

A COORDINATED MULTI-AGENCY APPROACH TO DEVELOPMENT OF CONTINUOUS EMISSION MONITORS

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ABSTRACT

The Department of Energy Office of Environmental Management (DOE-EM) currently operates four thermal treatment facilities for mixed waste that are permitted under regulations for hazardous waste combustors. As regulations become more stringent and public stakeholders become more influential, permitting these and other thermal treatment facilities is becoming increasingly difficult. This is a problem that is not unique to DOE-EM. The DOE Office of Fossil Energy is responsible for technology development for the utility boiler business, and the Department of Defense operates several incinerators for demilitarization of ordnance and chemical weapons. In addition, the Environmental Protection Agency is responsible for promulgating regulations concerning emissions of hazardous pollutants and for developing compliance assurance measures for such facilities. Continuous emission monitors (CEMs) offer the potential to help facility operators better understand their processes in order to reduce emissions, and will help to assure regulators and the public of the safe operation of those facilities. The DOE-EM Mixed Waste Focus Area has participated in a multi-agency program for the development and testing of a variety of CEMs that could have application to a wide variety of thermal processes.

INTRODUCTION

The Department of Energy operates several thermal waste treatment for the treatment of mixed hazardous and radioactive waste. These facilities are permitted as hazardous waste incinerators and will be subject to the new rule for Maximum Achievable Control Technology (MACT) for Hazardous Waste Combustors. DOE's mixed waste incinerators are not the only ones who are facing these or similar regulations in the near future. DoD operates several incinerators for chemical or ordnance destruction. DoD also operates incinerators for hazardous waste at other facilities. Private industry operates many incinerators for hazardous, municipal, and medical waste. The utility boiler industry, particularly those that are coal-fired, is a very large potential source of hazardous emissions.

Continuous emission monitors (CEMs) offer a better way to develop emissions controls and monitor compliance with emission regulations. For example, the MACT Rule provides incentives to use CEMs to reduce waste feed characterization and to reduce dependence on operating parameters for compliance verification. If a sufficient suite of

CEMs were available, EPA has publicly stated a willingness to eliminate comprehensive testing and reduce scope of trial burns and waste feed characterization. As part of the MACT Rule, EPA has published draft performance specifications that precede availability of CEMs. EPA appears open to creative, perhaps staged relaxation of these performance specifications to encourage implementation of CEMs as long as the risk to public health is not increased.

There are three principal drivers for development of CEMs:

1. CEMs offer the potential for simplified compliance in the face of increasingly stringent emission regulations.
2. CEMs can provide opportunities for process performance improvement.
3. CEMs can provide assurance for the public that thermal treatment processes are operating within permitted emission limits.

CEMs have been in use for years for some pollutants, such as oxygen, carbon monoxide, total hydrocarbons, nitrogen oxides, sulfur oxides and hydrogen chloride. However, CEM techniques for some analytes are much more complex than these commercially available CEMs. Three of the most difficult areas, and those that are of prime concern, are mercury, dioxins/furans, and multiple metals. Technical risks present serious barriers to successful deployment. Of these barriers, performance verification is one of the most important.

Because of the potential for widespread application of CEMs, there have been programs concerning CEMs from a number of federal agencies and from the private sector as well. Among the federal agencies involved are:

Department of Energy

- Office of Environmental Management
- Office of Fossil Energy
- Office of Environmental Health

Department of Defense

- Strategic Environmental Research and Development Program
- U.S. Army Defense Ammunition Center
- Air Force Armstrong Laboratory

Environmental Protection Agency

- Office of Solid Waste
- Office of Air Quality Planning and Standards
- Office of Research and Development

It is evident with so many potential technology development sponsors, that overlap and duplication would be inevitable if all these agencies acted independently. Therefore an Interagency CEM Coordination Committee (ICCC) was formed to coordinate the efforts of the many players. The mission of the ICCC is to help accelerate development of technologies that meet, or nearly meet clearly defined performance specifications, and to

minimize redundancy in CEM technology development among the various government sponsors.

The ICCC has members not only from technology developers, but also from potential end users and regulators. End users provide an important link to the facilities that will implement CEMs providing realistic goals for cost and performance that must be met for an instrument to be acceptable. Having regulators involved gives developers a better understanding of what performance requirements are being considered. In addition, the regulators obtain a better understanding of the state of a technology and what its capabilities and limitations are, which then leads to more realistic and achievable performance specifications.

The function of the ICCC is not to act as still another funding source, but rather to coordinate the ongoing and planned activities of the various agencies to maximize the impact of each individual program. Since its inception in 1997, the ICCC has been involved in several aspects of CEM development. These include analyzing the current status of various technologies to plan strategies for development, research for new technologies, pilot scale testing of developing technologies, and demonstrations of commercially-available technologies.

The remainder of this paper will discuss several of the programs that have been initiated under the ICCC.

MULTI-METALS

EPA regulates six hazardous metals in emissions from hazardous waste incinerators: mercury, lead, cadmium, arsenic, beryllium, and chromium. The current method for determining stack emission of multi-metals involves periodic manual sample collection followed by off-line sample analysis. This is a very time consuming and costly process. As such, they are only conducted during trial burns and other comprehensive tests, every 18 to 24 months. The remainder of the time process operating parameters and feed characterization must suffice for emission compliance. Several CEM development programs have been undertaken to overcome this limitation. EPA drafted Performance Specification 12 (PS12) for multiple metals, and while it will not be promulgated at this time, it forms the basis for required performance.

CEMs for real-time monitoring of hazardous trace metal emissions have been developed by organizations sponsored by DOE, DoD, and private industry. These CEMs have been tested in three comparative demonstration tests jointly funded by DOE and EPA, beginning in April 1996 and ending in September 1997. Three CEMs were tested in each of the first two tests. In the final test, seven CEMs were tested in a pilot-scale rotary kiln at the EPA Office of Research and Development facility in Research Triangle Park, NC. The intent of these tests was to determine if any of the monitors was ready to undergo long-term validation tests at an operating facility, such as a hazardous waste incinerator. Table 1 gives a listing of the seven CEMs that participated in the September 1997 tests¹.

These tests were designed to measure the performance of multi-metal CEMs for regulatory compliance applications. As such, CEM performance was measured against PS12. Results for those seven CEMs were compared with results from simultaneous flue gas sampling using conventional EPA Reference Method 0060 sampling trains and analytical procedures.

Table 1. Summary of multi-metal CEM technologies, organizations, and sponsors

CEM TECHNOLOGY	DEVELOPER	SPONSORING ORGANIZATION
Inductively Coupled Plasma (ICP)	U. S. Department of Defense (DoD) Naval Air Warfare Center	U. S. Army Demilitarization Technology Office Commercially available through Thermo Jarrell Ash
Air Inductively Coupled Plasma (Air ICP)	Diagnostic Instrumentation and Analytical Laboratory (DIAL) at Mississippi State University	U. S. Department of Energy Characterization, Monitoring, and Sensor Technology Crosscutting Program (DOE CMST-CP)
X-Ray Fluorescence	Private. Cooper Environmental Services, Inc.	Private. Cooper Environmental Services, Inc. Commercially available through CES, Inc.
Laser Induced Breakdown Spectroscopy (LIBS)	Diagnostic Instrumentation and Analytical Laboratory (DIAL) at Mississippi State University	U. S. Department of Energy Characterization, Monitoring, and Sensor Technology Crosscutting Program (DOE CMST-CP)
Laser Induced Breakdown Spectroscopy (LIBS)	Sandia National Laboratories, Livermore, CA	DOE CMST-CP and the U.S. Army Demilitarization Technology Office
Spark-Induced Breakdown Spectroscopy	Physical Sciences Inc.	U.S. Department of Energy, FETC
Microwave Induced Breakdown Spectroscopy	Massachusetts Institute of Technology	U. S. Department of Energy Mixed Waste Focus Area
Calibration Technique for LIBS	Laser Diagnostics, Inc.	U. S. Department of Energy Characterization, Monitoring, and Sensor Technology Crosscutting Program (DOE CMST-CP)

The most important performance issue for this test was whether a CEM could quantitatively measure all six metals. To address this issue, two parameters were measured: 1) detectability (at the concentrations tested, compared with required method detection limits (MDLs)), and 2) relative accuracy, which is the average CEM measurement compared with the EPA reference method measurement during the same time period.

Of the monitors tested, only the Navy/TJA ICP system was able to detect all six metals. The others were able to detect two to five metals. Only ICP and XRF were able to detect

mercury and arsenic, which have proven to be very problematic for other monitors. Table 2 shows the relative accuracies of the seven CEMs for each of the six metals at both the high and low target concentrations.

Table 2. Relative Accuracy of each multi-metal CEM at high and low concentrations.

Concentration	Navy / TJA ICP	CES XRF	DIAL ICP Mono	DIAL ICP HiRIS	DIAL LIBS	Sandia LIBS	PSI SIBS	MIT MIPS	Laser Diag.
High Target (75 µg/dscm)									
As	57%	31%							
Be	36%		38%	92%	49%	176%			128%
Cr	56%	43%	64%		42%	253%	151%	39%	101%
Cd	49%	22%	40%	84%	67%	341%			
Pb	64%	47%	19%		66%		89%	28%	
Hg	96%	53%	43%						
Low Target (15 µg/dscm)									
As	81%	39%							
Be	51%		46%	55%	37%	367%		37%	91%
Cr	76%	46%	76%		19%	196%	163%	98%	65%
Cd	(86%)	(55%)	(84%)		(78%)	(290%)			(112%)
Pb	(103%)	(48%)	(45%)		(37%)		(82%)	(50%)	
Hg	94%	66%	96%						

Based on the results of these tests, it was determined that no multi-metal CEM is currently ready for long term testing. All require additional developmental work, particularly in the area of field calibration. This was important to the EPA Office of Solid Waste, because it meant that multi-metal CEMs would not be required in the new Maximum Achievable Control Technology for Hazardous Waste Combustors Rule (MACT Rule).

MERCURY

Mercury is one of the six hazardous metals discussed in the previous section, but is such a pervasive problem that it is often considered alone. Mercury is a significant problem in many thermal processes, from incinerators to coal-fired utilities. In a thermal process mercury is volatilized and ends up in the offgas system. Although most offgas systems

will remove some mercury, efficiencies are generally less than 20% and often less. For incinerators, emissions of mercury are generally controlled by limiting the amount of mercury in the waste feed, which restricts the ability of facilities to process some waste streams. Also, characterizing waste feed for mercury is very difficult and costly. The MACT Rule has a provision that allows a facility to offset a portion of the feed characterization if a verified mercury CEM is installed. This potentially large economic incentive formed the basis of a test of commercially available mercury CEMs during 1996 and 1997.

Mercury CEMs are available and in use on European hazardous waste incinerators. They have been certified by the German TUV. In a joint program between DOE and EPA, three of these commercially available mercury monitors were tested during an extended period on an operating cement kiln burning hazardous waste². The monitors tested were the Perkin Elmer MERCER, the Seefelder Messtechnik Hg-Mat 2, and the Verewa HM-1400. Again, performance was measured against a standard reference method. None of the CEMs were able to meet the requirements of PS12 consistently. In general, the monitors gave acceptable results while they were operational, but the monitors required extensive maintenance to keep them running. Analysis after the test indicates that the offgas from the cement kiln was more severe than the monitors were designed for, particularly in the amount of SO₂ and particulate.

Based on the results of this test, EPA eliminated the requirement for mercury CEMs from the MACT Rule, but retained the incentive for using CEMs in lieu of extensive feed characterization. Most waste incinerators employ offgas scrubbers and particulate matter removal so the offgas is much less severe than was the case in the cement kiln. It may therefore be that a mercury monitor would operate satisfactorily at such facilities. To check this idea, DOE tested a mercury CEM at a DOE incinerator to assess its ability to reliably monitor mercury emissions. Although not an exhaustive test, results of that test showed that the monitor performed within specification of PS12. More testing may show that mercury CEMs are an acceptable alternative on incinerators.

PARTICULATE MATTER

Like mercury, European incinerators have been using particulate matter (PM) CEMs for several years. Several types have been verified by the TUV. In a joint DOE/EPA test similar to the long term mercury CEM test, five PM CEMs were tested on an operating hazardous waste incinerator. Unlike the mercury test, the PM CEMs showed that they could meet performance specifications, and EPA will require their use under the MACT Rule.

DIOXINS AND FURANS

EPA has established very stringent emission limits for dioxins and furans. A major problem for waste treatment facilities is understanding where in these systems dioxins and furans are formed. To better understand the formation mechanisms requires an ability to measure dioxins as a function of various operating parameters.

Currently, dioxin analyses can only be performed by manual methods, which require three to five weeks for the analysis results to become available. A near real-time diagnostic monitor would greatly aid in the development of dioxin control strategies. Compounding the problem of monitoring for dioxins is that there are 210 individual congeners of which only 17 are governed by regulations. The resulting requirements for sensitivity and selectivity severely challenge the abilities of any monitoring technique.

A 1996 scoping study was funded by EPA and DOE to test a resonance enhanced multi-photon ionization/mass spectroscopy (REMPI/MS) system to see what its potential might be for dioxins³. This very preliminary test showed that the system can detect up to tetra-chlorinated dioxins at concentrations as low as 10 ppt. Although this detection limit is not sufficient, the test at least showed that there is some potential for the technique.

Based on the results of that test, a program has been initiated to develop a coordinated program of monitor development and mechanistic studies leading to control strategies. The monitoring effort, funded by DOE, will develop an improved REMPI monitor that can be used to obtain diagnostic and research data from both test facilities and operating facilities. SRI International will perform this work. In a parallel effort funded jointly by EPA, DOE, and private industry mechanistic studies will be conducted to better understand how to prevent the formation of dioxins. Part of the mechanistic study will also be to develop correlations relating the 17 toxic congeners with other indicator species that are present in larger, more easily detected concentrations. A CEM for these indicator species could be used to assure compliance with dioxin emissions, but should be a simpler and less expensive instrument.

CONCLUSIONS

Continuous emission monitors offer thermal processing facilities the opportunity to assure regulators and the public that they are operating safely and within permitted emissions limits. Developing CEMs to meet these needs is a costly and complicated process. By bringing together developers, end users, and regulators, it is possible to address all aspects of this difficult problem and accelerate implementation of this valuable technology.

Draft Mercury Continuous Emissions Monitor System Demonstration

REFERENCES

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