METAL EMISSIONS MONITOR FOR MIXED WASTE THERMAL TREATMENT

TECHNOLOGY NEED

A continuous emissions monitor (CEM) for metals is applicable to incinerators and other thermal treatment devices and offers several potential benefits to DOE end-users. The benefits include process performance verification and subsequent risk reduction, permitting the selection of operational strategies that maximize efficiency while assuring continued compliance, and the promotion of public confidence in thermal treatment units. Current EPA methods to measure metal emissions are very costly (upwards of $10,000 per stack per triplicate sample), and because they utilize extractive batch samples, they provide no real-time emissions data. DOE needs identified by the Site Technology Coordination Groups and addressed by this project include the following:

- OR WM-13, Metals Monitoring of Gaseous Emissions at the Toxic Substance Control Act (TSCA) Incinerator at the Oak Ridge K-25 site.
- SR-1004, Need for Continuous Emissions Monitors for Measurement of Hazardous Compound Concentrations in Incinerator Stack Gas at the Consolidated Incineration Facility (CIF) at the Savannah River Site.
- ID-3.2.32, Develop Thermal Treatment Unit Offgas CEM Monitors at the Waste Experimental Reduction Facility Incinerator.

TECHNOLOGY DESCRIPTION

The metal emissions monitor makes use of the laser-induced breakdown spectroscopy (LIBS) technique, an atomic emission spectroscopy diagnostic that uses a pulsed laser to create a small microplasma in air. All metal species, both in the gaseous or particulate phase, are dissociated and excited within the plasma, and the resulting spectral emissions are used for quantitative elemental analyses. The LIBS technique can be performed *in situ* and in real time.

BENEFITS

Current EPA regulations require characterization of the waste fed to hazardous waste incinerators. Such characterization can cost in excess of millions of dollars per year per facility. It is anticipated that these costs could be reduced or eliminated with regulator acceptance of CEM technologies. In addition to monitoring and compliance assurance, the developed LIBS technology may be readily adapted to process control applications. Such process control capabilities could result in additional cost savings through enhanced efficiency, system response, and lowered worker or public risk.

CAPABILITIES AND LIMITATIONS

The LIBS technology is consistent with the draft EPA emissions limits proposed for the Resource Conservation and Recovery Act (RCRA) metals beryllium (Be), cadmium (Cd), chromium (Cr), mercury (Hg), and lead (Pb), which range from 20 to 50 micrograms per dry standard cubic meter. As implemented, LIBS is an *in situ* technique that requires no extractive sampling and transfer lines. Improvements made during FY 1998 have reduced the equipment costs for the entire LIBS system to less than $40K. Upcoming work will focus on increasing the LIBS sensitivity to arsenic (As), the remaining RCRA metal with a LIBS detection limit that is insufficient for monitoring at the level of the draft emission standards.

COLLABORATION/TECHNOLOGY TRANSFER

- Sandia has maintained an exchange of technical information with the LIBS group at SRI International, in Menlo Park, California.

- Three patent applications related to the LIBS technology have been filed with the U.S. Patent and Trademark Office.
- The Sandia National Laboratories Principal Investigator has traveled to the BHA Group, Inc. headquarters in Kansas City to discuss the status of the LIBS technology and potential opportunity for its application in monitoring emissions from the incineration of obsolete munitions.

ACCOMPLISHMENTS

The LIBS metal emissions monitor program has participated in a number of field trials:

- Measured manganese (Mn), Cr, and iron (Fe) emissions in real time with excellent agreement with EPA method 29 at the Balboa-Pacific Corporation in Santa Fe Springs, California during March 1997.
- Measured Be, Cd, Cr, Mn, and Hg emissions in a saturated stack at the Toxic Substance Control Act (TSCA) Incinerator at the DOE K-25 site in Oak Ridge, Tennessee during August 1997.
- Measured Be, Cd, Cr, and yttrium (Y) in a fly-ash-laden rotary kiln duct at the EPA Rotary Kiln Incinerator Simulator (RKIS) in Research Triangle Park, North Carolina, during September 1997.
- Measured single particulates containing Fe, silicon (Si), magnesium (Mg), sodium (Na), and calcium (Ca) at the Chevron USA Kern River co-generation gas turbine facility in Bakersfield, California, during November 1997.
- Measured Na, Ca, Mg, and silicon (Si) in the exhaust duct of glass furnace, including the discrete detection of micron-sized particles in an overall particle laden flow at Gallo Glass in Modesto, California, during December 1997.
- Measured transient concentrations of lead ranging from 50 to 50,000 micrograms per cubic meter in the Total Containment Vessel (TCV) at the Naval Air Weapons Station in China Lake, California during January and February 1998.
- Developed a software integrated conditional data analysis routine that can increase the LIBS sensitivity to particulate metal species by one order of magnitude or more under certain effluent stack conditions.
- Significantly enhanced LIBS sensitivity to the RCRA metals by optimizing the temporal gating of the LIBS detection scheme. Utilized the new time gating schemes with a new series of detectors to reduce the LIBS system weight by approximately 250 pounds and the total system hardware cost to below $40K.

Recent journal publications:

- D. W. Hahn, W. L. Flower, K. R. Hencken, Discrete particle detection and metal emissions monitoring using laser-induced breakdown spectroscopy, *Appl. Spect.,*51:1836-1844 (1997).
- D. W. Hahn, Laser-induced breakdown spectroscopy for sizing and elemental analysis of discrete aerosol particles, *Appl. Phys. Letters,* in press, Vol. 72 (June 1998).

TECHNICAL TASK PLAN (TTP) INFORMATION

TTP No./Title: AL33C231 - Metal Emissions Monitor for DOE Mixed Waste Thermal Treatment

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Laser-Induced Breakdown Spectrometer (LIBS) System Hardware Developed by CMST

LIBS Metal Emissions Monitor installed on Toxic Substances Control Act Incinerator at DOE K-25 Site, Oak Ridge, Tennessee