



Implementation of laser-induced breakdown spectroscopy as a continuous emissions monitor for toxic metals

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Abstract

Laser-induced breakdown spectroscopy (LIBS) has been considered for some time as a potential CEM method for toxic metals. Recently, improvements in sampling methodology and signal processing have allowed LIBS to achieve detection limits below the proposed MACT limits for 5 out of 6 of the RCRA metals. This paper discusses performance improved by nearly 2 orders of magnitude of this in situ monitoring technique following implementation of conditional analysis. Results from trial burns at two incinerators and at a DoD contained burn facility are highlighted. At the incinerators, implementation of conditional analysis yielded much lower detection limits than previously reported using the LIBS technique. At the contained burn facility, reproducible, transient Pb measurements were recorded in real-time for concentration values that varied by more than two orders of magnitude. Method detection limits of between 2 and 100 $\mu\text{g}/\text{dscm}$ are reported for toxic metals Be, Cd, Cr, Hg, and Pb. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) has been used as an analytical technique for gases, liquids, and solids for some time [1–3]. Applications of LIBS typically employ a pulsed laser with a high peak power to form a spark (breakdown) in the medium to be examined. In gases, the temperature of the resulting plasma at short times ($< 10 \mu\text{s}$) is in the range of 10,000–25,000 K [4], hot enough to dissociate molecules into their constituent atoms, and to excite the electrons in the neutral atoms and ions formed in the plasma out of the ground state and into excited electronic states. As the plasma cools, excited electrons and ions relax back into their ground states, emitting light at characteristic atomic frequencies. Identification of the atoms present in the sample volume occurs using well-known atomic emission lines, and quantification of the elemental species concentration occurs via quantification of the

intensity of the emission lines. Sensitivities range from parts-per-billion (ppb) for some species, such as Be, to well above the parts-per-million (ppm) level for other species, such as Sb. LIBS detection limits are slightly higher compared with inductively-coupled plasma diagnostics and some other toxic metals monitoring methods [5], but LIBS has in situ, real-time advantages (e.g. avoiding extractive sampling lines that can introduce significant errors and uncertainties) that offer significant benefits.

This paper will discuss the implementation of LIBS as a continuous emission monitor (CEM) for toxic metals [6–8]. We will use illustrative data obtained at field trials at the EPA rotary kiln incinerator simulator (RKIS) in Research Triangle Park (NC), at the DOE TSCA Incinerator in Oak Ridge (TN), and at a contained burn of Shillelagh rockets at the Navy's contained burn facility (CBF) at China Lake Naval Air Weapons Station (CA). In the RKIS and TSCA tests, several metals were individually spiked into the exhaust stream. The LIBS monitor was placed downstream of the injection point, and concurrent sampling was done using the EPA Multi-Metals Sampling Train, known as EPA Method 29. In the CBF test, the LIBS monitor was placed before a bank of HEPA filters during a contained burn of Shillelagh rockets, which contain approximately 2% Pb (by mass) in the propellant as a burn rate modifier. The Army has approximately 40,000 of these rockets to destroy.

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2. LIBS data acquisition and analysis

2.1. Conditional analysis

In the stack of a typical combustion device following the air pollution control equipment, temperatures are such that most of the toxic metals (with the notable exception of Hg) have a negligible vapor pressure. As a result, at stack temperatures, most metals are present in condensed phase on discrete particles, the loading of which is often very low. Using a fixed-frequency LIBS instrument under these conditions, the sampling rate of toxic metal particles (i.e. the particle hit rate) can be very low, resulting in a very poor detection limit when signals are ensemble-averaged in the traditional manner. To improve LIBS response at low concentration levels, a conditional data analysis routine was incorporated into the Sandia metal emissions monitor in 1997 [6]. The conditional analysis approach implemented for the LIBS-based metals monitor is based on independent, fixed-rate sampling combined with the analysis of each laser pulse in an overall sequence of pulses. Hits corresponding to targeted elements are identified using a threshold criteria applied to the atomic emission lines. With this approach, spectra are recorded and analyzed in real-time for a total number of desired shots, typically 600–1200 total pulses. An average spectrum is generated based on the ensemble average of the spectra recorded for all shots identified as hits (i.e. those exceeding the threshold). An equivalent metal concentration is then calculated from this average spectrum using the integrated line intensities and calibration curves as described below. The true or actual metal concentration is then calculated from the product of the equivalent concentration for hits only and the frequency of hits (i.e. number of hits/total number of pulses). For low particle loadings, this separation of LIBS spectra containing the desired metal signals (i.e. hits) from the many spectra containing no information (i.e. misses) can greatly increase the signal-to-noise ratio for the selected metal emission lines. When the frequency of identified hits equals 100%, the conditional analysis technique converges to a conventional ensemble-averaging scheme. This can be accomplished at any time by setting the hit threshold sufficiently low such that all shots are designated as hits. The current system can also operate simultaneously in both conditional analysis and ensemble-averaging modes.

2.2. Calibration

Using either the conditional analysis scheme or conventional ensemble-averaging, the resulting output spectrum contains a continuous background emission signal with superimposed discrete atomic emission line signals. For each targeted analyte emission line, a LIBS

signal is calculated based on the integrated emission line peak divided by the surrounding continuous background intensity level. A concentration is calculated from a library of linear calibration curves entered for each target analyte atomic emission line, as determined in the laboratory using a calibration flow stream of known mass concentration, and with identical LIBS parameters (e.g. lens focal length, laser power) as utilized for the field measurements. Recent work has shown that ambient conditions (humidity, temperature, gas composition, particulate levels) have little effect on the laser spark [4], hence we expect that a calibration at laboratory conditions will be suitable for analysis of stack gases. For the September 1997 field test at the RKIS facility, the Sandia LIBS-based metal emissions monitor was calibrated for the following elements for the elements listed in Table 1.

2.3. Hardware and data acquisition

The Sandia LIBS-based metals CEM utilizes a 1064-nm Nd:YAG laser (Continuum Surelight) as the excitation source, with a nominal pulse width of 10 ns and pulse energy of 350 mJ. This relatively high pulse energy contributes to the stability and repeatability of the LIBS measurement, for example, by eliminating particle-triggered breakdown when operating at near-threshold intensity levels. The laser beam is expanded to 12 mm and then focused to create the plasma using a 75-mm focal length, 50-mm diameter UV-grade quartz lens. The 50-mm lens also functions to collect the plasma emission. A schematic of the LIBS monitor system is presented in Fig. 1. LIBS spectra are collected at 5.0 Hz using an Acton 1/4 meter spectrometer and a Princeton Instruments time-gated CCD array. The CCD intensifier gate width used for the RKIS field test was 3.5 μ s, with a time delay of 18.0 μ s from the laser pulse. These parameters are somewhat longer than those commonly used in LIBS analysis, but were found to yield better signal-to-noise ratios for many elements. A similar configuration

Table 1
Calibrated atomic emission lines for the RKIS facility

Element	Calibrated atomic line (nm)
Antimony (Sb)	252.9
Arsenic (As)	286.0
Beryllium (Be)	313.0
Cadmium (Cd)	228.8
Chromium (Cr)	283.6
Iron (Fe)	238.2
Mercury (Hg)	253.7
Lead (Pb)	220.4
Silicon (Si)	288.2
Yttrium (Y)	294.6

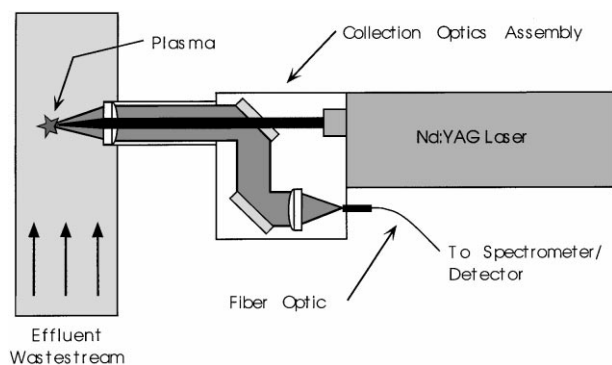


Fig. 1. Schematic of LIBS monitor system probe.

was employed in the CBF test, with the exception that the CCD intensifier gate width was 100 ns, following a delay of 50 ns from the laser pulse, allowing much improved sensitivity for the Pb atomic emission line at 405.8 nm. A more detailed treatment of CCD delay and gate choices can be found elsewhere [9].

The LIBS system is controlled remotely by a PC-based computer. For the RKIS test, the computer was situated downstairs about 50 ft. from the duct, and was linked to the stack-mounted probe and instrument rack by a fiber optic communications cable. The Sandia monitor is controlled with a single LabVIEW based program that was designed and coded specifically for the LIBS system. Using a 2400 groove/inch grating, the spectral bandwidth is 30 nm, with a spectral resolution of about 0.035 nm per detector array element (i.e. pixel). To cover all of the atomic emission lines listed in Table 1, four spectral windows were utilized during the RKIS field test. The four spectral windows and targeted species are summarized in Table 2. The conditional data analysis interface allows the selection of up to six separate species for subsequent analysis in any given spectral window. In real-time, each spectrum is analyzed sequentially for each of the designated species using the corresponding hit thresholds.

External requirements for the LIBS monitor system include a 110 V, 5 A power supply; a 220 V, single-phase, 10 A power supply; and a 5 l/min supply of purge gas such as nitrogen or argon. The purge flow is blown across the outer surface of the 2-inch diameter lens as a preventive measure to keep the optic clean.

For a typical test in a low-particle-loading situation, 600 laser pulses are used for each data point, corresponding to

2 min per data point, respectively, at the 5 Hz acquisition rate. At the end of each pulse sequence, the data are analyzed automatically using the calibration procedure outlined above, the concentration data are entered and stored on disk in a sequential log file, and the spectral data are stored on disk. The analysis and file writing process takes about 2 s for completion, at which time a new pulse sequence can be initiated immediately. The four spectral windows listed in Table 2 were cycled through once for each of the individual 1 h test runs. Using either 800 or 1200 laser pulse sequences, 5 or 8 data points were generated for a given window, after which the spectrometer was rotated to the next window and the process repeated. The changing of spectral windows is also controlled remotely with the LabVIEW program and takes about 1–2 min to accomplish. With this procedure, concentration measurements comprised of 5–8 2 min averages were recorded for each element during each hr test period. This corresponds to the monitor being on-line nearly 100% of the test period, with resulting data for any given targeted species covering about 25% of the test period.

3. Instrument installation

3.1. Probe installation

The Sandia LIBS monitor is placed in a test section of the duct being sampled, ideally far from bends in the duct and other flow disturbances. The LIBS laser assembly is inserted through a specially designed flange that functions to anchor the probe and to seal the exhaust stack gases. The flange mounts to an existing standard 4-inch NPT pipe nipple. The entire laser probe module (see Fig. 1) is mounted on a self-supporting table that enables the probe to easily slide into and out of the process stack. The entire laser probe module weighs about 75 lb. One supporting instrument rack (30"×30"×48", 300 lb.) is stationed nearby on the floor, and contains the laser power supply, the spectrometer, and the CCD detector and controller. It takes approximately 6 h to unload and install the equipment and to perform a system check.

3.2. System check

The system check to ensure proper operation of the LIBS monitor is comprised of two primary tasks: wavelength calibration of the spectrometer and CCD array, and a check of system response and calibration. Because the spectral data from the CCD array corresponds to light intensity as a function of detector element, or pixel number, all data analysis within LabVIEW is done in pixel-space rather than wavelength-space. Accordingly, each atomic emission line corresponding to a targeted

Table 2
Spectral windows and corresponding species

Window center (nm)	Targeted species
225	Cd, Pb,
250	Hg, Fe, Sb
277	As, Cr, Si
305	Be, Y

metal is assigned a pixel location number corresponding to a given spectral window. The pixel locations are entered into the software calibration file. However, the absolute pixel location of a given emission line can shift by several pixels during instrument shipping, during extended instrument shutdown, or during wide temperature fluctuations. The carbon atomic emission line at 247.86 nm is used for instrument wavelength calibration. Sufficient signal can be obtained from the CO₂ in the ambient air to perform the spectral calibration. During the nearly two-week test period at the RKIS, the pixel shift ranged from 1 to 2 pixels with respect to the laboratory calibration performed in California prior to shipment. The pixel offset from the wavelength calibration is entered in the LabVIEW program for automatic correction of all atomic emission line locations.

The system response and calibration check is accomplished with a calibration cell of known gas composition. A helium gas cell at ambient pressure is used for the system check in the field. Helium has a strong atomic emission line at 388.86 nm. The concentration of helium gas within the calibration cell is calibrated in the laboratory prior to shipping and entered in the software calibration file. In the field, the concentration of helium within the cell is calculated and compared to the pre-shipment calibration value. This calibration check allows correction for changes in the system throughput after shipping or after use, such as dirty or misaligned windows or lenses. Typically both of these system checks are done at the beginning of each day.

4. Field test results — RKIS and TSCA

4.1. Data collection modes

The Sandia LIBS-based metals monitor was operated in a conventional ensemble-averaging mode for beryllium and iron due to the strong spectral responses recorded. Lead was also monitored using ensemble-averaging as well as conditional analysis. Arsenic and antimony were not monitored during the actual tests due to the presence of spectral interferences either recorded or expected on the most accessible atomic emission lines. The strong arsenic emission lines at 228.81 and 234.98 nm have interferences with much stronger emission lines from cadmium at 228.80 nm and beryllium at 234.86 nm, respectively. A much weaker arsenic emission line at 286.0 nm was determined to lack sufficient sensitivity. Similarly, the strongest antimony emission lines at 252.85 and 259.81 nm have interferences with much stronger lines from silicon at 252.85 nm and iron at 259.94 nm, respectively. The very large spectral contribution from silicon and iron, attributed to the fly ash, made antimony analysis unfeasible with the available emission lines. The most suitable atomic emission

lines for these two elements are 189.04 nm for arsenic, and 206.84 nm for antimony. Both of these lines are deeper into the ultraviolet wavelength region than can be accessed with the fiber-optic coupled detector system used in the current Sandia monitor. These short wavelengths require working with vacuum-UV spectrometers and purged or evacuated optical paths, which are not practical with a stack-mounted, in situ LIBS probe package.

The conditional data analysis scheme was used for cadmium, chromium, lead, and yttrium throughout the formal test period at the RKIS and TSCA. The relatively low targeted concentration levels provided an excellent test of the conditional analysis mode as a means to enhance signal response.

4.2. LIBS data

The species measured at the RKIS facility were beryllium, cadmium, chromium, iron, and yttrium. While none of the candidate metal emissions monitors (including ICP and other LIBS instruments) tested at the EPA RKIS or at TSCA during these tests met the goal of agreement with the Reference Method 29 to within 20% for all tests, the Sandia LIBS monitor performed well. On a time-averaged basis, the overall agreement between the LIBS CEM data and the Reference Method 29 data was rather good, with an average difference of 63% for all species, feed rates, and test periods. Excluding the beryllium data, which exhibited the largest differences, the average difference between the LIBS data and Method 29 data is 37%.

In addition to the average values, it is useful to assess how well the LIBS CEM data tracked the individual Method 29 test results. The average LIBS data for each 1 h test period are presented along with the Method 29 results for cadmium and chromium in Figs. 2 and 3, respectively. Overall, the data are observed to track rather well with the Method 29 data.

4.3. Conditional analysis results

The conditional analysis technique was successful in significantly enhancing the signal-to-noise ratios for cadmium, chromium, and yttrium. Non-detects would have been reported for cadmium, chromium on the low spiking days, while yttrium would not have been detected on any day, using a conventional ensemble-averaging scheme as currently configured. An example of conditional analysis is presented in Fig. 4 for the detection of cadmium. The ensemble-averaged spectrum corresponds to 600 laser pulses. The conditionally analyzed cadmium spectrum corresponding to the subset of 24 laser pulses that triggered on cadmium, a hit frequency of 4%. A significant increase in signal-to-noise is apparent with conditional data analysis. Another interesting feature is that the spectral features attributed to

iron (a relatively refractory metal) are present at comparable levels in both the ensemble-averaged spectra and in the conditional analysis spectrum. This suggests no correlation between the presence of iron and either cadmium or chromium. In fact, the comparable signal levels of iron in both spectra suggest that iron may be appearing on ultrafine particles dispersed with a high

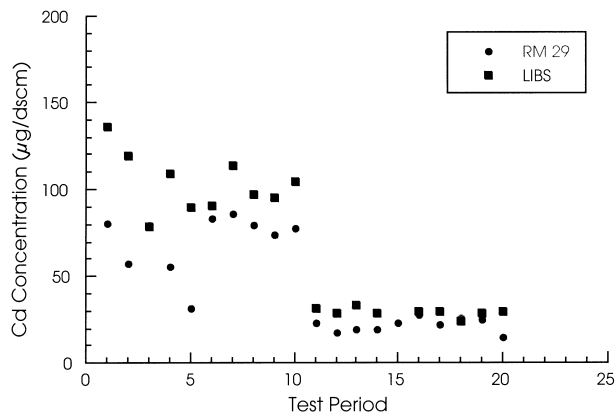


Fig. 2. Comparison of Method 29 and LIBS Cd concentration data at the RKIS.

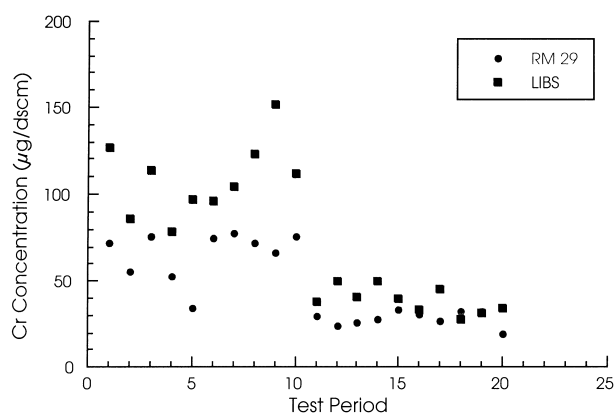


Fig. 3. Comparison of Method 29 and LIBS Cr concentration data at the RKIS.

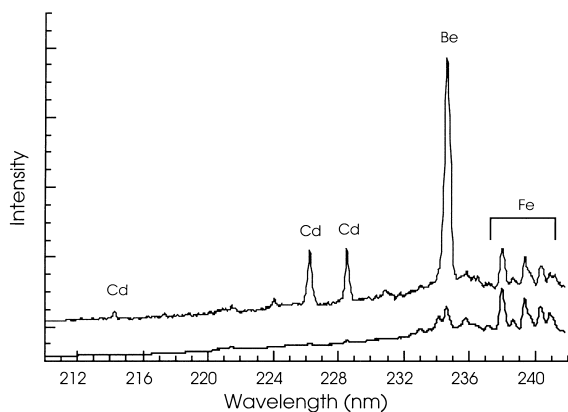


Fig. 4. Spectrum of Cd hits ($n=24$) and corresponding ensemble-averaged spectrum ($n=600$). Spectra have same intensity scale and are shifted for clarity at the RKIS.

number density. However, the beryllium emission lines are enhanced significantly with the presence of cadmium (and also with chromium in other conditionally-analyzed spectra). This strong correlation was recorded consistently, and suggests that cadmium and chromium are present with beryllium on specific particles, likely small particles formed during the nucleation/condensation process.

Fig. 5 shows periodic measurements of chromium at the TSCA incinerator; each point represents a 2-min (600-point) conditional analysis concentration measurement. The solid line indicates the average measurement as would be indicated by a conventional, integrating, extractive method such as the EPA Reference Method 29. Times for which there are no periodic chromium measurements are times that the spectrometer was investigating other spectral windows besides the chromium window. The striking thing about Fig. 5 is the spike in the chromium concentration that occurred at approximately 14:30. This periodic increase in concentration, which was observed at other times for other metals, was found to correspond to periodic washing of the electrostatic precipitator. Such a brief, transient event would contribute little to the average value (and little to overall emissions) and would not be measurable with an integrating sample method. Subsequent process changes at TSCA have minimized the impact of the ESP wash on emissions. This is an example of the benefits of real-time, rather than extractive monitoring for air toxics.

5. LIBS sensitivity

5.1. Conditional analysis

As discussed above, the conditional analysis method as a means to increase LIBS sensitivity was very successful during the EPA RKIS field test. The conditional

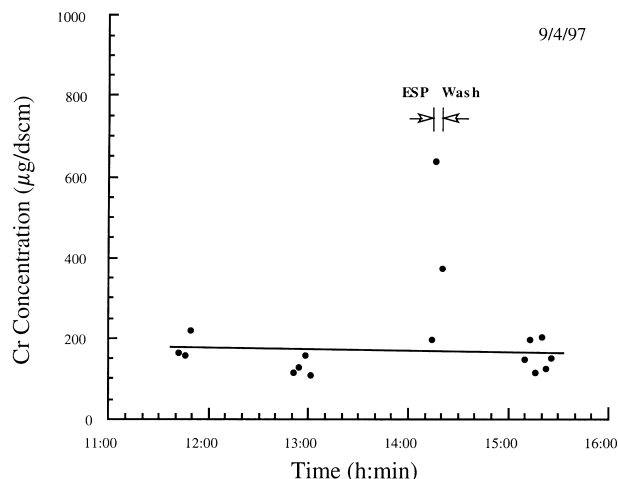


Fig. 5. Detection of the ESP wash cycle at TSCA incinerator.

analysis technique consistently detected discrete particle hits during the formal test period. On average, the hit rates were in the range of 2 to 5% throughout the test. To first order, this corresponds to an increase in signal-to-noise by a factor of 25, as is apparent in Fig. 4. Working with enhanced signal-to-noise ratios can extend the lower detection limits of a LIBS instrument and provide improved accuracy at near detection limits.

5.2. Signal sensitivity and detection limits

The sensitivity of the LIBS technique to the targeted species under the RKIS and TSCA stack conditions can be elucidated through comparison of LIBS spectral data and reported concentration values with the Method 29 reference data. A careful analysis was performed with regard to the targeted metals beryllium, cadmium, chromium, lead, and mercury.

Using the test data generated at the RKIS facility as described above, in combination with laboratory work and prior field experience, the lower detection limits for the Sandia LIBS monitor were determined for the RKIS facility and are summarized in Table 3. The values reflect a signal-to-noise ratio of 3-to-1 at the method detection limit (MDL) for 600-shot (2 min at 5 Hz) measurements. It is noted that the detection limits summarized in Table 3 are in the units of micrograms per dry standard cubic meter, which reflect values approximately 1.8 times greater than those at actual stack conditions (micrograms per actual cubic meter). In addition, the detection limits presented below are based on a combination of conventional ensemble-averaging and conditional analysis modes of operation. Considerable improvements in sensitivity have been made since the September 1997 test by using alternative emission lines in combination with very long delay times. The arsenic, lead, and mercury detection limits in Table 3 reflect these recent results utilizing the 278.0, 405.8, and 253.7-nm emission lines, respectively.

Table 3 does not include detection limits for the element antimony. It is noted also that despite the improvements in arsenic, the MDL of Table 3 is still relatively high. Spectral interferences combined with

relatively low emission signals were discussed above for antimony and arsenic. Suitable atomic emission lines are available at 206.83 nm for antimony, and 189.04 and 197.20 for arsenic. These lines are not accessible with the fiber-coupled configuration currently used for the in situ Sandia LIBS system; however, recent work with a second (photomultiplier tube) detector coupled to a bandpass filter suggests that arsenic could be measured using LIBS if a second single-channel detector were employed. A dedicated single-channel detector would only minimally impact the cost of the overall LIBS system.

6. Field test results — CBF

The Sandia LIBS instrument was deployed at the China Lake Naval Air Weapons station to measure lead emissions during a contained burn of Shillelagh anti-tank missiles, for which the Naval Air Warfare Center and Lockheed Martin are working together to develop a demilitarization procedure. The primary environmental concern is generated by the solid propellant in the Shillelagh, which contains 32 g of lead. In the prototype process, the rocket motor is fired into a sealed chamber and high-efficiency particulate filters are used to scrub the subsequent gaseous and particulate emissions. The LIBS system was mounted in a 10-inch duct at the entrance of the filtration system to measure the total airborne lead generated by a burn. The LIBS system measured lead using the 405.8 nm emission line, a delay following the laser pulse of 50 s, and an integration gate of 100 s. An ICP system with a lower detection limit of 2 g/m³ was mounted at the exit of the filtration system.

Fig. 6 shows the LIBS measured lead concentrations during four individual Shillelagh rocket motor burns spaced over a period of a month. These data were taken

Table 3
Estimated LIBS method detection limits

Element	Detection limit (ug/dscm)
Antimony (Sb)	NA
Arsenic (As)	400
Beryllium (Be)	2
Cadmium (Cd)	5
Chromium (Cr)	5
Mercury (Hg)	80
Lead (Pb)	20

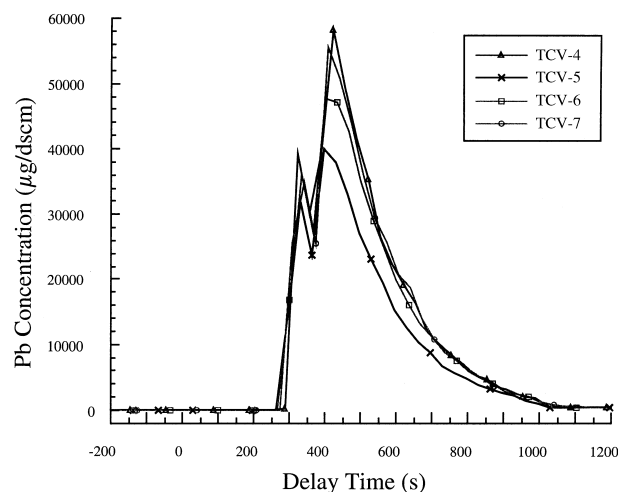


Fig. 6. Time series of Pb concentration measurements in the CBF during a Shillelagh rocket motor burn.

with one data point every 30 s, corresponding to an ensemble average of 150 laser shots. The lead concentration data are reported as a function of delay time with respect to the firing of the motor at $t=0$ s. At 300 s, positive pressure was vented from the tank through the 10-inch exhaust duct and into the filtration system. Starting at $t=390$ s, the tank was continually flushed with ambient air at approximately 1500 scfm until $t=1020$ s. The lead emission profiles are very similar for all four tests shown in Fig. 6. The concentration rises rapidly when the tank is vented, resulting in a peak of between 30,000 and 40,000 $\mu\text{g}/\text{acm}$ (approximately 30–40 ppm by mass). The lead concentration then decreases slightly until the blower is turned on at $t=390$ s, after which all of the curves hit their peak value of between 40,000 and 60,000 $\mu\text{g}/\text{acm}$. The Pb concentration then decays steadily while the tank is continually flushed.

The data in Fig. 6 demonstrate the ability of the in situ Sandia LIBS monitor to (a) respond rapidly to changes in concentration, (b) work over wide ranges in concentration, and (c) operate in high concentrations and low concentrations without residual signal from the high concentration measurements. The Pb measurement in the tank spanned approximately three orders of magnitude in signal, from 50 $\mu\text{g}/\text{acm}$ to 50,000 $\mu\text{g}/\text{acm}$. The rapid rise in signal was captured very well by the real-time data from the LIBS instrument. The instrument had the dynamic range to capture all of the pertinent data from this test, and unlike extractive methods, the LIBS instrument was not fouled by the high concentrations. Other candidate CEM methods have reported being unable to use their instruments following a high concentration spike of Hg or Pb, until their extractive probes were cleaned. The in situ LIBS instrument, however, does not have a problem with a wide range of metal concentrations, and yielded consistent data over a period of a month. Table 4 summarizes average, peak, and time-integrated lead concentration measurements made using the Sandia LIBS instrument during the four Shillelagh rocket motor runs. The time-integrated LIBS measurements agreed very well with time-averaged extractive sampling techniques.

7. Summary

The tests of the LIBS-based continuous metal emissions monitor at the EPA RKIS facility and at the DOE

Table 4
Lead concentration values before particulate scrubber on the CBF

	TCV-4	TCV-5	TCV-6	TCV-7
Average ($\mu\text{g}/\text{acm}$)	20,700	15,000	18,500	19,600
Maximum ($\mu\text{g}/\text{acm}$)	58,200	39,900	47,600	55,500
Time-integrated (g)	10.15	6.80	9.59	9.85

TSCA incinerator were successful in demonstrating a real-time response to targeted metal species. All data analysis and data reporting procedures were fully automated and performed in real-time, with the instrument being on-line during 100% of all test periods. It is noted that the Sandia monitor utilizes an absolute pre-test calibration that requires no on-site adjustment, post-processing, or post-test calibration. Overall, consistent stack concentration readings were recorded with the LIBS monitor, in good agreement with independent Method 29 reference data. The Method 29 data enabled determination of overall accuracy of the LIBS technique, as compared with the only EPA-accepted sampling protocol, and establishment of lower detection limits for the RKIS stack conditions.

The conditional data analysis approach was evaluated in the RKIS and TSCA tests and concluded to be very useful in increasing the LIBS sensitivity through discrete particle detection. The conditional analysis approach was successful in detecting single particulates under normal operating conditions, yielding signals with significantly enhanced signal-to-noise ratios as compared to conventional ensemble averaging. The Sandia monitor also accurately tracked transient changes in metals feed rates. Overall, the RKIS and TSCA tests have demonstrated that a LIBS-based continuous emissions monitor for metals can provide real-time response and concentration measurements in a pilot-scale treatment facility with a soot-laden stack gas.

The CBF tests of the LIBS monitor illustrate the combination of rapid response, large dynamic range, and hysteresis-free measurements that are possible with the Sandia CEM. Together, these measurements illustrate the present status of the LIBS-based toxic metals CEM under development at Sandia. Further work will focus on the integration of an arsenic detector into the LIBS monitor, improvements in calibration and accuracy, and on finding opportunities to test and deploy the metals CEM for emissions monitoring, process monitoring, and control.

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