

IMPLEMENTING MERCURY CEMS IN DOE MIXED WASTE TREATMENT SYSTEMS

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ABSTRACT

This paper examines the current state of the art of mercury continuous emission monitors (CEMs), and their usability for monitoring effluent from mixed waste treatment systems. EPA's Office of Solid Waste (OSW) is not mandating mercury CEMs in the draft Maximum Achievable Control Technology (MACT) Rule for hazardous waste incinerators. However, voluntary use of mercury CEMs can be negotiated on a site-by-site basis to reduce up-front waste feed characterization, compliance testing, and operational costs.

It is important to evaluate the usability of mercury CEMs for two reasons. First, mercury is a ubiquitous pollutant for DOE, and has unique ramifications in treatment systems. Second, recent DOE/EPA field test results may have unfairly branded mercury CEMs as unworkable for hazardous waste applications.

In this paper we compare 17 different mercury (and multi-metal) CEMs both under development and commercially available. We base these comparisons on results from field tests, direct discussions with vendors, and literature. We also discuss performance requirements (e.g. calibration and detection limits) in the EPA/OSW draft MACT rule, compared to requirements in German TUV regulations. This paper also includes a discussion on some practicalities and terminology regarding speciating mercury CEMs.

With no regulatory-based market for mercury CEMs, implementation will depend on clear, achievable performance specifications and validation tests. Individual permit writers can work with a facility to make site-specific decisions how to use mercury CEMs where practical. Draft EPA performance specifications, PS12, will undoubtedly play a role in site-by-site implementation. EPA and DOE can also work together to define and conduct more realistic validation tests.

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INTRODUCTION

We are interested in mercury CEMs as they might be applied to the three DOE mixed waste incinerators:

1. Waste Experimental Reduction Facility (WERF), at INEEL, near Idaho Falls, Idaho.
2. Toxic Substance Control Act Incinerator Facility (TSCA), at Oak Ridge, near Oak Ridge, Tennessee, and
3. Consolidated Incineration Facility (CIF) at Savannah River, near Aiken, South Carolina.

Approximate stack conditions at each facility are compared in Table I. These numbers, based on trial burn and/or typical operating data, show WERF to have dry, hot stack gas, while TSCA and CIF have wet and relatively cooler stack gas. The SO₂ concentration shown for CIF is misleading. CIF does not actually measure SO₂ in the stack, so the number given is based on minimum detection limit for sulfur in the feed. In practice, CIF expects to have very little sulfur in any waste feed. SO₂ concentrations are not available from WERF. Average mercury emissions for the three facilities vary considerably, based primarily on mercury concentrations in the feed. Individual waste packages can vary from less than 1 ppm to greater than 20,000 ppm. However, with waste blending and time averaging of emissions, actual mercury emissions tend to be in the range of 5 µg/dscm to 1000 µg/dscm.

Table I. Summary of approximate stack conditions at 3 DOE mixed waste incinerators.

Effluent Parameter	WERF	TSCA	CIF
Moisture, %	3	50	60
Particulate Matter (gr/dscf @ 7% O ₂)	0.007	0.004	0.002
NO _x , ppmv	?	60	90-360
SO ₂ , ppmv	?	<0.5	<220
CO ₂ , %	2	7	7
HCl, lb/h	<4	0.008	0.048
Cl ₂ , lb.h	?	0.01	?
O ₂ , %	19	9	11
Gas Flow, dscm	10,000	7200	7000
Stack Temperature, °F	350	180	220

MERCURY REGULATIONS: EMISSION STANDARDS & COMPLIANCE (MACT Rule)

What the regulations require.

The draft MACT rule for hazardous waste combustors will be promulgated in April, 1999. Subsequent to this law, facilities will have 3 years to comply, with an optional one-year extension. Regardless of whether mercury control technologies are used, compliance will at least partially be based on mercury limits in the waste feed. The final rule will specify a mercury emission standard somewhere between 50 and 100 µg/dscm. For a facility without mercury control, this would result in a mercury feed limit of about 0.5 ppm. This is equivalent to about 0.1 gm of mercury in one 55-gallon drum. Once this limit is set, it must be monitored on a periodic basis to demonstrate compliance.

Alternative compliance options.

As an alternative to relying solely on waste feed monitoring, EPA will allow a facility to demonstrate compliance using a mercury CEM. Provisions for this type of compliance will be negotiated on a site-by-site basis with regulators. Guidance for this type of compliance will come from a combination performance specifications, PS12, found in a 1997-draft version of the MACT rule, and other requirements deemed important by individual regulators. Incentives or tradeoffs for using CEMs can be negotiated on a site-by-site basis. We expect that using CEMs would reduce or eliminate waste feed characterization, reduce compliance testing, and perhaps reduce facility operational costs.

PS 12 Requirements.

Early drafts of the MACT rule contained draft performance specifications for mercury monitors, PS 12. PS 12 emphasizes short-term performance evaluation and site-specific validation. By contrast, German regulations (as found in the German TUV certification program) require calibration against manual methods, with no internal reference standard.

PS 12 requires that a CEM measure total (elemental + speciated) mercury with a Method Detection Limit (MDL) of 20% of the emission standard (e.g. 10 µg/dscm if the emission standard is 50 µg/dscm). PS 12 also requires a relative accuracy test audit (RATA) every 3 years, with results less than 20% compared with standard EPA reference method measurements. Other PS 12 procedures include weekly calibration & zero drift checks for Hg⁰ only, an absolute calibration audit (ACA) every 3 months for both Hg⁰ and HgCl₂, and interference response during each ACA and RATA using an interference test gas containing SO₂, CO, NO_x, Water, HCl, and Cl₂.

PS 12 also requires that the effluent be sampled continuously, which may pose a problem for CEMs that use a gold trap followed by thermal desorption to isolate the mercury from interfering gases.

The draft MACT rule specifies that compliance using a mercury CEM would be based on the rolling 9-hour average of the CEM data. The concept of a rolling average is important when discussing implementation options.

Furthermore, even though the draft MACT rule regulates emission of total mercury, it may be possible to monitor only elemental mercury in cases where it can be shown that all or nearly all the emissions are elemental. If this option were possible, it would allow for cheaper, simpler mercury CEMs.

What are the challenges in meeting MACT regulations?

The MACT regulatory scenario presents a particular challenge to DOE incinerators, which are not currently designed for mercury removal. Previous trial burns have shown that these facilities may have difficulty meeting the emission limits established by MACT. Compliance with MACT could mean an expensive retrofit of their air pollution control systems.

Another challenge is measuring mercury in waste feed. At concentrations as low as 0.5 ppm, DOE has little faith in mercury waste feed characterization, particularly for heterogeneous debris. Representative sampling of debris for mercury is virtually impossible, and mercury is notorious for not being evenly distributed. Also, feed characterization in mixed waste increases the risk of personnel exposure to radionuclides.

BENEFITS OF USING MERCURY CEM FOR COMPLIANCE

CEMs offer a better way of compliance for two reasons. First, it is a better way protect human health and the environment. CEMs monitor continuously, unlike periodic waste feed monitoring. And especially for mercury, CEMs are more accurate than waste feed monitoring. Without a CEM most emission excursions would go undetected. As an example, a pool of waste in the bottom of a drum could result in an emission excursion, even though the facility thought they were in compliance by feed rate controls. A mercury CEM could alleviate this concern by giving the facility instantaneous data, allowing them to make changes that compensate for the increased mercury in the feed stream before emissions become excessive. Although implementing CEMs will require decisions about how the data is to be used (by facility operators as well as by regulators), the assurance provided by continuous emissions measurements is more protective than periodic waste feed measurements.

Another advantage of using CEMs is the potential to increase waste feed rates by directly monitoring emissions and showing they are below the standard. This is probably not as much an issue for DOE mixed waste facilities, as none are metal-feed rate limited. However companies like WTI, in Ohio, have cited this as an economic advantage of installing their multi-metal CEM.

Some people might argue that CEM data at the stack exit is "too late." By the time a facility knows that mercury emissions are above the limit, it would be too late to allow the facility to correct for emission limit excursions.

This argument is flawed. Instantaneous CEM data is not used for compliance. Rather, a 9-hour rolling average of instantaneous CEM data is used. A momentary excursion above the emission limit would not immediately affect the 9-hour rolling average. However, the instantaneous data is useful to the facility operator, allowing strategies such as waste blending or operational changes to correct emission surges before they become a compliance problem. Instantaneous data gives a facility plenty of time to optimize performance before safety is affected. This assumes that the facility response time to waste feed perturbations is much shorter than 9 hours. The amount of time between a CEM measurement and the event that triggered the measurement is much shorter than the amount of time required for non-compliance. The exception is catastrophic failure of an air pollution control component, e.g. a baghouse filter bank. But such a failure would be detected by other system instrumentation. We would not rely on CEM data to detect such failure, thus it is not relevant.

In a similar argument, some people have questioned whether or not emissions can be controlled without monitoring mercury in the waste feed. It may be that "process knowledge" of the waste is enough, along with instantaneous emissions data, to control emissions. More experience with mercury CEMs will help address this question.

MERCURY CEM VENDORS

Five commercial vendors offer dedicated mercury CEMs:

- Seefelder Messtechnik (SMT),
- Perkin Elmer (PE),
- Semtech,
- Verewa, and
- Opsis, Inc.

All of these systems are TUV-certified in Germany. In fact, all are European technologies with distributors in the U.S.

In addition, six systems are under development, in some cases with U.S. government funding:

- ADA Technologies, Inc. (2 different technologies),
- EEI (with Princeton Plasma Physics Lab),
- PS Analytical,
- Sensor Research & Development Inc.,
- Tennessee Valley Authority (TVA), and
- Tekran, Inc.

In addition, Physical Sciences, Inc. (PSI) conducted a Phase I SBIR evaluating another technology, which we include for completeness, even though PSI has since abandoned the technology.

Finally, two commercial vendors offer multi-metal CEMs, which also measure mercury. These are:

- Thermal Jarrell Ash
- Cooper Environmental

And several multi-metal CEMs are under development, including several efforts focused on laser-based atomic emission spectroscopy, MIT's development of a microwave AES, and PSI's development of a spark-based AES system, all under government funding.

KEY FEATURES OF HG CEM SYSTEMS

Measure, Convert, Separate, & Desorb

Mercury measurement is only one part of a mercury CEM, although the part sometimes most distinctive. Different mercury measurement techniques include: cold vapor atomic absorption (CVAA), UV differential optical absorption spectroscopy (UV DOAS), atomic emission spectroscopy (AES), or atomic or laser induced fluorescence (AF or LIF). By far the majority of dedicated mercury CEMs (i.e. those that measure just mercury) use CVAA to measure mercury.

An important feature of CVAA (and UV DOAS) is that this technique can only detect elemental mercury (denoted Hg^0). Therefore, all systems that use CVAA or UVDOAS must first *convert* ionic mercury to its elemental form. The second differentiating feature of CEMs, therefore is the method used for conversion: wet chemistry (a traditional approach), dry chemistry (under development), or heat.

The third distinction among these dedicated mercury CEMs is how they *separate* the mercury from other interfering gases, especially SO_2 . Separation is most commonly achieved using a gold trap, but can also be accomplished using carbon filtration, or even a Zeeman correction. The TVA Hg CEM uses a separation technique (gold filter) to generate a baseline signal of interfering gases. Rather than measuring the pure mercury stream desorbed from the gold filter, the TVA system measures the interfering gases after all the mercury has been removed, giving them a baseline reference signal.

A fourth, less significant distinction would be the phase of the mercury measured. All mercury CEMs discussed in this report measure only vapor-phase mercury. Desorbing particle-bound mercury is a complexity not warranted by current mercury partitioning data.

An alternative to dedicated mercury monitors is a multi-metal monitor, which has the capability to measure all six metals (including mercury) covered by the MACT Rule.

Multi-metal CEMs offer the additional incentive of even greater reduction in waste feed characterization than mercury CEMs. The two commercially available multi-metal systems are Thermo Jarrell Ash's inductively coupled plasma atomic emission spectroscopy system (TJA ICP/AES), and Cooper Environmental Services hazardous element sampling train with x-ray fluorescence (HEST/XRF). Other systems under development with government funding are laser induced breakdown spectroscopy (LIBS or Laser AES), MIT's microwave AES system, and PSI's spark AES system. Mississippi State is developing another ICP/AES system. None of the multi-metal detection systems require conversion of speciated to elemental mercury. It is important to note that none of these monitors has been validated to date. Features of the multi-metal CEMs are summarized in Table 2, along with those for dedicated mercury CEMs.

Another option for mercury monitoring is be an AES-based measurement system dedicated just to mercury measurements, either laser based, or microwave based (as is under development at EEI). Such a system could take advantage of all that has been learned from multi-metal AES based technology development. The primary goal would be simplification of a dedicated AES-based system, resulting in substantially reduced up-front costs, and significantly lower operational costs. Ideally, such a system would also be easy to calibrate. Another option would be to use a simple elemental mercury monitor, such as the Opsis UV DOAS system, in facilities with wet scrubbers with little or no mercuric chloride in the effluent.

Table 2. Summary of techniques for dedicated mercury CEMs and multi-metal CEMs.

Developer/vendor	Separate	Convert	Measure	Other notes
Dedicated Hg CEMs:				
Commercially available				
Opsis	none	none	UV DOAS	• measures elemental only
Seefeldler Messtechnik (SMT)	none	wet chemistry	CVAA	• autocalibration • desorbs particle-bound mercury
Semtech	zeeman	wet chemistry	CVAA	
Perkin Elmer	gold trap	wet chemistry	CVAA	
Verewa	none	thermal + wet chemistry	CVAA	• autocalibration
Developing technologies				
Tennessee Valley Authority	gold trap	dry gas-phase chemistry	UVDOAS	• gold trap used to create baseline for zero.
ADA Technologies	zeeman	thermal cracking	CVAA	
EEI	none	N/A	AES (microwave)	• in-situ
Sensor R&D	gold trap	N/A	SAW	• early research
PSI	none	none	AF (ANET)	• technique abandoned by PSI
ADA Technologies	none	none	Cavity Ring-down	• early research, ultra sensitive
PS Analytical	gold trap	none	AF	
SRI International	N/A	N/A	2-laser	• research concept only – capable of true speciation &
Multi-metal CEMs:				
Commercially available				
TJA	none	N/A	ICP AES	
Several	none	N/A	Laser AES	
Developing technologies				
MIT	none	N/A	mwave AES	
PSI	none	N/A	Spark AES	
Cooper	carbon	N/A	XRF	

Speciating Capabilities

Another capability that some of these CEMs have, is the “plumbing” and software to make differencing measurements. This means that an “unconverted” gas stream is sent to the (UV) analyzer, which measures the amount of elemental mercury in the gas stream. This can be subtracted from the “total” mercury measurement to infer the amount of mercury that is NOT elemental, i.e. is speciated. To date, ADA Technologies and Tennessee Valley Authority are the only two mercury CEMs that incorporate this feature. However, it is not probably not a difficult feature to add to other CVAA systems.

This capability is sometimes referred to as a “speciating” mercury CEM. It would be more accurate to call it a “total speciated” measurement. A true “speciating” mercury CEM would be one that actually identifies individual mercury species in the gas stream. At this time, there is no need, aside from research, for real-time true mercury speciation of combustion flue gas.

RESULTS FROM MERCURY CEM PERFORMANCE TESTING

TUV Certification and European Operational Experience.

The following companies offer instruments that are TUV certified, with units operating throughout Europe: Perkin Elmer, Verewa, Semtech, Seefelder Messtechnik, and Opsis. Each of these vendors has several instruments operating at municipal and hazardous waste incinerators throughout Europe.

1997 EPA/DOE Test at Holly Hills, NC.

This 1997 joint EPA/DOE test was conducted to validate mercury CEMs for inclusion as mandatory compliance instruments in the then-draft MACT rule. The test accomplished the opposite. None of the three commercially available, Germany-TUV-certified mercury CEMs passed the performance criteria from the test. In hindsight, the test facility was not the ideal choice. Due to the lack of a scrubber, the SO₂ and particulate matter were substantially higher than would be experienced at a hazardous waste incinerator. SO₂ concentrations were between 150 and 500 ppm with excursions up to 1500 ppm. A typical HWI usually operates at concentrations less than 100 ppm. DOE facilities will be lower than this due to low sulfur in the waste and the fuel. SO₂ is especially worrisome to the CVAA techniques because without an upstream separation technique (such as a gold trap), CVAA suffers from strong interference from SO₂ at concentrations above 100 ppm.

1997 DOE/Univ. of North Dakota Energy and Environmental Research Center (EERC).

EERC tested the Perkin Elmer MERCEM, the Semtech Hg 2000, and the PS Analytical Sir Galahad. Their test gas contained 5000 ppm SO₂ and 1250 ppm chloride to emulate the offgas resulting from burning coal with high-sulfur and high-chlorine. They did not report PM loading during the test. EERC developed a pre-treatment cell for the instruments to remove acid gases. Although the PS Analytical converter and the ADA

Technologies system did not work, the remaining CEM data was within 20% of the reference method (Ontario Hydro) data. The instantaneous CEM data was "quite variable."

1998 DOE Test at DOE/TSCA Incinerator.

During September and October, 1998, the DOE TSCA incinerator tested the Perkin Elmer MERCEM unit that had been tested previously at EERC (see paragraph above).

Quantitative results from this test are not yet available, although operationally, the instrument performed very well with little maintenance. Preliminary results indicate relative accuracy near 20%, despite the fact that an on-site calibration was not performed.

General Results of Performance Testing to Date.

Two general observations can be made relative to mercury monitoring.

- Operational and design simplicity is always better if performance is adequate. Simpler is better, and results in less maintenance, especially in harsh field environments such as acid gases, particulate matter, and moisture.
- Sampling and sample-handling, especially for mercury, is prone to difficulty. Mercury is known to adsorb onto synthetic materials such as PVC, PE, PTFE and stainless steel and titanium. It must be done with care and rigid procedures. For this reason in-situ monitoring would inherently be better than a sampling monitor, if the performance is comparable.

HG CEM IMPLEMENTATION PLANS

Each site should develop a plan to implement mercury CEMs. Such a plan should include logical arguments to their state permit writer as to why a mercury CEM provides better compliance assurance than conventional waste feed characterization. A phased-in approach, where waste feed is measured simultaneously with a stack gas CEM could be used to demonstrate the increased compliance accuracy with the CEM. In addition, the plan should address the issue of increased radionuclide exposure risk to workers from waste feed characterization. Also included should be a discussion about technology selection, CEM verification data, and how the CEM data will be used to demonstrate compliance.

Technology Selection.

At least 3 commercially available mercury CEM technologies show promise of meeting performance requirements: the Perkin-Elmer MECEM, the Seefelder Messtechnik, and the Semtech Hg 2000. Technology selection should include careful consideration of interferents, such as SO₂, in the flue gas, other flue gas components that might cause corrosion and plugging, and maintenance requirements for each technology. As mercury CEMs come into wider use, we expect the systems to get simpler and less expensive to own and operate.

It may be possible that a facility could use a simpler, less expensive technique such as the in-situ Opsi UV-DOAS system. This would require that the facility can demonstrate that the majority of their mercury is in elemental form or that the relationship between elemental and total mercury is well established and constant.

Site Specific Calibration

During site-specific verification testing, tests should be conducted comparing 9-hour rolling average CEM data to data from standard reference method measurements and "instantaneous" CEM data to better understand typical variations in the 9-hour rolling average compared to "instantaneous" CEM data.

Problems with PS12.

There are three areas of potential concern with PS12 as it relates to implementation of mercury CEMs in DOE facilities. The first is that PS 12 does not provide a protocol for reference sources of Hg^0 and HgCl_2 for the absolute calibration audit (ACA) test, which requires testing with both Hg^0 and HgCl_2 . The basis for this requirement is the need to test the ionic mercury conversion step in the monitor. All other PS12 tests involve only Hg^0 (or total Hg for the RATA). Since HgCl_2 calibration gas and even permeation tubes are not readily available in concentrations necessary for tests such as these, the ACA test is not easily implemented. By contrast, Hg^0 is now becoming available as a cylinder reference test gas and as a NIST-traceable permeation tube.

The second issue with PS12 is the frequency of quantitative checks. PS12 requires daily calibration and zero drift tests. By contrast, TUV requires only a daily qualitative "state of health" check. PS12 requirements for daily absolute calibration are reminiscent of SO_2 and CO monitors, where calibration gas is readily available. Depending on the performance of the new Hg^0 calibration gas, this may or may not be easily implementable for Hg CEMs.

Finally, PS12 requires a concentration of 500ppm SO_2 in the interference test gas. This high SO_2 concentration may be typical for an unscrubbed cement kiln effluent, but is much higher than one would find in a HWI, which typically operates below 100 ppm. Above 100ppm, SO_2 is a strong interferant for cold vapor atomic absorption (CVAA) instruments, unless a separation technique such as a gold trap is used.

SUMMARY & CONCLUSIONS

For DOE applications, at least three commercially available CEM systems show promise of meeting performance requirements. Prior to implementation, each site should prepare an implementation plan that includes how the technology was selected, verification data for the technology, and how the CEM data will be used for compliance assurance.

Besides commercially available mercury CEM systems, several other technologies are under development that could result in less expensive, more reliable mercury CEMs. If these types of technology improvements are funded, there should be a clear understanding of performance requirements. True speciation and ultra-sensitivity ($<1\mu\text{g/dscm}$) should not be priorities. Rather, lower cost, lower maintenance, ruggedness, and perhaps in situ monitors are what are needed. Also to be considered should be the use of multi-metal CEMs if they become validated, which offer the additional incentive of reducing waste feed characterization even further.

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