waste feed characterization (i.e., for incinerators)
- Greater public assurance

These approaches have largely driven the advancement of the Hg CEM technologies in the U.S., despite the lack of a clear regulatory incentive.

Hg CEMS are currently used in Europe for compliance purposes, primarily in Germany. Hg CEMS are installed at over 100 facilities, including fossil-fuel boilers and municipal waste combustors.¹ The types of pollution control devices associated with combustors have a significant impact on Hg CEM measurement ability. A representative German site has eight separate devices to control emissions: two electrostatic precipitators (ESPs), two scrubbers, a spray dryer, a carbon adsorber, a catalytic oxidizer, and a baghouse.¹ The effects of potential interferants such as carbon dioxide (CO₂), carbon monoxide (CO), nitrogen oxides (NO_x), water vapor, sulfur dioxide (SO₂), ammonia (NH₃), hydrochloric acid (HCl), chlorine (Cl₂), hydrocarbons, and particulate are minimized, if not eliminated. After passing through the control devices, particularly ESPs, baghouses, and wet scrubbers, most, if not all, of the Hg remaining in the flue gas is in the elemental phase.¹ Measuring elemental Hg is much less difficult than measuring the other forms of Hg associated with combustion processes.

Extrapolating European Hg CEM measurement performance to U.S. applications is difficult due to the diversity in combustion sources and pollution control device availability and configuration. As a result, the U.S. measurement environment is likely to be much more severe and diverse as well. In order for Hg CEMS to be considered for regulatory compliance assurance, acceptable performance will need to be demonstrated. Hg CEMS are not likely to be required unless sufficient performance data are available to justify the promulgation of a CEM-based standard.

It is this lack of demonstrated performance that caused EPA's Office of Solid Waste (OSW) to propose the use of total Hg CEMS for compliance assurance only as an option in the Phase I Maximum Achievable Control Technology (MACT) rule for Hazardous Waste Combustors (HWCs).² Without a mandatory requirement for Hg CEMS, Hg CEM vendors and potentially regulated facilities appear to be reluctant to invest in their further development. Further, there is little incentive to generate the data necessary to support regulatory consideration. As a result, few opportunities exist to demonstrate CEM performance, and those demonstrations that have been conducted have not been sufficiently robust to fully support a Hg CEM-based standard. As a result, the developmental progress of Hg CEMS in the U.S. has been hindered.²

HOW Hg CEMS WORK

Mercury CEMS are similar to most combustion process CEMS in that the emission sample typically must be extracted from the stack and then transferred to the analyzer for detection. However, Hg monitoring is complicated by the fact that Hg exists in different forms (particulate-bound, oxidized, elemental) and that quantitative transport of all these forms is difficult.

Typically, Hg CEMS directly measure (detect) only elemental Hg. Hg CEMS measure total Hg through the use of a conversion system that reduces the nonelemental or oxidized Hg to elemental Hg for detection. Mercuric chloride is considered to be the primary oxidized form of Hg. Although particulate-bound Hg can also be reduced to the gaseous elemental form, particulate sample delivery issues make this impractical. As a result, for most commercially available CEMS, the total Hg measured is in fact total gaseous Hg (TGM).

Nonelemental Hg is commonly converted using a liquid reducing agent (e.g., stannous chloride). This technique is least preferable, though more established. The use of wet chemical reagents is considered to be a significant limitation to Hg CEM use. The wet chemicals typically possess corrosive properties and require frequent replenishment. The spent reagents commonly possess hazardous properties that result in waste disposal concerns. In addition, the reducing ability of reagents such as stannous chloride is affected by high levels of SO₂.³

In addition to the more established wet chemistry conversion methods, dry conversion methods are now available. These techniques use high-temperature catalysts or thermal reduction units to not only convert nonelemental Hg to the reduced form, but also condition the sample for analysis by removing selective interferants. This approach does much to minimize the size of the conversion system as well as maintenance requirements.

Because the particulate form is difficult to transfer and is also often a measurement interferant, the particulate is typically filtered out and remains unmeasured. This could potentially impart a negative bias to the total Hg measurement. This bias could be further amplified as certain types of particulate may actually capture gas-phase Hg. This may not be significant for sources where particulate-bound Hg is not present in appreciable quantities, but may be significant for high-particulate-emitting sources (e.g., sources with minimal particulate control). Therefore, the ability to measure the particulate component is important and should not be ignored.

Similarly, there are known complications with the quantitative transfer of mercuric chloride (HgCl₂). HgCl₂ is water soluble and reactive with many surfaces. Losses due to adsorption are a major concern. As a result, recent emphasis has been placed on locating the nonelemental Hg conversion system as close as possible to the source so that the less reactive elemental form is transferred from the source to the detection unit.

In general, Hg CEMS can be distinguished by their Hg measurement detection principle. Detection systems include: cold-vapor atomic absorption spectrometry (CVAAS); cold-vapor atomic fluorescence spectrometry (CVAFS); *in-situ* ultraviolet differential optical absorption spectroscopy (UVDOAS); and atomic emission spectrometry (AES).

Most Hg CEM systems employ CVAAS or CVAFS as the detection technique. These detection techniques are susceptible to measurement interferences resulting from the presence of common combustion process emissions. Gases such as NO_x, SO₂, HCl, and Cl₂ can act as measurement interferants as well as degrade the performance of concentrating devices (e.g., gold amalgams).

As such, conditioning systems and/or techniques that remove or negate the effects of these interfering gases are required prior to sample delivery to the detector. SO₂ is a major spectral interferant with most CVAA detection systems. The effects of SO₂ are commonly negated through the use of a gold trap. The sample gas is directed through a gold trap, where the Hg forms an amalgam with the gold surface. Once the trap is loaded, it is heated and flushed with a SO₂-free carrier gas to the detector. The trapping also serves to improve measurement sensitivity by concentrating the sample. A trapping device is required of CVAFS systems to achieve optimum sensitivity: not because of the concentrating aspect, but because the carrier gas will enable maximum sensitivity. Oxygen and nitrogen, present in combustion flue gases, have spectral quenching effects that suppress measurement sensitivity. Conditioning of the sample gas prior to reaching the gold trap is often required. In addition, HCl and NO_x in combination can poison the gold surface, affecting Hg capture. Removal of both or either of these constituents is required.

An alternative to the Hg measurement approach is AES. With this technique, Hg is ionized by a high energy source (e.g., plasma) and the emission energy detected. A major advantage of this technique is that all forms of Hg, including particulate-bound Hg, are capable of being ionized and detected. Another advantage of AES is that the ionization source and detector can be located directly at the source, avoiding sample delivery issues. In addition, AES is less susceptible to spectral interferences from common flue gas constituents as compounds are ionized to their elemental form prior to detection.

Speciated Hg measurements are becoming increasingly important with respect to characterizing combustion process emissions and evaluating Hg control strategies. While no commercially available CEMS measure the various speciated forms of Hg directly, several commercially available total gaseous Hg CEMS have been enhanced to measure speciated Hg (the elemental and oxidized forms) indirectly by determining the difference between elemental Hg and TGM. This difference is recognized as the oxidized form. Separate Hg measurements are made before and after the conversion step in order to calculate the oxidized form. This indirect speciation method is referred to as "speciation by difference." Based on the current understanding that the oxidized species of primary interest is HgCl₂ and that HgCl₂ is the dominant form of oxidized Hg present, the speciation by difference technique is considered an acceptable approach to obtaining speciated Hg measurements.²

The key to performing the speciated Hg measurement is being able to perform reliable elemental Hg measurements. The oxidized form must be removed without affecting the true elemental component. This is often accomplished using a liquid reagent of some sort to quantitatively remove the water-soluble oxidized Hg forms and allow the insoluble elemental Hg to pass through, unretained. These reagents may also neutralize the effects of measurement interferants. The greatest concern is the reliability of the speciated Hg measurement. Measurement artifacts exist that bias the speciation, primarily by over-reporting the level of the oxidized species. The largest cause of this bias is the reactivity of certain types of particulate matter (PM). PM may possess catalytic properties that, at the conditions of Hg CEM PM filtering environments,

elemental Hg can be oxidized across the PM surface.^{2,4} This is not an issue from a TGM measurement standpoint (unless transport of oxidized Hg is an issue). However, it may have major implications when measuring environments possessing high PM loadings. This bias is minimized in low PM-loading environments, consistent with post-particulate control measurement locations.⁴ Another potentially significant source of speciated Hg measurement bias takes place in the liquid phase. In combustion flue gas environments where Cl₂ is present, under certain conditions the Cl₂ may react in the liquid phase to oxidize elemental Hg.⁵ There is evidence that this problem can be mitigated by modifying the liquid reagent.⁵

Hg CEM APPLICATIONS AND PERFORMANCE EVALUATION ACTIVITIES

Hg CEMS in the U.S. have been used primarily to support combustion research objectives and characterize the emissions from various combustion sources. These have largely been independent efforts. More recently, collaborative efforts have been used to further knowledge of Hg emissions from coal-fired utilities, including Hg emission control.

The Department of Energy (DOE) and EPA, in conjunction with the University of North Dakota (UND), have conducted a number of laboratory studies and field tests evaluating the measurement performance of select Hg CEMS to support research characterizing Hg emissions from coal-fired utilities, including the evaluation of viable Hg control techniques.^{3,4} These tests have done much to investigate measurement issues specific to this combustion source category, particularly with respect to the quality of speciated Hg measurements. This research has investigated alternative sample conditioning and Hg conversion systems, the catalytic effects of PM, and the quality of reference method (RM) measurements used for comparative purposes.

Similarly, the EPA's Office of Research and Development, National Risk Management Research Laboratory (NRMRL) has conducted research examining the measurement performance of select Hg CEMS in support of fundamental Hg control studies. This research has investigated the quality of speciated Hg measurements including liquid-phase oxidation of Hg,⁵ sample conditioning approaches, and the development and evaluation of tools necessary for the conduct of field performance testing. Quality Assurance/Quality Control (QA/QC) tools such as elemental and oxidized Hg gas standards have been investigated.

A number of tests have been conducted specifically to evaluate Hg CEMS as a compliance assurance tool. The first such test, sponsored by EPA's OSW, evaluated the performance of three total Hg CEMS at a cement kiln that also burned hazardous waste.⁶ Measurement performance was evaluated following Draft Performance Specification 12 (PS 12) entitled *"Specifications and Test Procedures for Total Mercury Continuous Monitoring Systems in Stationary Sources."*⁷ At the time, this was a relatively new test procedure and had yet to be implemented. In fact, the guidance called for elemental Hg and HgCl₂ gas standards that had yet to be developed and proven. The tests were only marginally successful. None of the Hg CEMS met the performance test requirements. OSW concluded that Hg CEMS would not be considered as a compliance tool for HWCs.⁶ In retrospect, the harshness of the kiln's emission environment

was concluded as a major cause of the test program's lack of success.^{6,8} The cement kiln chosen lacked acid gas control and had relatively high PM loading, resulting in severe interferences and operational difficulties.

The DOE Mixed Waste Focus Area (MWFA) has sponsored several tests determining the measurement performance of a single total Hg CEM under hazardous waste incineration conditions.^{9,10} Measurement performance was also evaluated following PS 12. These tests demonstrated not only Hg CEM performance, but also that additional elements of the PS 12 test procedures could be implemented. A prototype elemental Hg compressed gas standard was used for the first time. While these tests have been relatively successful, they are still limited in scope and application.

Recently, the EPA's Environmental Technology Verification (ETV) Program, in collaboration with NRMRL, has completed testing of four commercially available Hg CEMS from three vendors using the unique capabilities of NRMRL's pilot-scale combustion test facility. These tests examined the measurement performance of both total and speciated Hg CEMS under two distinct and diverse combustion conditions. Coal and chlorinated waste combustion conditions were simulated. These verification tests used PS 12 as guidance, but also considered specific measurement issues of interest and innovative approaches that better examined these issues. The pilot-scale tests were unique in that specific measurement issues were investigated as variables. The pilot-scale combustion facility enabled independent control of Hg concentration and species. As a result, the total Hg measurement could be challenged by the distribution of oxidized and elemental Hg. Interference flue gas constituents were also independently examined. The ETV testing made use of several new QA/QC tools. Newly developed elemental Hg compressed gas standards were used to determine Hg CEM calibration drift and system bias. As a result, not only were Hg CEMS evaluated, but improved techniques for evaluating Hg CEMS were demonstrated. Performance data for the participating Hg CEMS are not yet available.

FUTURE DIRECTIONS AND NEEDS

Interest in the use of Hg CEMS for a variety of monitoring purposes is increasing. This includes interest from the regulatory perspective at the federal, state, and regional levels. Of course, in order to be considered for regulatory applications, acceptable performance must be demonstrated first. The generation of Hg CEMS measurement performance data has been hindered by the lack of accepted test procedures to accomplish this objective. PS 12, proposed by OSW to support the collection of Hg CEMS performance data from HWCs for regulatory monitoring consideration, remains in draft form. Application of PS 12 to multiple source categories was not intended. The particular demands placed on Hg CEMS by the emissions characteristics of each Hg emissions source category or subcategory must be considered. Furthermore, successful demonstration of one particular category, does not convey necessarily to other categories. As a result, a variety of measurement performance data representing these source categories are needed.

The Office of Air Quality Planning and Standards (OAQPS) Emission Measurement Center (EMC) has recently initiated a study to determine the measurement performance of two commercially available Hg CEMS at a coal-fired utility, which represents a source category currently under regulatory consideration. Measures of performance will be recorded to determine potential monitoring applications based on measurement performance achieved. Data from this study, and future studies of Hg CEMS measurement performance at additional source categories, should aid in the future crafting of a performance specification for application of Hg CEMS at a variety of source categories. In the interim, OAQPS may consider publishing a source-category-specific performance specification.

In addition, the ETV pilot-scale tests, the availability of elemental Hg and HgCl₂ gas standards, and advancements in Hg CEMS technologies provide evidence that techniques and tools suitable for assessing Hg CEMS measurement performance are now available. However, further demonstration of these new tools is necessary for them to be accepted. While the stability of the elemental Hg compressed gas standard has been confirmed, techniques for establishing the standard's true concentration have not. As a result, quantitative use of the standard is limited. Similarly, acceptance of a HgCl₂ standard is valuable: this standard is used to assess Hg conversion system effectiveness as well as overall sampling system delivery efficiency and reactivity, parameters not challenged by an elemental Hg gas standard. This is particularly relevant in measurement applications where oxidized Hg may be the predominant Hg form present.

Additional Hg CEMS research and measurement performance data are still needed to truly demonstrate the viability of the technology under all potential applications. As a process control monitor or as a tool to evaluate Hg control strategies, there are still measurement obstacles to be overcome, particularly with respect to speciated measurements. Sampling at pollution control inlet locations presents unique measurement challenges. When considering Hg CEMS as a potential compliance assurance tool, the obstacles do not appear to be technological as much as lack of performance demonstration. Data are needed that demonstrate not only measurement abilities, but also CEMS reliability, maintenance and operational requirements, and long-term performance. These performance elements will be the focus of future EPA Hg CEMS field testing.

SUMMARY

Currently, at least 10 Hg CEMS vendors exist. Half of them offer speciating versions. Total Hg CEMS appear to be a more mature technology than has been widely perceived in the past. The units are becoming simpler to operate and maintain. The techniques employed to reduce oxidized species to the detectable elemental form are less reliant on wet chemical approaches. In addition, techniques for managing potential interferants are also more advanced. Moreover, several Hg CEMS vendors have developed QA/QC capabilities to perform their own instrument calibration drift and system bias checks from internal elemental Hg gas sources. These capabilities are needed for routine daily operational performance verification.

Hg CEMS for both total and speciated Hg measurements are now becoming an integral component of EPA's and DOE's Hg combustion research programs. It is through these research programs that the techniques and tools necessary for evaluating measurement performance have been improved. The development of gas standards for elemental Hg and HgCl₂ are significant advancements. These improvements should be valuable inputs to any EPA efforts to revise PS 12 or develop other Hg CEMS performance specifications and to develop QA/QC requirements for Hg CEMS operation for compliance assurance purposes.

In order for Hg CEMS to be considered for compliance assurance purposes, acceptable performance will need to be demonstrated. However, opportunities for demonstrating measurement performance to provide the necessary data have been limited and little incentive exists to support such activities. Also, the procedures necessary for evaluating measurement performance are viewed as less than adequate. As a result, the developmental progress of Hg CEMS is hindered.

REFERENCES

- 1) Parker, B., "European Mercury Monitoring Trip Report," U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Emission Measurement Center, Research Triangle Park, NC, October 10, 2000
- 2) Hedges, S., J. Ryan, and R. Stevens, "Workshop on Source Emission and Ambient Air Monitoring of Mercury," September 13-14, 1999, Bloomington, MN, U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Cincinnati, OH, June 2000, EPA/625/R-00/002 (NTIS PB2001-100963)
- 3) Laudal, D. L., T. D. Brown, and P. Chu, "Testing of a Mercury Continuous Emission Monitor at Three Coal-Fired Electric Utilities," 92nd Annual Meeting and Exposition of the Air and Waste Management Association, St. Louis, MO, June 1999
- 4) Electric Power Research Institute, "Evaluation of Flue Gas Mercury Speciation Methods," Final Report TR-108988, Palo Alto, CA, December 1997
- 5) Linak, W. P., J. V. Ryan, B.S. Ghorishi, and J. O. L. Wendt, "Issues Related to Solution Chemistry in Mercury Sampling Impingers," *Journal of the Air and Waste Management Association*, 2001, 51:688-698
- 6) U. S. Environmental Protection Agency, "Draft Mercury Continuous Emissions Monitor System Demonstration, Volume I: Holnam, Inc., Hazardous Waste Burning Kiln, Holly Hill, SC," Office of Solid Waste and Emergency Response, Washington, DC, March 1998

- 7) U. S. Environmental Protection Agency, "Draft Performance Specification 12 - Specifications and Test Procedures for Total Mercury Continuous Monitoring Systems in Stationary Sources," Office of Air Quality Planning and Standards, Emission Measurement Center, Research Triangle Park, NC, <http://www.epa.gov/ttn/emc/propperf/ps-12.pdf> (accessed July 2001)
- 8) French, N., S. Priebe, and W. Haas, Jr., "State-of-the-Art Mercury CEMS," *Analytical Chemistry News & Features*, July 1, 1999, 470-475A
- 9) Gibson, L. V., J. E. Dunn, R. L. Baker, W. Sigl, and I. Skegg, "Field Evaluation of a Total Mercury Continuous Emission Monitor at a U. S. Department of Energy Mixed Waste Incinerator," 92nd Annual Meeting and Exposition of the Air and Waste Management Association, St. Louis, MO, June 1999
- 10) Baker, Ronald L. "Are We Ready for Meeting Continuous Emission Monitoring Requirements for Total Mercury Combustion Sources?" 93rd Annual Meeting and Exposition of the Air and Waste Management Association, Salt Lake City, UT, June 2000

TECHNICAL REPORT DATA <i>(Please read instructions on the reverse before completing)</i>		
1. REPORT NO EPA/600/A-01/079	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Development and Evaluation of Mercury CEMs for Combustion Emissions Monitoring	5. REPORT DATE	
	6. PERFORMING ORGANIZATION CODE	
7. AUTHORS Jeffrey V. Ryan	8. PERFORMING ORGANIZATION REPORT NO	
9. PERFORMING ORGANIZATION NAME AND ADDRESS See Block 12	10. PROGRAM ELEMENT NO.	
	11. CONTRACT/GRANT NO. NA (Inhouse)	
12. SPONSORING AGENCY NAME AND ADDRESS U. S. EPA, Office of Research and Development Air Pollution Prevention and Control Division Research Triangle Park, North Carolina 27711	13. TYPE OF REPORT AND PERIOD COVERED Published paper;	
	14. SPONSORING AGENCY CODE EPA/600/13	
15. SUPPLEMENTARY NOTES APPCD project officer is Jeffrey V. Ryan, Mail Drop 4, 919/541-1437. For presentation at 17th Annual Waste Testing and Quality Assurance Symposium, Arlington, VA, August 12, 2001.		
16. ABSTRACT The paper discusses the increased attention and focus being received by continuous emission monitors (CEMs) for mercury (Hg). Their potential use as a compliance assurance tool is of particular interest. While Hg CEMs are currently used in Europe for compliance purposes, use of Hg CEMs in the United States (U.S.) has focused on combustion research and Hg control technology evaluation applications. Hg CEMs are now receiving increased attention as compliance assurance tools. Several programs exist to evaluate Hg CEM measurement performance. It is through these efforts that application-specific measurement issues are investigated. Collectively, these efforts have advanced the state-of-the-art of the technology as evidenced by the number and types of CEMs now available and the various applications in use.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution Mercury (Metal) Emission Monitors Evaluation Combustion	Pollution Control Stationary Sources	13B 07B 14G 21B
18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES 8
	20. SECURITY CLASS (This Page)	22. PRICE