

SANDIA REPORT

SAND97-8270 • UC-402

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Printed July 1997

Performance Testing of a Laser-Induced Breakdown Spectroscopy (LIBS) Based Continuous Metal Emissions Monitor at a Pyrolytic Waste Treatment Facility

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Prepared by
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for the United States Department of Energy
under Contract DE-AC04-94AL85000

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**Performance Testing of a Laser-Induced
Breakdown Spectroscopy (LIBS) Based
Continuous Metal Emissions Monitor
at a Pyrolytic Waste Treatment Facility**

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Abstract

A program was initiated at Sandia National Laboratories to develop and demonstrate an advanced continuous emissions monitor that will provide real-time measurement of metal emissions in the wastestreams of thermal treatment facilities. This effort led to the development of a prototype metals monitor based on an optical technique referred to as laser-induced breakdown spectroscopy (LIBS). The measurements are performed *in situ*, and are both noninvasive and real-time. The automated software incorporates a new conditional analysis algorithm that utilizes single particle detection. The metal emissions monitor was tested during March 1997 at a pilot-scale pyrolytic waste processing facility in Santa Fe Springs, California. This report describes the field test, including the monitor installation, test cycle, and overall instrument performance. The Clean Air Act metals chromium and manganese were recorded at concentrations from approximately 2 to 5 parts per billion. Iron was recorded at concentrations from 40 to 140 parts per billion. The overall accuracy was in very good agreement with contracted EPA Reference Method 29 results. Overall, the LIBS-based metals monitor performed exceptionally well on a waste treatment facility with very low metal emissions levels.

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Preface

This work was sponsored in part by a Memorandum of Understanding (MOU) between the U.S. Department of Defense, Office of Munitions, Joint Services Demil Technology Office, and the U.S. Department of Energy, Defense Programs Office, and in part by the U.S. Department of Energy, Office of Science and Technology, Characterization, Monitoring, and Sensors Technology Crosscutting Program (CMST-CP).

The field test was performed at Balboa Pacific Corporation in Santa Fe Springs, California. Activities related to this field test were done in cooperation between Sandia National Laboratories and Balboa Pacific Corporation. We would like to acknowledge Dr. Shapoor Hamid and Mr. Jerry Holt of Balboa Pacific for providing access to their facility and for their assistance throughout the entire test.

Nomenclature

acm	actual cubic meter of gas
AES	atomic emission spectroscopy
APCS	air pollution control system
CCD	charge-coupled device
CEM	continuous emissions monitor
Hz	measure of frequency, cycles/sec
ICP	inductively coupled plasma
LIBS	laser-induced breakdown spectroscopy
MACT	maximum achievable control technology
µg	microgram, 10^{-6} g
ppb	part per billion (mass)
RCRA	Resource Conservation and Recovery Act
RM	reference method

Introduction

In recent years, considerable resources have been directed toward the development and testing of new continuous emissions monitors (CEM's) for metals in process wastestreams. The motivating factors that drive CEM development are diverse and include regulatory compliance, public assurance of treatment technologies, and process optimization and control. Recent draft maximum achievable control technology (MACT) standards encourage the development and use of continuous emissions monitors for metals.¹ One goal is the reduction or elimination of expensive compliance testing, thereby facilitating the permitting process. Furthermore, with waste treatment processes often coming under increased public scrutiny, continuous or near-continuous emissions data may be beneficial in promoting public confidence in treatment technologies. An additional application that has gained attention is the use of CEM data for process control and optimization. Cost benefits can be realized by curtailing often expensive front-end waste characterization, and through enhanced process efficiency via CEM data feedback. The broad scope of CEM incentives and potential benefits has led to a wide range of technologies and development efforts.

The technologies in the forefront of metals CEM development include inductively coupled plasma atomic emission spectroscopy (ICP/AES), microwave induced plasma atomic emission spectroscopy (MIP/AES), and laser-induced breakdown spectroscopy (LIBS), also referred to as laser-spark spectroscopy (LASS). The report will focus only on LIBS, the one technology of the three that has been demonstrated in the field as a real-time monitor that is both *in situ* and noninvasive. LIBS is an atomic emission spectroscopy diagnostic that utilizes a high power, pulsed laser beam as the excitation source. The resulting optical breakdown, also referred to as a laser-induced plasma or laser spark, dissociates molecules and excites all atoms within the probe volume. The resulting atomic emission then enables determination of elemental composition. The origin and uses of the LIBS technique have been summarized in several publications,²⁻³ and literature reviews of a wide range of LIBS studies have been published.⁴⁻⁶ The specific applications of LIBS for the analysis of aerosols,⁷⁻¹¹ vapors,¹² and combustion particulates¹³⁻¹⁵ include a number of metal species such as beryllium, lead and mercury, coal particles, and metal hydrides. Nonetheless, while much progress has been made in both understanding the LIBS process and its particular application for metals sensing, important issues, e.g. lower detection limits, remain regarding its use as a metals CEM in thermal treatment processes.

The nature of the metal species in thermal treatment process effluent streams becomes a fundamental issue in the implementation of a LIBS-based CEM.

Specifically, in waste combustion systems, the fate of metals is a complex phenomenon controlled by mechanisms such as particle entrainment, chemical interactions, vaporization, condensation, particle coagulation, and particle collection by air pollution control system (APCS) devices.¹⁶⁻¹⁷ Important parameters include the volatility of metal species and the treatment process temperature profile. As the combustion products cool downstream of the primary reactor, vaporized metals are expected to nucleate homogeneously or condense onto other particles. Homogeneous nucleation typically produces submicron-sized particles; heterogeneous condensation also favors enrichment of metals onto the smallest particles due to their higher surface-area-to-mass ratios. APCS devices such as venturi scrubbers, high efficiency particulate air (HEPA) filters, and electrostatic precipitators (ESP) are characterized by decreased collection efficiencies for submicron-sized particles.¹⁷ Although new devices offer improved collection efficiencies for submicron-sized particles, particulate metals in typical post-APCS wastestreams are most frequently of the submicron size. The resulting particulate-metal emissions may include both homogeneous and multispecies metals, and metal-enriched fly ash. In view of these comments, the successful implementation of the LIBS technology as a metals CEM must consider and make use of the discrete, particulate nature of most metal species under applicable wastestream outlet conditions.

To address the particulate nature of metal effluents, an approach based on independent LIBS sampling and the conditional analysis of the resulting data was incorporated into the Sandia monitor. The purpose of the Balboa Pacific field test was to assess the conditional analysis approach on a waste treatment facility with characteristically low metal emission levels (Åseveral ppb). In this paper we report the results of the LIBS-based metals monitor and compare the performance test data with contracted EPA Reference Method 29 extractive sampling results.

LIBS-Based Metals Monitor

The original LIBS instrument developed by Sandia operated in a straightforward time-averaging mode. Specifically, 100 or 200 laser pulses (i.e., sparks) were collected and ensemble-averaged to produce a representative spectral signal. The averaging technique is very useful for eliminating random signal shot-noise. However, our calculations demonstrated that for metal concentrations and particle size ranges expected within the normal operating range of effluent streams, the probabilities of sampling metal particles can become limiting.¹⁸⁻¹⁹ The time-averaging of metal analyte signals with a low particle sample rate (Å1%) can reduce the signal-to-noise ratio to well below the detection threshold. To avoid these problems, a technique was devised that enables the separation of laser spark particle “hits” from those laser pulses that sample no metal particulates, (i.e. “misses”).

The approach implemented for the LIBS-based metals monitor is based on independent, fixed-rate sampling combined with the conditional analysis of each single laser pulse in a overall sequence of pulses. Using our current software package, a ratio is calculated in real-time for each spectrum collected. The ratio is defined as the average intensity around the expected metal emission line, divided by the average intensity in a baseline region well removed from any species line emissions. A threshold value for the ratio is selected that allows each laser pulse and spectrum to be classified as either a hit (exceeds threshold) or a miss. The threshold value is usually set by first recording a time-averaged spectrum for a number of sequential pulses, nominally 100. If the metal line of interest is weak or not apparent in the time-averaged spectrum, then conditional analysis is required and the ratio, as discussed above, is calculated for the time-averaged spectrum. The time-averaged spectrum is also useful for selecting an appropriate baseline region to use for the ratio calculation. A threshold value may then be selected using the ratio value of the time-averaged spectrum. The threshold value is typically set to a value 20 to 30% greater than the ratio of the time-averaged spectrum.

The hit criteria is applied in real-time for the total number of desired shots, typically 1000, and then an average spectrum is generated based on the arithmetic average of the spectra recorded for all hits only. An equivalent metal concentration is then calculated using the same methods as with any time-averaged LIBS technique, which for our system is based on intensity information as described below. The true or actual metal concentration is then calculated from the product of the equivalent hit concentration and the frequency of hits (i.e., number of hits/total number of pulses).

As implemented, the Sandia LIBS system runs at 5.0 Hz. This allows 1000-pulse sequences to be completed in about 3 minutes, which is sufficient for true real-time

analysis. The current laser is limited to 10 Hz operation, however, operation at higher repetition rates must also consider issues such as laser pulse-to-pulse interactions. The ratio and threshold may always be selected such that each laser pulse and spectrum are classified as a hit, in which case the systems operates in a conventional time-averaging mode. By running the system at a fixed frequency of about 5 Hz, an independent and random sample selection is realized. This corresponds spatially to samples separated by about 40 cm each for a nominal effluent duct flow of 2 m/s. By sampling at a fixed rate, it is expected that the frequency of hits is representative of the true particle loading for a sufficient number of hits. This eliminates a significant source of sample bias that may be introduced by trying to actively trigger the laser spark based on a *priori* particle detection. In other words, for this application any attempt to detect particles in the target volume (e.g., using light scattering) and then initiate a laser spark would be prone to both particle size biases and to particle species biases.

The Sandia LIBS-based metals CEM utilizes a 1064-nm Nd:YAG laser as the excitation source, with a nominal pulse width of 10 ns and pulse energy of 500 mJ. 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 and atomic emission. A schematic of the LIBS monitor system is presented in Figure 1. LIBS spectra are collected at 5.0 Hz using a spectrometer and time-gated CCD array. The CCD intensifier gate width used for this field test was 3.5 μ s, with a time delay of 6.0 μ s from the laser pulse. These settings were used for all metal analytes. The complete system is controlled remotely by a single Macintosh PowerPC computer. The computer is linked to the stack-mounted probe and instrument racks by a 500-ft fiber optic cable.

External requirements for the LIBS monitor system include a 110 V, 5 amp power supply; a 220 V, single-phase, 10 amp power supply; and a 5 lpm supply of purge gas such as nitrogen or argon.

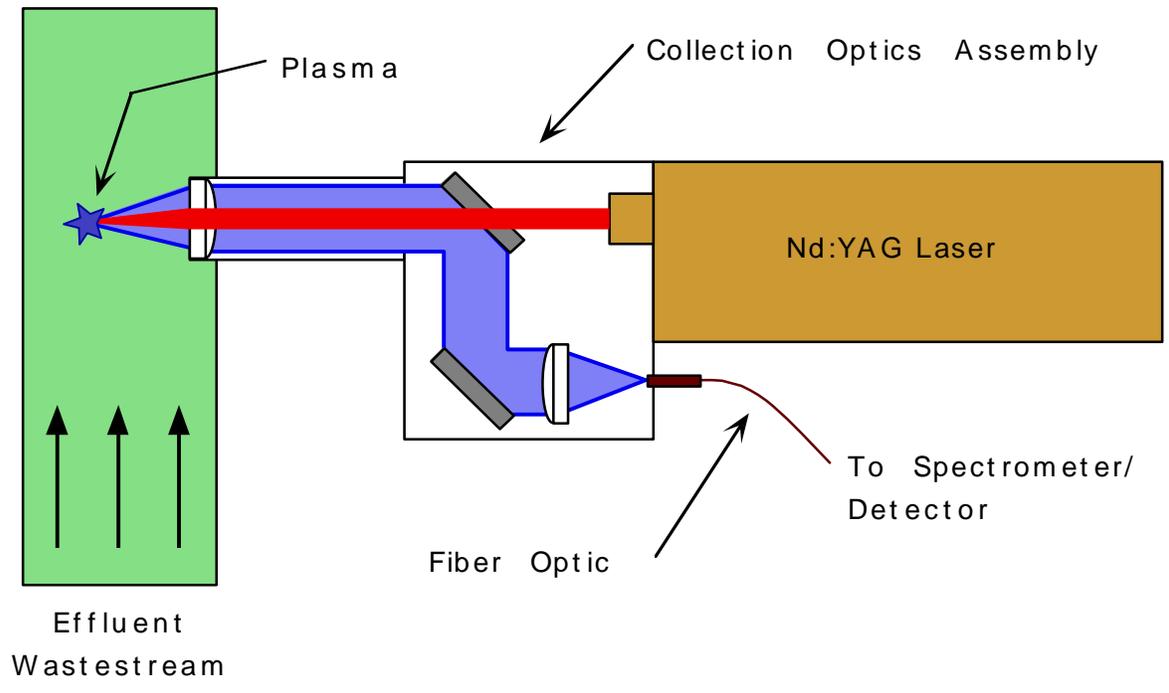


Figure 1. Schematic of LIBS monitor system probe.

Installation and Test Plan

Balboa Pacific Pyrolytic Conversion System

The field test was conducted at Balboa Pacific Corporation located in Santa Fe Springs, California. The Balboa Pacific Thermal Conversion System is a natural gas fired, pilot-scale pyrolytic waste processing unit. A 220 kW burner was partially fired for this series of tests. The pyrolytic processing chamber can be operated at temperatures from 1200 to 1800°F, under either oxidizing or non-oxidizing conditions. The gaseous exhaust stream from the pyrolytic chamber enters a direct-fired secondary combustion chamber, then passes through a waste-heat recovery unit, and finally through a wet-gas scrubber before exiting the stack. A schematic of the pyrolytic processing unit is presented in Figure 2. Because of the relatively low operating temperatures of the primary pyrolytic unit, nearly all metal components of the waste feed are removed in a separate, solid-waste exit stream. The resulting metal concentrations in the stack effluent gas stream have been historically low, from 10's of ppb to sub-ppb levels.

Installation and Sampling Locations

The exhaust stack from the wet gas scrubber has a rectangular cross-section of 16 inches by 21 inches. The locations of the LIBS sample port and the EPA Reference Method 29 sample ports are shown in Figure 3. The LIBS sample port was located 35 inches downstream from the Method 29 sample port. The LIBS laser assembly was inserted through a specially designed flange that functioned to anchor the probe and to seal the exhaust stack gases. The flange mounted to a standard 4 inch NPT pipe thread, as shown in the Figure 4 photograph. A nitrogen purge line is also visible in Figure 4. Approximately 5 lpm of nitrogen was blown across the outer surface of the 2 inch lens as a preventative measure to keep the optic clean.

Overall, the LIBS monitor was installed on the process waste stack approximately 43 inches upstream from the stack discharge, on an access platform about 20 ft. above the ground. Two instrument racks (30" x 30" x 38") were stationed nearby on the platform, one containing the laser power supply, and one containing the spectrometer and CCD detector equipment. The two instrument racks must be within 12 feet of the laser probe. The Macintosh computer was situated in a van parked nearby. Photographs of the LIBS probe installation are shown in Figure 5. It took approximately 5 hours to unload and install the equipment and to perform a complete system check.

Figure 2. Schematic of Balboa Pacific Thermal Conversion System

Following installation of the LIBS probe, one test day was designated for instrument shakedown. Approximately 1-hour test runs were conducted sequentially utilizing each of the three target waste feeds (see Table 1). This allowed the identification of relevant spectral lines and potential spectral interferences, and the assessment of signal strengths and available analytes.

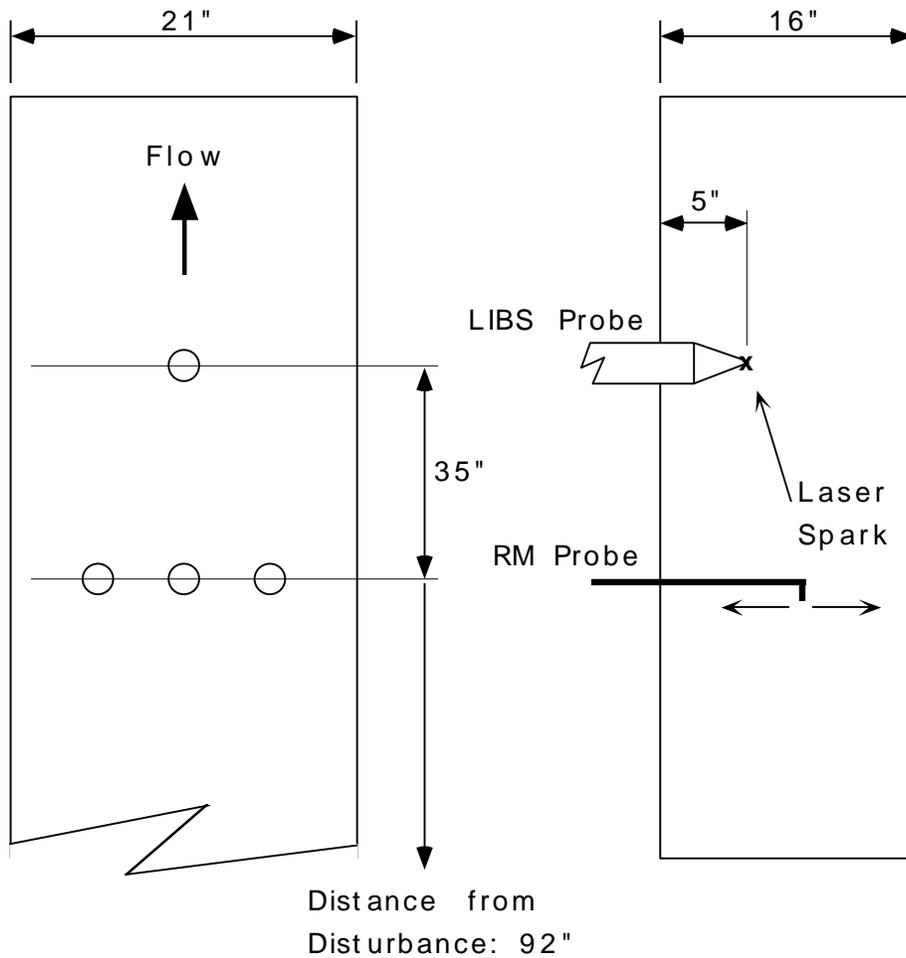


Figure 3. Configuration of sample ports



Figure 4. Photograph of LIBS probe flange mount.

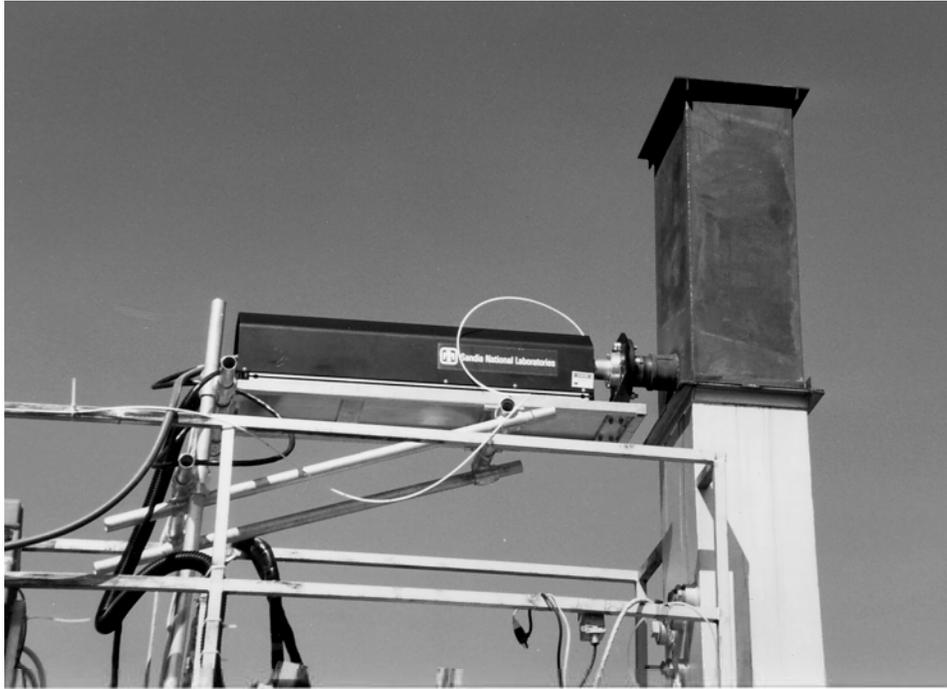


Figure 5. Photographs of LIBS probe installation.

Test Plan

Three days of formal testing were conducted at the Balboa Pacific pyrolytic unit utilizing the LIBS-based CEM in coordination with traditional EPA Reference Method 29 extractive sampling. Dames & Moore of Santa Ana, California was contracted by Sandia to perform the reference method sampling. The test conditions for the three test days are summarized in Table 1.

Table 1. Operating conditions and waste feeds.

Test Day	Waste Feed Material	Feed Rate (lb/hr)	Process Temperature (°F)	Stack Temperature (°F)
3/10/97	Municipal Solid Waste	21	1600	138
3/12/97	Shredded Tires	30	1475	138
3/14/97	Spent Catalyst	10	1700	138

On each test day, the reactor was stabilized at steady operating conditions and the waste feed was then initiated. When the solid-waste discharge stream was established, the LIBS monitoring and the extractive sampling were conducted simultaneously for a 2-hour test interval. It is noted that the pyrolytic unit is operated under near steady-state conditions, but that some mass did accumulate in the pyrolytic retort chamber throughout the 2-hour waste feed period.

Calibration and Operation

The LIBS-based metals CEM was calibrated using a laboratory facility located at Sandia National Laboratories. For each target metal analyte, the spectral response was determined over a concentration range from as low as 20 µg/acm up to 2000

$\mu\text{g}/\text{acm}$. The processed signal is the integrated metal analyte peak normalized by an integrated baseline about the peak. Linear least square calibration curves were calculated and loaded into the software package calibration file. The output of the CCD detector array contains spectral intensity as a function of array pixel number. The spectral window is approximately 36 nm, with a spectral resolution of 0.035 nm per pixel.

Each target analyte atomic emission line is assigned a pixel location number corresponding to a given spectral window. The pixel locations are entered into the software calibration file. The absolute pixel location of a given analyte line can shift by several pixels during instrument shipping or during extended instrument shutdown. Calibration cells with known gases were used in the field to calibrate the pixel line positions on each test day. A photograph of the calibration cell installed on the LIBS system at Balboa Pacific is shown in Figure 6. The cell shown contained helium, which has a strong atomic emission line at 388.86 nm. The concentration of He gas within the calibration cell was also calibrated in the laboratory and entered in the software calibration file. In the field, the concentration of He within the cell was calculated and compared to the calibration value. The normalized He concentrations ranged from 93.6 to 102.1% (97.4% average) of the reference value throughout the test week.

In addition to the He reference cell, the carbon atomic emission line at 247.86 nm resulting from carbon species present in the stack gases was also used for instrument spectral calibration. Spectra corresponding the carbon line measured in the stack, and to the He calibration cell are presented in Figure 7.

The LIBS system was operated at 5 Hz, typically for 1000 total laser pulses. The current system was designed for monitoring of one metal species at a time. At the end of a laser pulse sequence, the metal concentration was evaluated instantaneously within the software using the pre-loaded calibration files, and then logged into a data file. During the two-hour reference method test periods, the LIBS monitor was cycled through the species of interest. The metals that were monitored during the test week included the Clean Air Act metals chromium and manganese, in addition to iron. Periodic attempts were made to monitor cadmium and nickel, but no significant analyte signals were detected.

EPA Method 29 was used to collect samples for multiple metal determination. Multi-point isokinetic sampling was conducted at five minutes per traverse point for a total of 120 minutes per reference method. The sampling train consisted of a glass-lined, heat traced probe with a glass, button hook nozzle with an attached thermocouple and pitot tube assembly. Five 500-ml impingers were connected in series with leak-free ground glass joints. All recovered fractions; probe rinse, moisture dropout, and impinger contents, were combined for subsequent analysis.

The collected samples were sent under chain-of-custody to West Coast Analytical, Santa Fe Springs, CA for predetermined target metal determination.

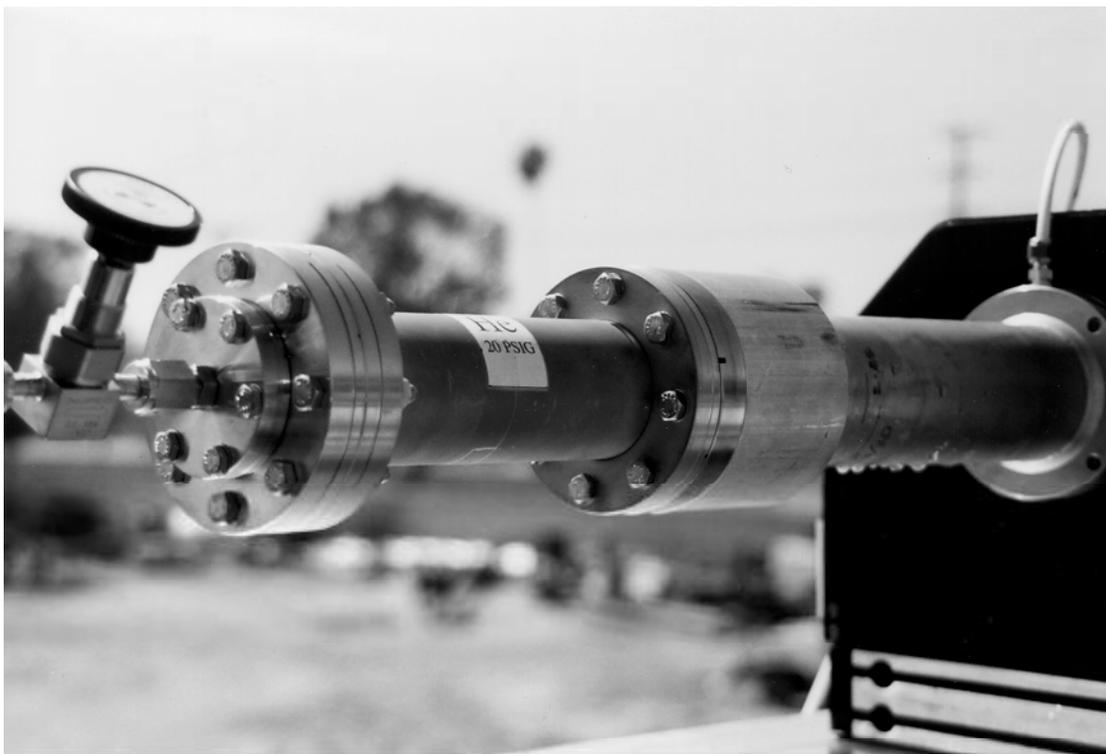


Figure 6. Photograph of LIBS probe calibration cell.

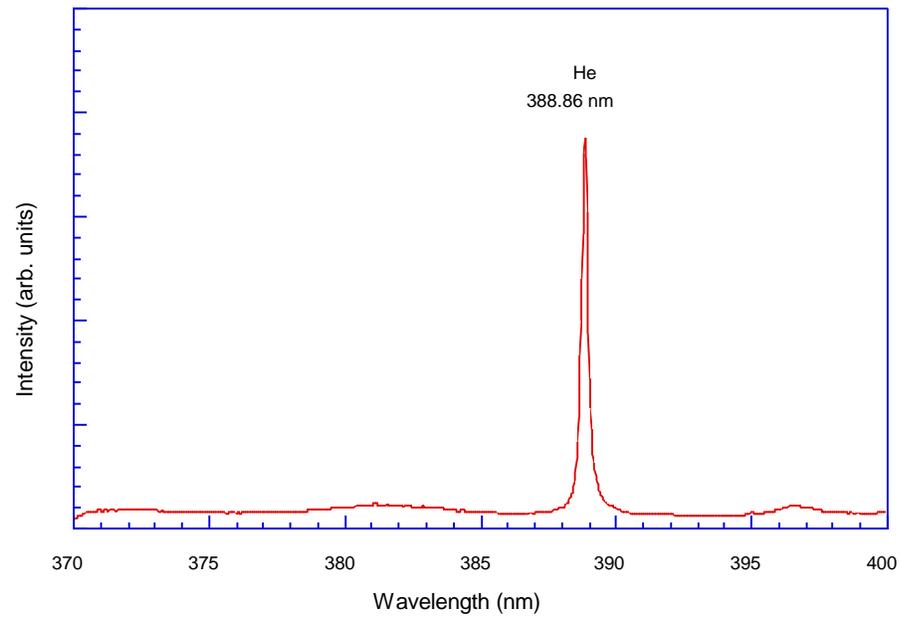
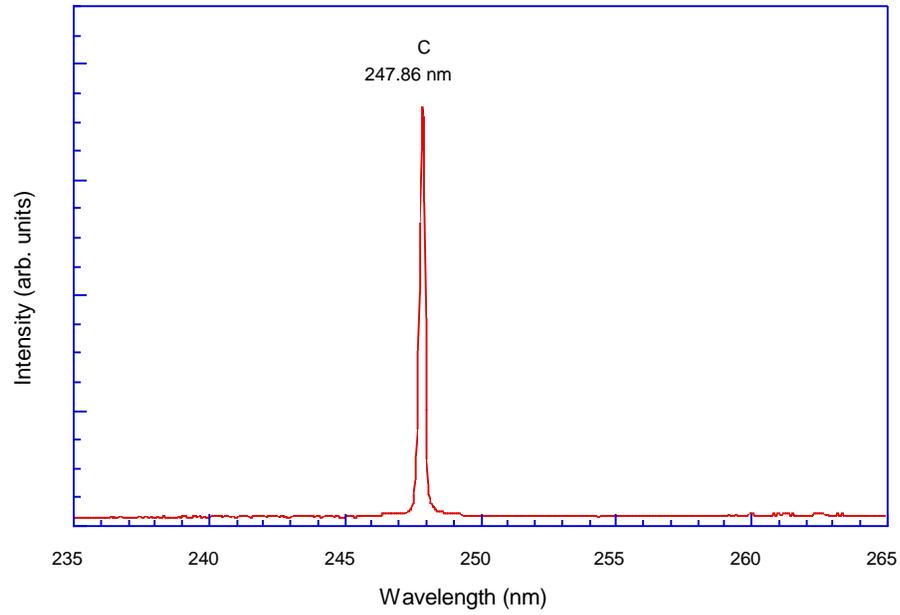


Figure 7. Calibration spectra: (upper) carbon line measured in stack, (lower) helium line measured in calibration cell (see Figure 6).

Test Results

Conditional Analysis

Chromium, manganese, and iron signals were measured consistently during all three test days using the conditional data analysis approach. The typical LIBS “hit” rates realized in the process stack were approximately 2%. For a sampling rate of 2%, to first order, the resulting signal-to-noise is improved by a factor of 50 with the conditional analysis data in comparison to an ensemble average. Representative spectra are presented in Figures 8 and 9 corresponding to the subset of hits for manganese and iron, respectively, along with the 1000-shot ensemble averaged spectra. The significant increase in analyte signal is apparent in the two figures, demonstrating the advantage of the conditional data analysis approach for LIBS-based metals monitoring.

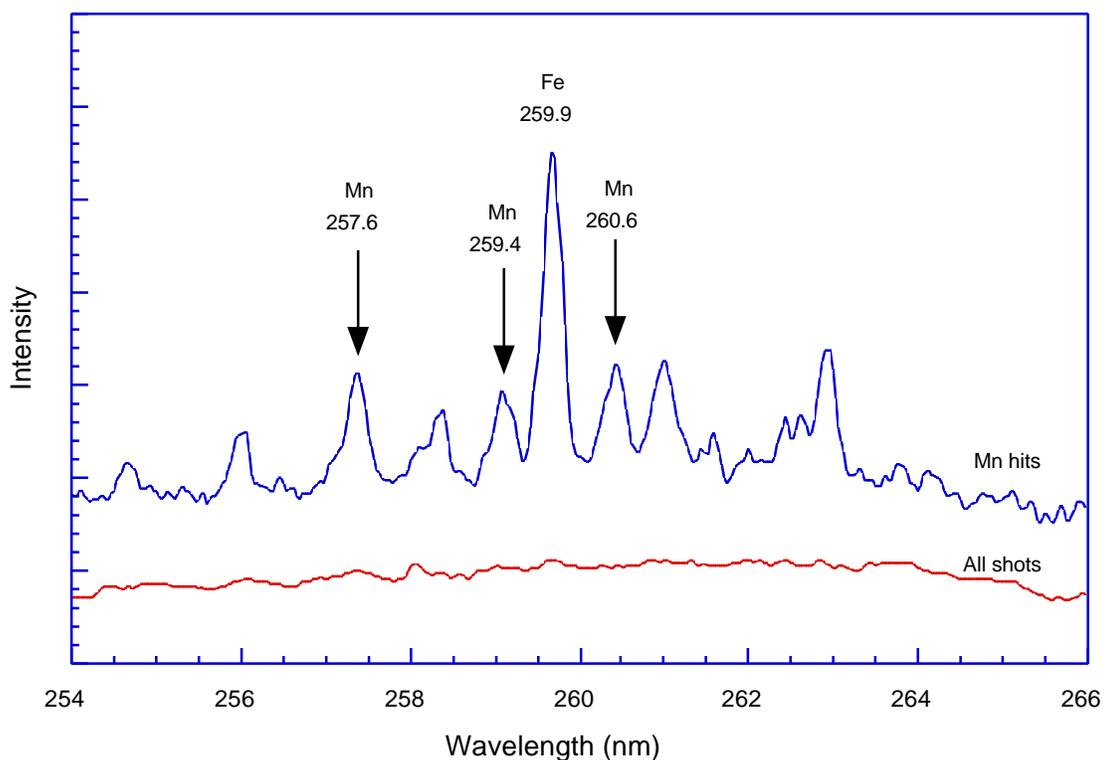


Figure 8. Spectrum of identified Mn hits ($n=15$) and spectrum of the average of all shots for a 1000-shot LIBS pulse sequence. Upper spectrum has been

shifted vertically for clarity. Both spectra have same intensity scale.

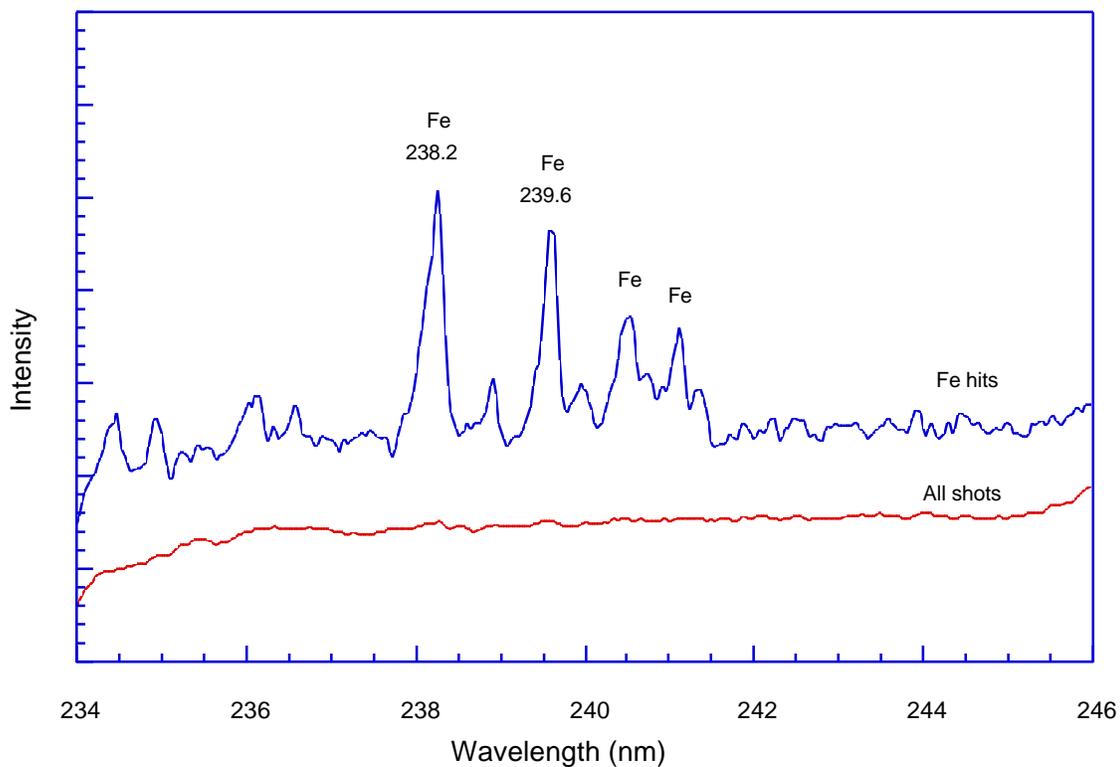


Figure 9. Spectrum of identified Fe hits ($n=20$) and spectrum of the average of all shots for a 1000-shot LIBS pulse sequence. Upper spectrum has been shifted vertically for clarity. Both spectra have same intensity scale.

Metals CEM Data

On each test day, the metal concentration values were sequentially logged throughout each 2-hour reference method for the metal analytes of interest. Because of the single-species detection mode in which the current prototype system is operated in, a limited set of target metals were identified during the shakedown test period. The selected metal analytes and the corresponding atomic emission lines are summarized in Table 2. After each 1000-shot laser pulse sequence, the metal concentrations were automatically calculated and logged immediately into the data log file. Included in the log files were the sample time, the species and atomic emission line, the sample (i.e., hit) frequency, and the metal concentration value. At the completion of each test period, hardcopies of the data log files were printed, signed, and turned in to Dames & Moore field personnel for inclusion in their field test logs. The LIBS-based CEM log sheets are presented in the Appendix for all three test days.

Table 2. Selected Metal Analytes.

Metal Analyte	Emission Line (nm)
Chromium (Cr)	283.56
Iron (Fe)	238.20
Iron (Fe)	259.94
Manganese (Mn)	257.61
Nickel (Ni)	243.79

Representative concentration data recorded for manganese, chromium, and iron on 3/10/97 (municipal solid waste feed) are presented in Figures 10 through 12, respectively. We note that the reported concentration unit of $\mu\text{g}/\text{acm}$ is approximately equal to a part per billion (ppb) on a mass basis. Also included in the figures are the 2-hour average values reported for the Method 29 extractive sampling. The data reported for iron correspond to the 238.2 nm atomic emission line. For iron, the concentration values were calculated using both the 238.2 nm and the 259.9 nm lines. The current software enables the concentration values to be re-evaluated after initial data logging using an alternative analyte line. However, the recalculated values are not logged into the data logging file. For the most part, the iron lines were evaluated and logged using the 238.2 nm line, and then re-evaluated using the 259.9 nm line and recorded manually into our field note book. The iron concentrations

were consistently about 33% lower when calculated with the 259.9 nm line as compared to the 238.2 nm line.

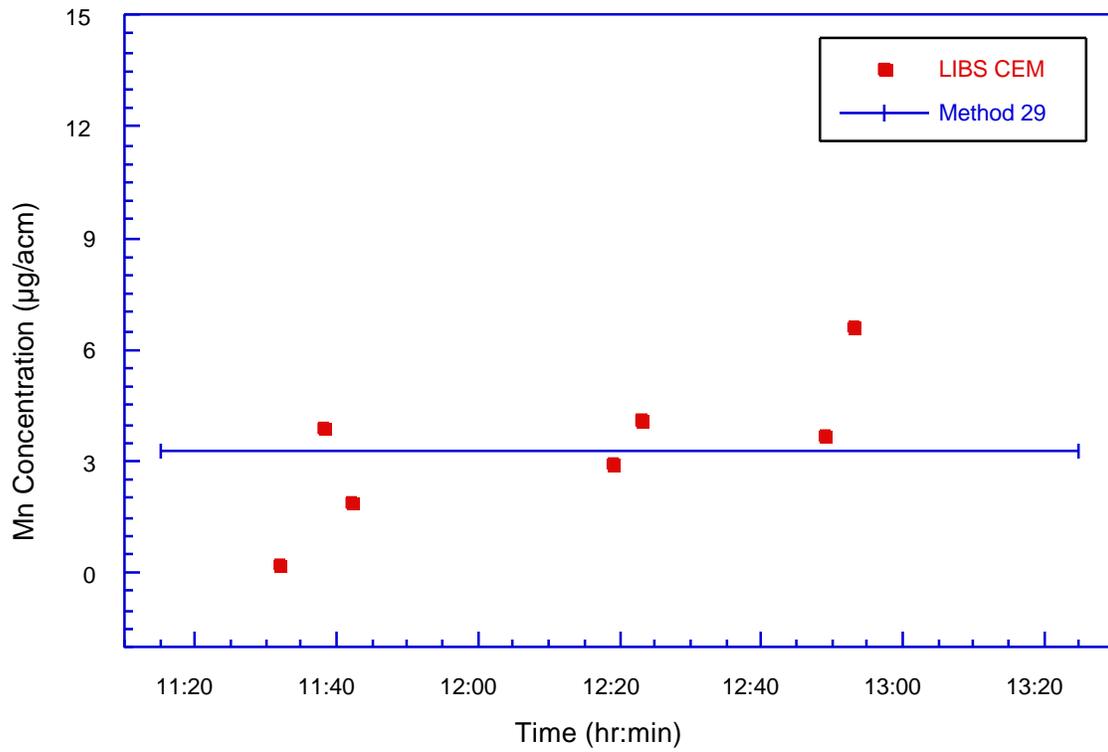


Figure 10. LIBS Mn concentration values reported for the 3/10/97 test day along with the 2-hour averaged Method 29 reference value.

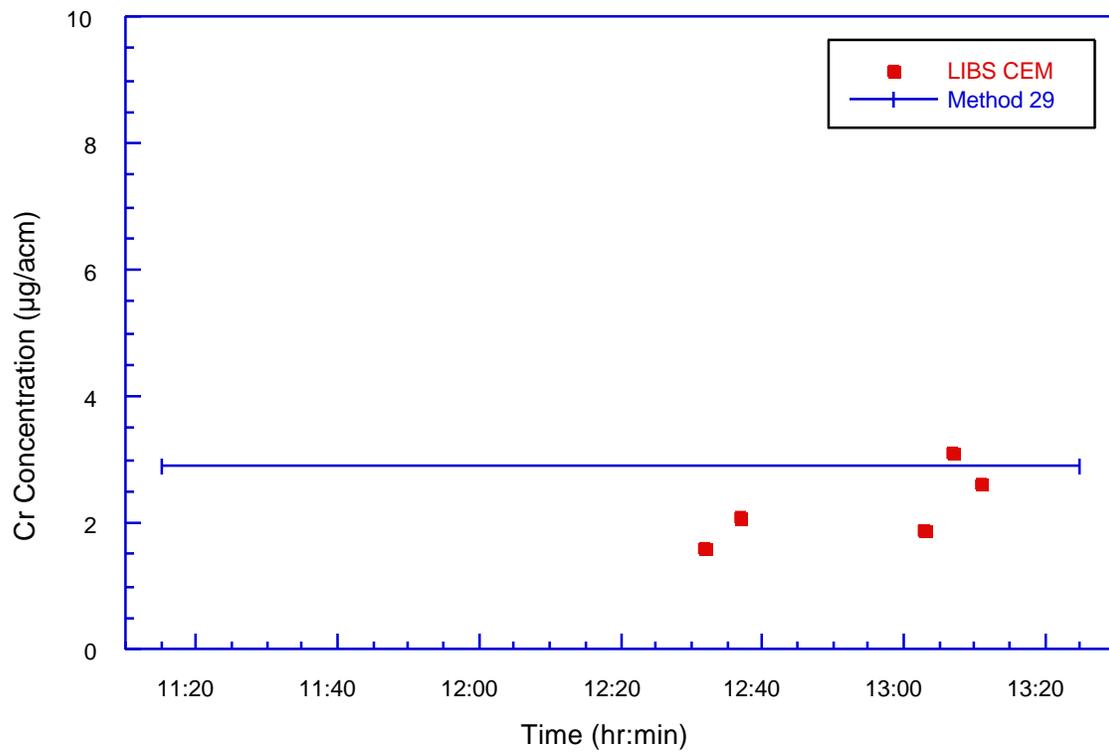


Figure 11. LIBS Cr concentration values reported for the 3/10/97 test day along with the 2-hour averaged Method 29 reference value.

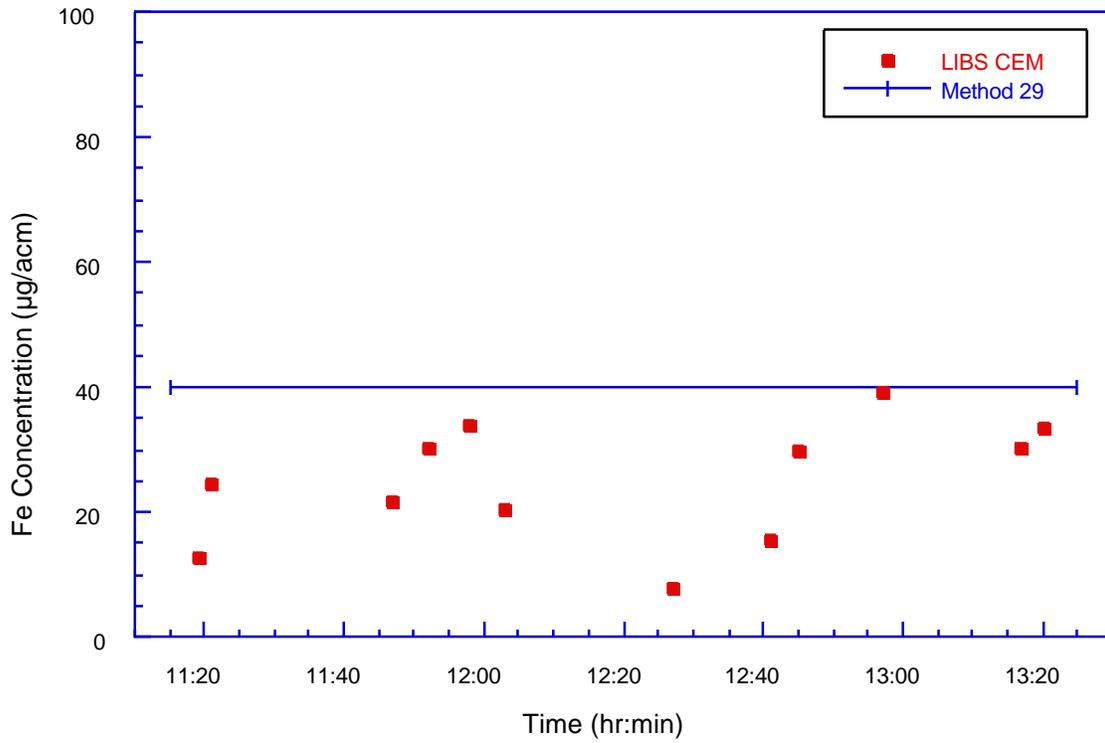


Figure 12. LIBS Fe concentration values reported for the 3/10/97 test day along with the 2-hour averaged Method 29 reference value.

The LIBS CEM test results and the Reference Method 29 test results are summarized in Table 3 for the three test days. In the Appendix we have included the Executive Summary from the report of Dames & Moore, the reference method contractor. We note two differences between the Dames & Moore summary and the values in Table 3. On the test days of 3/10/97 and 3/12/97, in addition to the 238-nm Fe concentration values, several Fe concentration values were logged using the 259-nm line, and the Dames & Moore values reflect the ensemble average of all logged values. The iron concentration values reported in Table 3 were separated to reflect the concentration values that were calculated using the 238-nm and 259-nm lines. On the 3/10/97 test day, the final value logged for manganese was inadvertently recorded using a trigger threshold based on iron. This value was therefore omitted from the average manganese concentration value as reported in Table 3. Also included in Table 3 is the absolute deviation (and percentage) between the LIBS-based CEM concentration values and the Reference Method 29 concentration values.

Table 3. Summary of LIBS CEM and Method 29 results.

Date	Metal	LIBS (µg/acm)	RM 29 (µg/acm)	Deviation (µg/acm)
3/10/97	Fe, 238 nm	24.9	39.9	-15.0 (-38%)
3/10/97	Fe, 259 nm	17.9	39.9	-22.0 (-55%)
3/10/97	Mn, 257 nm	3.3	3.3	0.0 (0%)
3/10/97	Cr, 283 nm	2.3	2.9	-0.6 (-21%)
3/12/97	Fe, 238 nm	50.3	82.2	-31.9 (-39%)
3/12/97	Fe, 259 nm	33.0	82.2	-49.2 (-60%)
3/12/97	Mn, 257 nm	9.3	4.9	4.4 (90%)
3/12/97	Cr, 283 nm	1.5	1.9	0.4 (-21%)
3/14/97	Fe, 238 nm	91.3	139.7	48.4 (-35%)
3/14/97	Fe, 259 nm	56.3	139.7	83.4 (-60%)
3/14/97	Mn, 257 nm	7.0	4.5	2.5 (56%)

As presented in Table 3, the overall agreement between the LIBS CEM data and the Reference Method 29 data is very good. These values represent the absolute accuracy of the LIBS monitor as compared to the accepted standard reference method. The ensemble average of the absolute deviation for all species, emission lines, and test days is 43%. For the Clean Air Act metals chromium and manganese, the average agreement with Method 29 for all three test days was 1.6 $\mu\text{g}/\text{acm}$, an absolute accuracy of about 1 ppb. Furthermore, with the exception of manganese, the percentage deviation values (in parentheses) are very consistent over all test days, suggesting a fixed calibration offset. The consistency or precision of the CEM data may be quantified by calculating the standard deviations of the percentage deviations for a given species and emission line. The standard deviations, expressed as a percentage of the mean deviation, are 5.8%, 4.6%, and 1.7% for the two iron lines and chromium, respectively. At present we have a new *in situ* calibration method that is being developed that should enable the correction of fixed offsets.

In contrast to the iron and chromium results, the agreement between the CEM and RM concentrations values for manganese ranged from 0% to 89.9% deviation. We attribute this difference in results to the different conditional analysis approaches used for iron and chromium, and for manganese. Specifically, two emission lines were used for the conditional analysis scheme for the chromium and iron measurements; the first emission line was monitored for the hit threshold criterion, while the second emission line was used to evaluate the final concentration value. Because of the random nature of the spectral noise, the use of two lines decouples the susceptibility of the first emission line to false triggers and consequent false analyte signal, and therefore enables the use of a more sensitive threshold criteria. For the manganese measurements, a single emission line (257.61 nm) was used for both hit triggering and concentration calculations. During the course of the test week, we experimented with the optimal threshold criterion. Consequently, the manganese data reveal more variability as compared to the iron and chromium data.

We also note the test results for other Clean Air Act metals of interest. Both beryllium and arsenic were reported as non-detects by Dames & Moore, which corresponds to stack concentrations at sub-ppb levels. We did not attempt to monitor beryllium and arsenic during the test period. A few measurements were recorded throughout the week for cadmium and nickel, resulting in what we considered non-significant analyte signal levels. The Reference Method 29 results for cadmium and nickel were consistent throughout the test period at a level of about 1.5 ppb.

Other Issues

The entire LIBS monitor system performed very well during the test days of 3/10/97 and 3/12/97. The only problems were several brief interruptions (typically about one minute each) that resulted from electrical power fluctuations that necessitated resetting of the detector electronics. The total availability of the LIBS system, which we define as the percentage of the reference method period during which LIBS data were being recorded, was 77% for both 3/10/97 and 3/12/97. The remainder of the sample period (approximately one-fourth of the total time) was utilized to change between analyte lines, or is attributed to the above mentioned power-induced interruptions. The electrical power at the Balboa Pacific site was affected by the intermittent operation of high-amperage equipment, resulting in significant voltage spikes and fluctuations. On the last day of testing (3/14/97), a circuit board in the laser system failed, presumably due to a power surge on the 220V line, that resulted in our discontinuation of testing approximately 30 minutes into the 2-hour reference period.

Summary

The test of the LIBS-based metals CEM at Balboa Pacific Corporation was successful in demonstrating the significant improvements made available by the conditional analysis approach. Furthermore, all data analysis and data reporting procedures were fully automated and performed real-time. Overall, consistent results were produced that were in very good agreement with reference method values at extremely low overall metal effluent levels.

The important issues of metal particle sampling with a LIBS-based effluent monitoring system have been further elucidated with this field data. From our present analysis, two observations can be made; that the discrete nature of metal particulates in effluent waste streams can potentially be a limiting factor in LIBS monitoring, and that appropriate conditional data analysis schemes can greatly enhance the sensitivity and applicability of a LIBS-based metals monitor. The latter point is significant, because while LIBS offers the advantage of noninvasive, *in situ* monitoring, the overall LIBS sensitivities to targeted RCRA metals have lagged somewhat behind those of more mature technologies such as ICP/AES. However, this field test has demonstrated that a LIBS-based metals CEM can provide accurate, real-time concentration measurements in actual treatment facilities at metal effluent levels of a few ppb.

Recommendations

As a result of the March 1997 field test at Balboa Pacific Corporation, the Sandia LIBS-based CEM project team has identified the following issues for improvement and incorporation into the current LIBS system:

- 1) Use of one central 220 V input, conditioning power supply. This unit will be used to supply all electrical equipment in the LIBS system.
- 2) Modification of the LIBS system software to allow simultaneous detection of metals using the conditional analysis approach. Essentially, the software would operate in series for multiple species as it operates currently for a single species.
- 3) Modification of the LIBS system software to allow storage of threshold criteria and creation of monitoring scripts. The goal is to extend the CEM availability to near 100%.
- 4) Development of an *in situ* calibration technique to allow for correction of the fixed offsets as realized in this field test. A concept has been identified and will be developed at Sandia during the remainder of 1997.

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Appendix

**Executive Summary, Introduction, and CEM field logs
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