D I A L

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LASER-INDUCED BREAKDOWN SPECTROMETER

APPLICATION: Quantitative real time measurements of elements in off-gases.

UTILITY: Laser-induced breakdown spectroscopy (LIBS) is a stand-off or remote sensing technique which permits non-intrusive qualitative and quantitative measurements of metals. A high intensity pulsed visible-or infrared (IR) beam is focused in the gas stream and the signal is collected with the same focusing lens. Thus an optical port is needed on one side of the analyte stream only. The measurement takes from seconds to minutes depending on the number of laser pulses that are averaged, thus flowing streams can be monitored in near real time. Parts-per-billion (ppb) concentrations can be made for many metals, and multiple species can be detected using the same system. The technique can be applied to waste gas streams as a process monitor anywhere in the waste processing environment.

PRINCIPLE: The principle of the LIBS technique is illustrated in Figure 1. A pulsed laser beam is focused at the test point and produces a spark due to the high electric field. The spark generates a high density plasma which excites various atomic elements present in the focal volume. The atomic emission from the plasma is collected with a collimating lens and sent to the detection system. The intensity of the atomic emission lines observed in the LIBS spectrum are then used to infer the concentration of the atomic species.

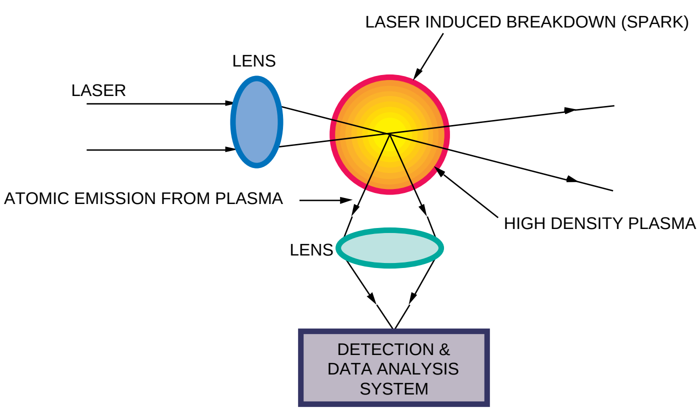

Figure 1. Principle of laser-induced breakdown spectroscopy.

TECHNOLOGY DESCRIPTION: A frequency doubled ND:YAG laser beam is focused at the probed volume through an optical port. The port is purged with nitrogen to keep the window clean and cool. The same port is used to collect the LIBS signal. A beam dump mounted on the opposite port across the gas stream is used to dump the laser energy. A third port normal to the laser beam is used to monitor the spark in the gas stream and also to align the spark with the sample injection probe for calibration. The later two ports, though convenient, can be omitted if needed. The emission from the spark is collected with a UV optical fiber bundle coupled to a spectrograph. An intensified diode array detector (IDAD) or CCD detector is attached to the spectrograph to record the LIBS spectrum. A computer interfaced to the detector controller is used for data acquisition/analysis.

FIELD EVALUATION/MATURITY: DIAL's LIBS system for off-gas emission monitoring has been successfully demonstrated at the Western Environmental Technology Office (WETO)/MSE (Oct. 1996). It has also been successfully used to monitor various toxic metals in the off-gas emission of a PT-150 Plasma Energy Corporation plasma torch during test runs of a Savannah River simulated test feed at DIAL/MSU (Feb. 1995). The LIBS system has also been demonstrated as a real time metal emission monitor during tests at the STAR Center (June 1995), the Transportable Vitrification System developed by the Westinghouse Savannah River Company (WSRC) (February 1996) and the DOE and EPA continuous emission monitoring test at EPA's National Risk Management Research Laboratory (NRMRL), RTP, Raleigh (April 1996).

OPERATING PROCEDURE: The spectral regions which give the strongest emission lines with minimum interference from other lines are selected for metal monitoring. The sample, or data rate, depends on the concentration of the toxic metals in the test medium. To obtain a good signal-to-noise ratio, the typical sample time is 26 seconds which corresponds to an average of 260 laser pulses. The intensity of the atomic emission lines observed in the LIBS spectrum are used to infer the concentration of the atomic species using the calibration data obtained from a nebulizer. User developed macro programs are used to collect, analyze and display LIBS data in near-real time.

CALIBRATION: The DIAL/LIBS system is calibrated with an ultrasonic nebulizer system. The calibration is based on the peak height and peak area of each selected analyte line. The peak area, or peak height, of the analyte lines from the test LIBS spectra are normalized with the calibration factor to obtain the metal concentrations. In general, peak height calibration and peak area calibration give about the same result for interference-free lines. For different types of spectral interferences, either peak height or peak area must be selected for best results.

PERFORMANCE CLAIMS: The detection limits of the selected analyte lines of ten RCRA metals are listed in Table 1. The detection limits were determined from the LIBS calibration data obtained with an ultrasonic nebulizer. The precision and accuracy of these measurements were estimated from the calibration data and are also listed in Table 1. Accuracy is the degree of agreement between a measured analyte concentration and the known concentration. Precision is a measure of the agreement among multiple measurements of a single analyte. The precision and accuracy greatly depend on the laser spark pulse-to-pulse fluctuation and the concentration variation in the metal flow from an ultrasonic nebulizer. The accuracy and precision of LIBS measurements can be improved by increasing the signal integration time. Continued improvements of the system performance are part of our development program.

Table 1: DIAL/LIBS minimum detectable concentration limits for selected metals.

Element	Minimum Detectibility (μg/acm)	Relative Precision (%)	Relative Accuracy (%)
As	600	25	9
Cr	6	10	15
Co	24	20	8
Hg	680	8	13
Mn	4	18	4
Ni	30	3	9
Pb	68	8	13
Sb	120	20	9
Be	<0.1	13	6
Cd	39	12	9

SOFTWARE: The present LIBS software can be used for real-time LIBS data collection and analysis. The analysis results and data file are updated after every set of data acquisition/analysis. The plots of concentrations versus time and the latest acquired spectrum are displayed on the screen in real time. If desired, TTL signals may be sent to an alarm/interface system and a warning message is shown on the bottom of the computer screen whenever the concentration of a probed species is above the alarm level during the LIBS measurements. This software will be upgraded with time and can be modified depending on a particular application.

MECHANICAL SPECIFICATIONS: The DIAL/LIBS system is mobile and versatile. It weights approximately 220 lb. The instrument requires a space of 42 in. X 24 in. X 30 in. near the optical port. The laser power supply occupies a space of 21 in. X 11 in. X 20 in. which can be kept ~13 ft from the laser head.

ELECTRICAL SPECIFICATIONS: 220V, 10A Single Phase and 110V, 10A

MAINTENANCE: Maintenance will be required on a monthly basis. This requires checking the optics and perhaps replacing the laser flashlamp(s).

AVAILABILITY: The instrument is currently available for field applications. The system will operate unattended, will provide outputs for process control and for compliance verification of certain metals.

COSTS: DIAL will provide the instrumentation, software, system integration, facility interfacing, calibration procedures, technical training, and will continue to update the system as developments warrant. This system along with others developed or under development by DIAL will be provided to the DOE user at a cost. Inquires from industrial users or commercial instrument companies are also welcome.

Additional information about LIBS can be obtained by contacting:

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