Continuous Emissions Monitoring Demonstration Program

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ABSTRACT

Continuous emissions monitoring of hazardous and mixed waste thermal treatment processes is desired for verification of emission compliance, process control, and public safety perception. Species of particular interest include trace metals and organic compounds resulting from incomplete destruction. Continuous real-time monitoring of these pollutants would permit measurement of real-time (actual) hazardous compound emissions and allow accurate (realistic) human risk assessment from hazardous and mixed waste thermal treatment facility operation. This paper describes a joint DOE/ EPA program developed to identify and demonstrate emerging continuous emissions monitoring technologies ready for pilot-scale demonstration. The demonstrations will include burning simulated waste spiked with hazardous metals and organics in a pilot-scale rotary kiln incinerator while flue gas metals and organics concentrations are continuously monitored. Simultaneous manual flue-gas sampling using EPA reference method sampling trains and analytical procedures will provide a benchmark for the continuous monitoring technologies. Both method accuracy and short-term system reliability will be assessed. A program coordination committee consisting of representatives from DOE, EPA, academia, end-users, and technology developers will provide technical support in demonstration protocol development, technology selection criteria, and performance assessment.

INTRODUCTION

Continuous emissions monitoring of hazardous and mixed waste thermal treatment processes is desirable for several reasons: verification of emission compliance, enabling responsive process control, and increasing public confidence in thermal treatment process safety and regulatory agency credibility. Pollutants of particular interest include trace metals and organic compounds resulting from incomplete destruction of wastes. In particular, EPA plans to propose new rules in 1995 governing the emission of toxic metals from hazardous waste thermal treatment facilities, including hazardous waste incinerators, cement and aggregate kilns, and smelting, melting, and refining furnaces. Continuously monitoring of these species would permit real-time hazardous compound emissions measurement and realistic assessment of human risk associated with the atmospheric release of these compounds resulting from the operation of hazardous and mixed waste thermal treatment facilities.

Programs are currently being funded by the Department of Energy (DOE), the Environmental Protection Agency (EPA), and private industry to develop technologies and equipment for continuous emissions monitors (CEM)s. Continued advancement and future implementation of these technologies require pilot- and full-scale demonstrations in realistic process environments. The DOE and EPA have established a joint program to demonstrate emerging technologies for continuously monitoring metals and organic compound emissions from pilot-scale thermal treatment facilities. The objectives of this program include identifying promising emerging technologies for continuous monitoring of hazardous compounds in emissions from thermal treatment facilities. A demonstration protocol will be developed to evaluate each CEM technology against defined criteria and EPA reference methods. A series of technology demonstration tests will be performed at the EPA Incineration Research Facility (IRF), a pilot-scale rotary kiln incinerator. This program is not intended to provide a definite assessment of which CEM is best, but is intended to reveal potential advantages and disadvantages with each technology and identify issues that could be encountered in a process environment. This joint program will utilize a team of recognized experts in the CEM field to provide technical support of all program activities.

TECHNOLOGY REQUIREMENTS

Continuous monitoring of an emissions source by the strict definition requires continuous and real-time sampling, analysis, and reporting. Yet, the current EPA Office of Solid Waste (OSW) definition of continuous emissions monitoring requires continuous process sampling, while the analysis can be conducted in a batch operation. The batch analysis must be completed on-site and be integral to the CEM. The CEM should provide a concentration value for the species of interest at least once every three hours. The response time (the time interval between the start of a step change in the system input and the time when the monitor output reaches 95% of the final value) of the CEM should be less than three hours. For CEMs utilizing batch analyses, the delay between the end of the sampling time and reporting of the sample analysis should be no greater than one hour. Also, there should be no greater than a five-minute gap in sampling when the sample collection media is changed.[1] Thus, a CEM should be able to continuously sample facility emissions and have as close to real-time reporting of effluent concentrations as possible.

In addition to requirements for sampling and data reporting, the CEM must have detection limits low enough to assure ability to comply with the eventual regulatory limits for specific species of interest. A multi-metals CEM should be capable of measuring, at a minimum, the total elemental concentrations of two or more of the metals listed in Table 1. Although final detection limit requirements for each metal have not been determined (it will be based on the future regulatory emission limits for each metal or group of metals which is yet to be defined), a metals CEM should be capable of measuring concentrations of each metal (in both the solid and vapor form) at or approaching the detection limits listed in Table 1.

Table 1
Multi-Metals CEM Detection Limits

Metal	Detection Limit ($\mu g/m^3$)
Antimony	5.0
Arsenic	5.0
Barium	2.5
Beryllium	0.25
Cadmium	2.5
Chromium	2.5
Cobalt	2.5
Lead	25
Manganese	0.5
Mercury	0.5
Nickel	2.5
Selenium	25
Silver	2.5
Thallium	2.5

Organic CEMs should be capable of measuring stack gas concentrations of one or more of the organic compounds listed in Table 2 at a detection limit approaching 1 $\mu g/m^3$ for all compounds except dioxins. Concentrations of interest for dioxins are in the ng/m^3 range, or lower.

Table 2
Organic Species for CEMs

Benzene
Carbon Tetrachloride
Chlorobenzene
Chloroform
Dichlorobenzenes
Dichloroethanes
Dichloroethenes
Formaldehyde
Methylene Chloride
Polynuclear Aromatic Hydrocarbons
Tetrachloroethene
Toluene
Trichloroethanes
Trichloroethene
Vinyl Chloride
Dioxins

TEST FACILITY

All CEM demonstration tests will be conducted in the pilot-scale rotary kiln incineration system (RKS) at EPA's Incineration Research Facility (IRF) located in Jefferson, Arkansas. A process schematic of the RKS is shown in Figure 1. The RKS consists of a primary combustion chamber (a 590 kW rotary kiln with 1.04 m ID and 2.26 m length), a transition section, and a fired afterburner chamber (590 kW, 0.91 m ID, 3.05 m length). After exiting the afterburner, flue gas flows through a quench section followed by the primary air pollution control system (APCS). The primary APCS consists of a venturi scrubber followed by a packed-column scrubber. Downstream of the primary APCS is a redundant APCS to ensure facility permit compliance. The redundant APCS contains a demister, an activated-carbon adsorber, and a high-efficiency particulate air (HEPA) filter.

Currently, it is anticipated that up to four CEMs would be tested simultaneously. The CEMs would likely be located in the facility flue gas duct (0.36 m diameter, gas velocity approximately 6 m/s) between the primary and secondary APCS at the scrubber exit. At this location, the flue gas is saturated, approximately 60°C, and can contain 100-200 mg/m^3 particulates with a mean particle size below 20 microns. Also, the flue gas can contain up to 5 ppm acid gas at this location.

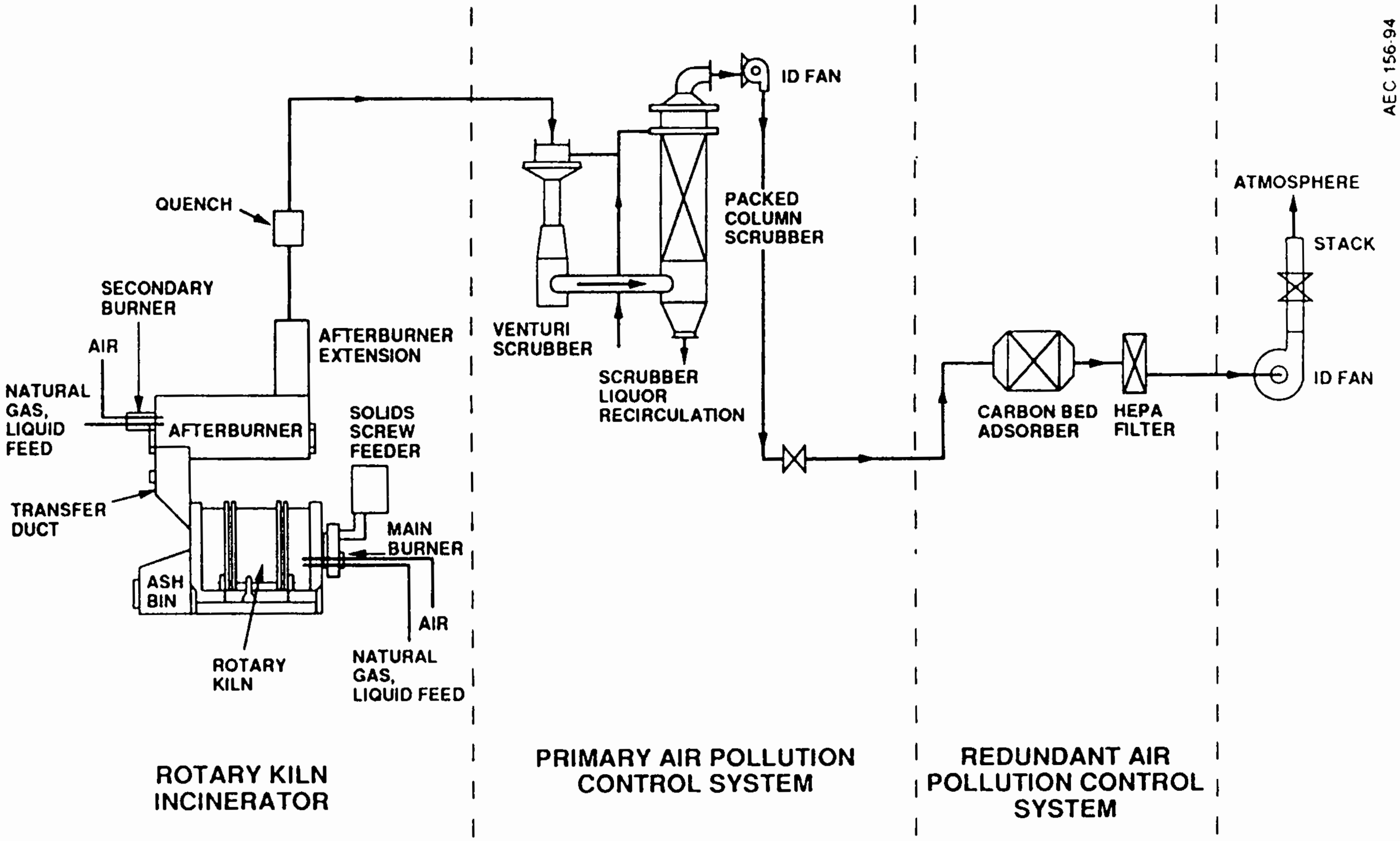

Figure 1. Schematic of the IRF rotary kiln incineration system.

Simulated waste will be incinerated during all CEM demonstration tests. Metals will be introduced by two different methods. A simulated hazardous solid waste will be generated by adding a concentrated aqueous metals solution (primarily soluble metal nitrates) to a clay-based oil sorbent material (< 1 mm particle diameter). A mixture of toluene, chlorobenzene, and tetrachloroethene will be added to the solid waste at a concentration of approximately 4 wt%. These organics will provide a source of chlorine which is present in most hazardous waste streams. This waste simulant will be continuously fed to the rotary kiln and burned at a nominal exit gas temperature of 870°C. In addition to the metal and organics-bearing solid waste, an aqueous metal solution will be injected directly into the kiln main burner, simulating the burning of liquid hazardous waste containing trace toxic metals.

Organics CEMs will be tested by metering a mixture of approximately 10 selected volatile and 3 semi-volatile organic compounds into the flue gas. The specific organic spiking compounds and their respective flue gas concentrations will be selected based on the CEMs being tested.

TEST METHOD

The CEM demonstration will be designed and conducted to assess each instrument for the following performance characteristics:

- Relative Accuracy - The absolute mean difference between species concentrations in the flue gas determined by the CEM and the value determined by the applicable reference method.

- Calibration and Zero Drift - The difference in the CEM output from the established reference values (including a blank) after a stated period of operation during which no unscheduled maintenance, repair, or adjustments took place.

- Response Time - The time interval between the start of a step change in the species concentration and the time when the CEM output reaches 95% of the final value.

- Instrument Robustness - A qualitative assessment of instrument applicability to a process environment. The criteria includes set-up time, ease of operation, percent downtime, maintenance requirements, calibration time, number of operators, etc.

The assessment of relative accuracy will consist of three separate runs at three concentration levels of the species of interest. For all metals CEM tests (including the monitors that measure only one specific metal), the gas stream will contain all the metals listed in Table 1. The target metal concentrations in the flue gas for each run is shown in Table 3.

TABLE 3
Target Metal Concentrations

Metal	Assumed Detection Limit ($\mu g/m^3$)	Run 1 Concentration ($\mu g/m^3$)	Run 2 Concentration ($\mu g/m^3$)	Run 3 Concentration ($\mu g/m^3$)
Antimony	5.0	10	40	400
Arsenic	5.0	10	40	400
Barium	2.5	5.0	20	200
Beryllium	0.25	0.5	2.0	20
Cadmium	2.5	5.0	20	200
Chromium	2.5	5.0	20	200
Cobalt	2.5	5.0	20	200
Lead	25	50	200	2000
Manganese	0.5	1.0	4.0	40
Mercury	0.5	1.0	4.0	40
Nickel	2.5	5.0	20	200
Selenium	25	50	200	2000
Silver	2.5	5.0	20	200
Thallium	2.5	5.0	20	200

The flue gas for the organics CEM tests will contain an assortment of volatile and semi-volatile organic compounds. The specific organic spiking compounds will be selected based on the CEMs being tested. The concentrations of each organic species in the flue gas stream will be defined based on the capabilities of the CEMs being tested, yet the organics concentrations should be in the range of 0.5, 2.0, and 20 $\mu g/m^3$for each of the three runs.

During each run, three manual Reference Method sampling procedures will be conducted. Each Reference Method sampling event is expected to last approximately three hours. Thus, the CEM will be exposed to nine hours of steady-state operation at each of the three target concentrations while three independent Reference Method samples are being taken. The Reference Methods planned for use are shown in Table 4.

TABLE 4
Test Reference Methods

Pollutant	Reference Method
Multi-Metals	M29
Mercury	M101A
Volatile Organics	M0030
Semi-Volatile Organics	M0010
PCDD/PCDF	M23

Calibration procedures, methods, and materials will be specified, supplied, and conducted by the respective CEM developer/operator. Only the analyzer, not the sampling interface, requires calibration with calibration and zero drift measurements. If, during the course of a run, or any time during the demonstration period, automatic or manual adjustments are made to the CEMs zero or calibration settings, a drift measurement must be taken. At minimum, zero and calibration drift measurements will be taken at the beginning and end of each set of three runs.

The instrument response to a process step change will be measured by two separate methods. The first method requires operation of the CEMs for a sufficient time period both before and after spiked feed is introduced to the facility. The second method will utilize injection of a spiked simulant directly into the flue gas duct. Since both of these methods also include some lag time inherent to the test facility, it is not a true CEM response time measurement. These response time tests are designed to demonstrate the instrument performance during a step change in facility operation. The CEM response to both of these transients will be recorded. Each CEM's resolution and response time will determine the ability to follow and recorded these events. This will also define how close these monitors are to "real time." There is no reference method for measuring response time.

For EPA/DOE test records, during the course of testing, each CEM operator will maintain a test log book documenting the time required for instrument set-up, shakedown, and calibration. All maintenance activities will be recorded, along with all calibration and zero drift data. The percent the instrument is off-line due to calibration or maintenance will also be recorded. In addition to the CEM operator log, test personnel will be conducting general observations of the ease of operation and the quantity of "hands on" attention each monitor requires. This type of qualitative data will allow estimation of the technology robustness and if or how soon the monitor will be ready for use in a commercial facility.

PROGRAM SCHEDULE

The request for interested CEM developers was published in the January 4, 1995 Commerce Business Daily. The draft test plan and protocol was sent to all potential participants in early April. The CEM developers are requested to respond with a commitment to participate by mid-May. The demonstrations are scheduled to begin in late June 1995 and be completed by the first of September. The program report is expected to be complete in early November 1995.

SUMMARY

Continuous emissions monitoring of hazardous and mixed waste thermal treatment processes is desired for verification of emission compliance. Species of particular interest include trace metals and organic compounds resulting from incomplete destruction. Continuous real-time monitoring of these pollutants would permit actual measurement of hazardous compound emissions and allow accurate human risk assessment from hazardous and mixed waste thermal treatment facility operation. A joint DOE/ EPA program has been developed to identify and demonstrate emerging continuous emissions monitoring technologies for metals and organics ready for pilot-scale demonstration. The demonstrations will take place at the EPA Incineration Research Facility in Jefferson, Arkansas. Simulated waste spiked with hazardous metals and organics will be burned in a rotary kiln incinerator while flue gas metals and organic concentrations are continuously monitored. Simultaneous manual flue gas sampling will provide a benchmark for the continuous monitoring technologies. The CEM demonstration will be designed and conducted to assess each instrument for relative accuracy between the CEM and the value determined by the applicable reference method. Calibration and zero drift will be measured at least every twenty-four hours during testing. Response time to step changes in the process will also be measured. Instrument robustness will be assessed for applicability to a process environment. A program coordination committee consisting of representatives from DOE, EPA, academia, end-users, and technology developers will provide technical support in the determination of demonstration protocols, technology selection criteria, and CEM performance assessment.

REFERENCES

1. "Draft Performance Specification - Specification and Test Procedures For Multi-Metals Continuous Emission Monitoring Systems in Stationary Sources," March 22, 1995.

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