CONTINUOUS EMISSIONS MONITORING USING SPARK-INDUCED BREAKDOWN SPECTROSCOPY (SIBS)

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Steven J. Davis, and Mark E. Fraser

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Spark-Induced Breakdown Spectroscopy (SIBS)

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IMPLICATIONS

The work presented here, and that performed by other technology developers, is being used by
the EPA to evaluate the ability of CEMs to meet the draft MACT (maximum achievable control
technology) rule for compliance monitoring as required by the 1990 Clean Air Act Amendments.

ABSTRACT

A new technology for monitoring airborne heavy metals on aerosols and particulates based on
spark-induced breakdown spectroscopy (SIBS) was evaluated at a joint EPA/DOE test at the
Rotary Kiln Incinerator Simulator (RKIS) facility at EPA/RTP in September 1997. The
instrument was configured to measure lead and chromium in a simulated combustion flue gas in
real time and in situ at target levels of 15 and 75 µg/dscm. Actual metal concentrations were
measured during the tests using EPA Reference Method 29.

The SIBS technology detected both lead and chromium at the low and high level
concentrations. Additionally, the hardware performed without failure for >100 hours of operation
and acquired data for 100% of the reference method tests. The chromium data were well
correlated with concentration increases resulting from duct operations and pressure fluctuations
that are known to entrain dust.
INTRODUCTION

The Environmental Protection Agency (EPA) and Department of Energy (DOE) have recently collaborated to survey available technologies for continuous emissions monitoring (CEM) of hazardous air pollutant metals. The interest of the EPA is to enable implementation of the 1990 Clean Air Act Amendments for compliance monitoring of several toxic metals. DOE has funded some of the new technologies and would be a CEM user for their hazardous waste incinerators and in other applications.

In September 1997, the EPA and DOE jointly sponsored a test of prototype and commercially available CEM technologies at the Rotary Kiln Incinerator Simulator (RKIS) facility at the EPA National Risk Management Research Laboratory in Research Triangle Park, North Carolina. A total of seven CEMs were tested side by side in a duct following the secondary RKIS combustion chamber. Two different target concentrations of six toxic metals were introduced into the incinerator - 15 and 75 µg/dscm of beryllium, arsenic, chromium, cadmium, lead, and mercury. The EPA chose these concentrations to span the emission standards in the draft maximum achievable control technology (MACT) rule (40 to 50 µg/dscm proposed for Hg, Cd, Pb).

The technologies represented in the metals CEM development include inductively coupled plasma atomic emission spectroscopy (ICP-AES), laser-induced breakdown spectroscopy (LIBS), microwave plasma AES and spark-induced breakdown spectroscopy (SIBS). As modified for this application, ICP-AES is an extractive methodology where a relatively large volume of particulate laden gas is isokinetically removed from the emission stream and injected into the plasma. LIBS is an atomic emission spectroscopy sensor that
employs a high power pulsed laser to provide excitation. When the pulsed beam is highly focused, an air breakdown results, vaporizing and exciting all materials in the spark volume. This allows elemental composition to be determined. This method has been widely used to measure metals in particles contained in a gas stream,\textsuperscript{2,3} as well as numerous reports of use in soils,\textsuperscript{4,5,6} water,\textsuperscript{7,8} and on surfaces.\textsuperscript{9}

This paper describes the performance results for the PSI Spark-induced Breakdown Spectroscopy technology. SIBS is a newly-developed in-situ measurement technique\textsuperscript{10-12} based on atomic emission resulting from a high energy (typically 5 J) electrically produced spark. The SIBS technology has been developed as a low cost CEM alternative. In its excitation process, SIBS is similar to LIBS, but with substantially greater energy deposition and excitation volumes (5 J and 10 mm\textsuperscript{3}) SIBS offers greater potential sensitivity and more representative sampling than LIBS. SIBS also uses an inexpensive spark power supply in place of a laser. The SIBS technology avoids the high capital and operating costs of the extractive ICP and microwave methods by operating in situ, without any consumables (i.e. large diluent volumes of Argon), and uses simple and inexpensive radiometric optical detection.

**EXPERIMENTAL SECTION**

**Basis of Spark-induced Breakdown Spectroscopy (SIBS)**

The basis of SIBS is the generation of a high energy electrical spark between two electrodes that vaporizes, ionizes and excites an air sample with metal-containing aerosols and particulates. Following the generation of the spark, optical detection of the atomic emission at characteristic optical wavelengths of the metal analyte species is performed. The concentration of the species of interest in the sample is proportional to the number of excited atoms, and to the intensity of the emission of the atomic features.
The necessary instrument components are two electrodes with appropriate gap (5 to 6 mm) between them, a power supply and the optical collection equipment. For sampling a gas stream, the spark gap is situated such that the gaseous sampling stream can flow unimpeded between the electrodes. Because the number of aerosol particles encompassed is dependent upon the volume of the spark, the sensitivity of the technique is a function of electrode gap.

The spark power supply contains an EG&G power supply (<2000V, 100 J/s) integrated with a capacitor bank. The total discharge energy can be varied from 1 to 5J with 5J typical. Once the spark has been struck (1 Hz typical), optical detection is delayed to discriminate against broadband plasma emission caused by Bremsstrahlung radiation. Following this delay, the optical signals are collected radiometrically with a pair of filtered, miniature photomultiplier tubes. The delay time is typically 20 to 50 µs with an equivalent integration time. The advantages of the filter and PMT approach include simplicity and low cost. The strategy behind the radiometer is to accumulate the signal associated with the atomic line (on-line) with one filter and to subtract any background signal with a nearby filter (off-line) that has no analyte atomic feature inside its bandwidth. For lead the Pb(I) line at 405.8 nm is used with 400 nm for background. For chromium the Cr(I) line at 427.5 nm is used with 420 nm for background. The filters are 1 nm FWHM (full-width, half-maximum).

The radiometer analog output signals are input into a PC (Pentium, 100 MHz) with a 1.2-MHz A/D data acquisition board. The temporal traces are evaluated by routines developed within a LabWindows CVI® architecture. The on-line and off-line temporal traces are subtracted and the difference is then integrated. For this test, the data were averaged and reported on 2-minute intervals.
The spark discharge heats the air between the electrodes to extremely high temperatures (10,000 to 20,000 K) making SIBS generally applicable to metals analysis. The metals that have been examined so far include lead, chromium, mercury, cadmium, uranium and thorium. Further experimental details of the SIBS technology have been published elsewhere.\textsuperscript{10-12}

**RKIS Test Conditions**

A block diagram of the test configuration is shown in Figure 1. Details of the previous test (1996) and the 1997 test conditions are provided in EPA reports\textsuperscript{1,13,14} and are only summarized here. The tests were performed at the rotary kiln incinerator simulator facility located at EPA in Research Triangle Park, NC. Prior to the test the RKIS incinerator was modified to accept up to seven CEM ports by extending the Schedule 8 exhaust duct.

The incinerator runs on natural gas with ash added through a screw feeder. Metals (Pb, Cr, Be, As, Se, Sb, Hg, and Y) were added through a nebulizer into the afterburner as acidified solutions. The test goal was to achieve metals concentrations of 15 and 75 µg/dscm in the duct. Typically, three times the mass of metals addition were required to reach the target levels due to losses within the duct.

The gas temperature at the SIBS sampling port was typically 230°C (450 F). The particle loading in the exhaust gas was 30 mg/acm and the stack gas velocity was 31 ft/s. The average particle diameter was 0.5 µm. There were no acid gases present and typical CO\textsubscript{2} and water concentrations were 2.9% and 7%, respectively.

The SIBS instrument interfaced with the duct through a 4-in. NPT port. Sampling for Reference Method 29 was performed at two ports, one located immediately downstream of the afterburner and at one located farther downstream. Ten reference method measurements were performed at each RM port location at each of the two target metals concentrations. The CEM
instruments acquired data simultaneously. The CEM measured concentrations in acm units were turned into the EPA test sponsors the morning following each day’s test.

**SIBS Interface**

To test in the duct shown in Figure 1 required the design and development of a specialized spark probe to perform the measurements in situ. The probe, shown in Figure 2, is an aluminum tube that houses a bundle of six high temperature, 400 µm diameter fiber optics, two high voltage leads, and the electrodes mounted on ceramic standoffs. The stainless steel front plate is equipped with a quartz window to collect the emission from the discharge and three small diameter holes to exhaust the cooling air and designed to prevent ash deposition on the window. The fiber optics and high voltage leads were chosen for elevated temperature resistance but the epoxy used to seal the fibers to the SMA connectors softens at 60°C. Thus, approximately 2.5 cfm of air cooling was needed to ensure the rear of the probe remained below this limit when the probe was mounted in the duct. The probe is 2 ft long, 3 in. in diameter and weighs less than 5 lb.

To connect to the Schedule 8 duct at EPA, the probe was designed to fit into a 4-in. NPT cap outfitted with a vacuum fitting to seal around the body of the probe. A schematic of the instrument interfaced in the duct is shown in Figure 3. The ports at 90 and 180 deg with respect to the probe port were used to install quartz viewing windows to enable visual alignment of the probe such that the electrodes were perpendicular to the flow and that the spark would occur at the centerline of the duct. Because the spark was completely enclosed in the steel duct, radio frequency noise from this source was substantially reduced.
The timing of the power supply was controlled by a function generator, which can drive
the power supply from about 0.5 Hz to over 10 Hz. The function generator was nearly always
used at a repetition rate of 1 Hz, as this was the rate used in the calibration arrangement.

An optical multichannel (OMA) system composed of a spectrometer, multichannel
analyzer array, and data acquisition board, software and computer (providing 0.3 nm resolution)
was also employed at the test. This system was used for semi-quantitative analysis and broad
spectral surveys only. The radiometer was used for the quantitative measurements.

**Calibration**

The instrument was calibrated in the laboratory prior to shipment to the RTP facility. The
calibration system is a dry aerosol generator containing a Berglund-Liu style droplet generator for
the production of a monodisperse liquid aerosol. Solutions of metal salts dissolved in water are
fed through the unit and used to create a metal-containing aerosol. This wet aerosol is then
passed through a drying column held above 100°C to remove the water. At the sampling point
the dry particles are typically sub-micron in diameter and have formed a volume-filling cloud.
This apparatus has been gravimetrically calibrated with known amounts of lead nitrate, and has a
throughput efficiency to the spark chamber near 90%. Further details of the calibration
procedure, including a detailed calibration curve for lead, have been published.\(^{10}\)

The laboratory calibrations for both lead and chromium exhibited 3σ detection limits of
9 ppbw which correspond to ~ 10 µg/acm for the CEM test conditions. The calibrations were
linear up to the maximum concentration tested, 1 ppmw, and had correlation coefficients (R²) of
0.99 for Cr and 0.90 for Pb. The SIBS CEM was tested at EPA/RTP using these laboratory
calibrations. An in-situ field calibration source for the SIBS CEM was not available. However,
through extensive laboratory testing, the key to obtaining optimal sensitivity and maintaining
calibration was determined to be precise, reproducible optical alignment of the viewing geometry
of the optical fibers with respect to the electrode orientation. We therefore developed a method to
return the system in the field to the geometry under which it was calibrated in the laboratory.
This was performed by imaging a small, battery-operated (two AA batteries) diode laser
(670 nm) through the collection fibers onto a flat surface at a fixed distance in front of the probe.
The image was then compared to an image obtained with the calibrated, optimized configuration.
This procedure was performed at the end of each day of testing. Post-test calibrations of the SIBS
CEM in the laboratory were within ±10% of the pre-test results for both lead and chromium.

We performed extensive tests in the laboratory with this aerosol calibration source and a
multispectral detector (Princeton Instruments OMA) to ascertain interference-free operation within
the bandwidths of the filters (1 nm FWHM) under the conditions likely to be encountered during
the RTP tests. These tests included simultaneous calibration for lead and chromium with high
concentrations of iron, aluminum and silicon representative of the same relative concentrations
encountered in the test (the ash contains 52.8% SiO2, 27.6% Al2O3, and 10.2% Fe2O3).14 These
tests confirmed that no silicon, aluminum or iron lines fall within the chosen filter bandpasses.

Test Procedures

The first task of each day during the testing period was the insertion of the probe into the duct.
Following the removal of the 4-in. NPT cap, the sleeve for the probe was inserted, the cooling air
was turned on, and the probe put into the duct. The probe was visually aligned at the centerline of
the duct and perpendicular to the flow using a flashlight and the two window ports positioned 90
and 180 deg to the probe. Once the probe was in place, spark discharges were initiated and
instrument data were acquired and saved.
Each morning during the test, immediately following power-up, the gas stream within the duct was tested before the addition of either flyash or metals. This enabled a zero calibration system comparison. This check showed no change from the laboratory calibration conditions.

Real-time determinations of the concentrations in the gas stream were performed by creating sparks in situ and processing the observed intensities. This was accomplished by the Lab Windows CVI-based software which subtracted the off-line PMT intensity (the spectral background at a wavelength similar to the atomic emission being used to quantify the metal) from the on-line PMT intensity (the intensity at the wavelength of the atomic feature of interest). These voltages were then integrated over a specific temporal regime and written to a file in strip chart fashion. EPA/DOE test requirements determined the data analysis and reporting procedures. After each days tests, the voltages were input into a spread sheet where backgrounds were determined, the calibration constant applied, and standard deviations determined. The finished files of date, time, concentrations, and standard deviations coincident with the RM29 measurement periods for each element were then copied and given to EPA/DOE personnel on the morning following each test.

RESULTS AND DISCUSSION

Entrained Flow Reactor Test Results

Prior to shipment of the SIBS instrument to EPA it was tested in an entrained flow reactor (EFR) at our facility. This facility contains a screw feeder for ash or other additives, a natural gas burner, and an electrically heated reactor. This system has been previously used to perform fundamental studies of combustion chemistry including removal of heavy metals from coal-burning boiler utility exhaust by sorbent addition. For this test, a horizontal exhaust duct was set up which had a port for the SIBS probe.
The temperature and flow conditions of the EFR were set at 180°C and 18 to 20 ft/s, respectively. The addition of metals was performed by adsorbing metal salt solutions onto chromatographic carbon powder and co-injecting the powder with ash. A 1 lb sample of the same ash used in the EPA/RTP test was obtained from EPA. The metals added were chromium, lead, and yttrium.

Preliminary testing of the probe inserted into the EFR exhaust duct confirmed reliable operation of the spark and the ability of the probe to withstand 180°C temperature. The metals and ash mixture were added at three different feed rates corresponding to three different metals concentration. During these additions the SIBS CEM acquired both lead and chromium data while the optical multichannel analyzer monitored broad spectral regions. The SIBS instrument measured chromium levels of 50, 200, and 600 µg/m³. Although lead was added by the same mechanism, and therefore should have achieved a concentration level roughly equivalent to that of chromium, the SIBS CEM did not observe lead. The absence of emission at the 405.7 nm wavelength was confirmed by the OMA system. The OMA did confirm the presence of yttrium, however. The explanation for this behavior may be that the lead re-condensed on a cold spot in the reactor after passage through the flame and it did not persist on the ash to the point of measurement.

Pretest Results

The entire test period at EPA/RTP was two weeks in duration. During the first week, the CEM developers installed, calibrated, and tested their instruments. The SIBS CEM was installed in the duct and verified to produce reliable, reproducible sparks on the first day. The system was also verified to be able to handle the thermal stress of normal operation. However, when the RKIS
system was placed in “overnight” mode, during which the flow velocity increased above 40 ft/s, the temperature on the rear of the probe approached 60°C even with additional external directed air cooling. For this reason, the probe was always removed at night after each test before the system was placed in the “overnight” mode.

The typical sequence in the RKIS for the pretest period was to bring the system to temperature and flow, then add the ash which was followed by metals addition. This afforded the developers the opportunity to gauge instrument performance at each stage. The SIBS CEM acquired data during all of these sequences and promptly responded to both the chromium and lead on the ash, verifying detection of these species.

**CEM Test Data**

The SIBS detector was operational for the full duration of all twenty reference method tests. During these periods data were collected and analyzed for both lead and chromium. Sample plots for these two elements are shown in Figures 4 and 5. The data in Figure 4 were taken during a high-concentration run. The upper plot shows the Cr results and the lower plot the Pb data. The average chromium results for this period were $96.0 \pm 13.2 \mu g/acm$ (actual cubic meter) and the average lead results were $22.7 \pm 4.3 \mu g/acm$ (one standard deviation). It is important to note that these standard deviations are representative of variability in duct conditions and are not indicative of instrument noise levels. Figure 5 shows the data from the a low-concentration run. The plot shows two high concentration spikes for chromium. Several of the data files contain such spikes. The spikes appear only in the chromium data and we believe they correspond to duct operations causing pressure pulses and particle entrainment. The large particle pulses, which are high in chromium, then cause short-lived, but substantially elevated chromium signals. All
chromium concentration spikes were correlated with changes in duct operations as confirmed by EPA personnel during the test. The measured chromium average concentration in Figure 5 was $38.6 \pm 15.6 \, \mu g/acm$ and that for lead was $5.2 \pm 4.2 \, \mu g/acm$.

**Comparison to RM Results**

A comparison between the reference method data and the SIBS CEM data is shown in Table 1. The concentrations have been corrected for temperature and water vapor content and are shown in $\mu g/dscm$ (dry standard cubic meters) units. The only reference method data shown are lead, chromium, and iron. Iron is included as its principal source was from the ash. The RM Nos. 1 through 10 are those that targeted the high metals concentration and Nos. 11 through 20 targeted the low concentration level. The reference method data are reported separately for each of the stations.

The reference method data exhibit a high degree of variability from run-to-run and from station-to-station within a run. An example of the latter is RM No. 2 which has iron concentrations of 1723.2 $\mu g/dscm$ at RM position 1 versus 697.5 $\mu g/dscm$ at RM position 2, lead concentrations of 62.4 $\mu g/dscm$ at RM position 1 versus 42.1 $\mu g/dscm$ at RM position 2, and chromium concentrations of 55.8 $\mu g/dscm$ at RM position 1 vs 34.0 $\mu g/dscm$ at RM position 2. An example of the run-to-run variability is evident when comparing RM No. 5 to RM No. 6. For this comparison the data variability ranges from 50% to a factor of three.

The run-to-run variabilities can be explained by poor reproducibility in the ash screw feeder and in the metals addition system (the nebulizer/injector would occasionally clog). However, the station-to-station variability is suggestive of systematic differences between the stations. This possibility has been examined by performing correlation plots of the data from
each station. An example for lead for RM Nos. 11 through 20 (low target metals concentration, Position 2 versus Position 1) shows the data to be poorly correlated with an $R^2$ value of 0.028. Similar results have been obtained for lead for RM Nos. 1 through 10 and for chromium.

The cause of the poor correlation may be that the ash loading is changing between the two stations. This would explain both the changes in iron concentration, which arise from the ash, and the various added metals if they have been deposited on the ash or behave similarly to the ash. Support for this hypothesis is provided by plotting the metals data against iron from the same station. When this is done the correlation has improved substantially with $R^2$ now equal to 0.81. Similar correlation improvements are noted for the high target concentration of lead for chromium at both concentration levels. Further evidence for real differences between the stations is provided by plots of metals data from one station against iron from the second station which produce poor correlations.

This analysis indicates that the metals injected in liquid solution are depositing on the ash or are forming particles that behave similarly to the ash. Also, variations in the ash mirror corresponding variations in the observed metals. The large variations in ash (iron) that are observed at identical sampling times between the two RM stations indicate there to be large localized concentration variabilities even at the long sampling times of the RM data collection (1 to 1.5 hours). Thus, the two RM stations behave as though they are nearly independent.

The identification of systematic variability between the two RM sampling stations, and, thus, along the entire length of the exhaust duct, complicates comparison to the CEM developers data since none of the CEMs were co-located at the RM stations. The CEM data therefore cannot be compared on a run-by-run basis, only averages over the entire test series can be employed. This is the approach taken by EPA in the final report. The averaged RM data are shown in
Table 1 with one standard deviation error. Note that, even with this approach, the relative errors are still large, often approaching 25%.

Our determination of variability between the RM sampling stations differs from a statistical analysis summarized in the 1997 report. The study in the 1997 report concluded that the differences between downstream and upstream samples did not prove to be statistically significant at the 95% confidence level. We have re-analyzed the statistics using the original work as a basis and have determined that a more thorough analysis incorporating critical experimental details leads to conclusions consistent with our observations. Our suggestions to improve future CEM tests include co-location of the CEMs and the RM stations, tracking iron to correct for systematic station-to-station variability, or expanding the 20% relative accuracy benchmark.

A principal conclusion in the EPA report is that no CEM developer of the six who participated in the test obtained data within the required 20% relative accuracy of the RM data. Considering the systematic RM variability identified here, it is unlikely that any technology could have met this benchmark. Expanding the relative accuracy goal to 50 to 75% will enable some of the CEM technologies to be judged compliant in future tests.

Comparison of the SIBS CEM averages against the average RM data in Table 1 indicate that the measured SIBS chromium values typically exceeded the RM chromium values by a factor of two and our measured Pb values were about a factor of three below the RM values. These differences are outside the target 20% relative accuracy but would be adequate for relaxed standards of 50% to 75% relative accuracy. To further improve the absolute accuracy of the SIBS CEM, we are considering an in-situ calibration system to introduce metals directly in the sampled environment (duct) to provide an unambiguous calibration.
The SIBS CEM acquired data for both lead and chromium, the only metals targeted, for all reference method test periods. The instrument operated for >100 hours without failure and without need for electrode maintenance. The acquired data do show some discrepancies against the absolute RM values, as discussed above, but such differences are typical for the first field test of a new technology. The absolute calibration and performance of the instrument will be improved such that the correlation to the RM data will be improved in the future.

ACKNOWLEDGMENTS

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LIST OF ACRONYMS

ACM - Actual Cubic Meter
EPA - Environmental Protection Agency
CEM - Continuous Emissions Monitor
MACT - Maximum Achievable Control Technology
RKIS - Rotary Kiln Incinerator Simulator
DOE - Department of Energy
RTP - Research Triangle Park
MDL - Method Detection Limit
PMT - Photomultiplier Tube
OMA - Optical Multichannel Analyzer
SIBS - Spark-induced Breakdown Spectroscopy
LIBS - Laser-induced Breakdown Spectroscopy
EFR - Entrained Flow Reactor
DSCM - Dry Standard Cubic Meter
RM - Reference Method
ICP-AES - Inductively-coupled Plasma Atomic Emission Spectroscopy
SMA - Standard Multi-purpose Adaptor
FWHM - Full-width Half-maximum

REFERENCES


**ABOUT THE AUTHORS**

Dr. Mark E. Fraser (corresponding author) is a Principal Research Scientist, Dr. Amy J.R. Hunter is a Principal Scientist, Mr. Joseph R. Morency is a Principal Scientist, Dr. Constance L. Senior is Area Manager for Chemical Process Technologies, and Dr. Steven J. Davis is Vice President for Applied Technologies. All are with Physical Sciences Inc., 20 New England Business Center, Andover, MA 01810.
Table 1. SIBS CEM comparison to reference method data (concentrations are shown in units of µg/dscm).

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<th>Pos. 1 Pb</th>
<th>Pos. 2 Pb</th>
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[List of Figures]

Figure 1. Schematic of the EPA RKIS test configuration.

Figure 2. Schematic of the SIBS probe design

Figure 3. Block diagram of SIBS CEM apparatus.

Figure 4. Plot of Cr and Pb results during high concentration conditions.

Figure 5. Plot of Cr and Pb results during low concentration conditions.
Figure 1.
Figure 4.