97045

LA-UR- 98-3689

Approved for public release; distribution is unlimited.

Title: Enhancing the Analytical Performance of Laser-Induced Breakdown Spectroscopy

RECEIVED
MAY 03 1999
OSTI

Author(s): David A. Cremers, Rosemarie C. Chinni, Alice E. Pichahchy, CST-1

Heidi K. Thornquist, CST-3

Submitted to: DOE OFFICE OF SCIENTIFIC AND TECHNICAL INFORMATION (OSTI)

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Los Alamos
NATIONAL LABORATORY

DISCLAIMER

97045

Enhancing the Analytical Performance of Laser-Induced Breakdown Spectroscopy

David A. Cremers*, Rosemarie C. Chinni,
Alice E. Pichahchy and Heidi K. Thornquist

Abstract

This is the final report of a one-year, Laboratory Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). The objective of this work is to enhance the analytical capabilities of laser-induced breakdown spectroscopy (LIBS). LIBS is a method of elemental analysis in which powerful laser pulses are focused on a sample to form a microplasma. LIBS is perhaps the most versatile elemental analysis method. applicable to a variety of different real-world analysis problems. Therefore, it is important to enhance the capabilities of the method as much as possible. Accomplishments include: (1) demonstration of signal enhancements of 5-30 times from soils and metals using a double pulse method: (2) development of a model of the observed enhancement obtained using double pulses; (3) demonstration that the analytical performance achievable using low laser-pulse energies (10 and 25 mJ) can match that achievable using an energy of 100 mJ; and (4) demonstration that time-gated detection is not necessary with LIBS.

Background and Research Objectives

Laser-induced breakdown spectroscopy (LIBS) is a method of determining the elemental composition of materials under conditions not possible using conventional analytical methods [1]. Examples include in-situ field screening of soils for contaminants, the detection of materials down boreholes and in other confined areas where access is limited, in-situ analysis of toxic materials in gloveboxes, and the remote (standoff) analysis of solids. LIBS is a form of atomic emission spectroscopy in which powerful laser pulses are focused on a sample to ablate material and to form a microplasma. The plasma light is spectrally resolved and analyzed to determine the elemental composition via the unique spectral "fingerprint" produced by each element. Unlike other forms of analysis, LIBS is totally non-invasive, only light touches the sample and the sample is analyzed in place. Although LIBS has been applied to a variety of analysis problems, the method does not, at present, have the detection

---

Principal Investigator, e-mail address: cremers_david@lanl.gov sensitivity and measurement accuracy and precision of conventional laboratory-based analysis techniques, thereby limiting its range of application. Based on recent measurements made by us using newly acquired diagnostic instrumentation and a laser with unique pulse-forming characteristics, it appears that novel methods can be developed that promise to significantly improve LIBS analytical performance. These previous measurements were the motivation for this work.

The interaction between a laser pulse and a solid target is a complicated process dependent on many parameters. A full study of these interactions was beyond the scope of this work. There are three related areas, however, which we believe are key to improving LIBS capabilities for the analysis of complex matrices. We addressed these topics here and we believe that useful results were achieved with the resources requested for this project. These tasks are listed below:

(1) Investigate the use of double-pulse excitation to improve detection limits and minimize matrix effects. The ability to decrease LIBS detection limits for some elements will greatly expand applications of the method. A double-pulse offered to provide such a method and so was examined here. In addition, double pulsing may reduce matrix effects that complicate the interpretation and quantification of LIBS measurements. Matrix effects such as a change in the chemical composition of the soils can alter laser ablation characteristics and change plasma characteristics, thereby affecting the analytical performance of LIBS.

(2) Investigate the use of low laser-pulse energies (<100 mJ) for LIBS measurements. The analytical figures-of-merit for LIBS measurements have been mainly studied using laser pulse energies of 100 mJ or above. Portable LIBS instruments that will be used in the field, however, will generally be limited to laser pulse energies <100 mJ because of size, weight, and cost restrictions. The capabilities of LIBS in this low energy regime were investigated.

(3) Investigate the use of non-gated detection of the plasma light. LIBS measurements are typically carried out using a gated detector so that the plasma light is only monitored during specific periods after formation. This is done to enhance measurement capabilities (e.g. reduce spectral interferences and lower detection limits). Unfortunately, detectors that can provide gated detection are more expensive, larger, and more complex than non-gated detectors. For field-based instruments, the smallest and lowest cost detectors are preferred. The use of non-gated detectors was examined and the analytical figures-of-merit achieved using non-gated detection was compared with those achieved using gated detectors.

Importance to LANL's Science and Technology Base and National R&D Needs

As noted above, LIBS is perhaps the most versatile method of elemental analysis, with application to a number of real-world monitoring needs. As a result, it has direct and indirect application to the mission of DOE and the Laboratory. These are described below.

Direct Benefits

This work benefits at least two of the core missions of DOE: national security and environmental quality. Successful completion of this work will permit the development of state-of-the-art instruments that can be used to determine the presence of harmful contaminants in the environment for application to DOE environmental clean-up and remediation programs. This instrumentation can also be used to monitor and ensure the health of workers that have potential for exposure to harmful materials as a result of their activities as employees of the DOE. These instruments will provide new and needed capabilities. In addition, the instrumentation can be used for stockpile stewardship because it can be used to monitor the presence of toxic materials used in the manufacture of nuclear weapons under conditions not possible using conventional analytical instruments.

In addition, the central mission of Los Alamos National Laboratory is reducing the global nuclear danger. This project will contribute to the following areas involved in this mission.

Nuclear Management/Pit Surveillance. Currently, the LANL LIBS User Facility is being funded by another project to develop an endoscopic probe to monitor the interior of pits for surface contaminants. The goal of this work is the development of a micro-LIBS probe to interrogate surface defects and stains on pit interiors. However, this work is not being funded to develop methods to enhance the analysis capabilities of LIBS. Therefore, the accomplishments of our LDRD project can be incorporated into the endoscopic probe to provide greater analysis capabilities (e.g. lower detection limits for some elements of interest). In addition, LIBS instruments can easily monitor elemental contaminants in the environment and workplace and this instrumentation can be readily adapted to ensure the safe disposition of radioactive and other materials used in nuclear weapons manufacture. The increased analysis performance resulting from our work will make these instruments more versatile.

Nonproliferation and Counterproliferation. Because of the compact nature of LIBS instruments, these devices can be readily adapted to monitor material in the field to detect activities related to nuclear weapons manufacture. These materials include Pb, Be, U, and maraging steels (steels with high Co and Mo content), which are used in the construction of nuclear materials processing facilities because of their resistance to radiation damage. In 1995, the LANL LIBS User Facility constructed a prototype remote sensor for DOE/NN-20 to be used for the remote determination of materials used in nuclear weapons manufacture.

The methods of enhancing LIBS capabilities that result from our LDRD project can be adapted to this and other instruments to provide increased performance in the field.

Environmental Stewardship. The LIBS User Facility at LANL has recently completed an evaluation of a backpack LIBS instrument as a screening tool for metal contamination in soils and on the surfaces of buildings for use at Formerly Utilized Sites Remedial Action Program (FUSRAP) sites. FUSRAP is a DOE program aimed at cleaning up sites contaminated over the past 50 years by U.S. atomic energy and weapons programs. The U.S. Congress mandated this cleanup. One FUSRAP site is the Luckey Site at Luckey, Ohio, which is contaminated by Be, Th, U, and other nuclear-related materials. DOE has contracted with Bechtel National, Inc. for the remediation effort at this and other FUSRAP sites. As a result, and to provide site characterization efficiently using limited funds, Bechtel National requested an evaluation of the LIBS prototype built by LANL for the characterization effort. This evaluation has been completed and the results were sufficiently encouraging that the LANL-developed LIBS backpack device is being used in the clean-up effort, which began in September 1997. This effort will last approximately 8 months. The LIBS prototype will be used in the FUSRAP sampling and analysis plan (FUS162P/042997) for the Luckey Site, which was prepared by the DOE Oak Ridge Operations Office. There are 45 other FUSRAP sites across the country and Bechtel National has requested the use of LIBS instruments at some of these other sites. The method of enhancing element signals from soils, a direct result of this LDRD effort, can readily be incorporated into the LIBS backpack system to increase its field performance.

Indirect Benefits

Los Alamos is the recognized leader in the application of laser-induced breakdown spectroscopy. This capability has been developed over the past 16 years and has been used for a variety of applications. Many of these applications have direct relevance to DOE as noted above. Past applications to DOE needs have included: (1) the development of a real-time beryllium aerosol monitor for EH-412 and DOE-DP and (2) the rapid analysis of uranium in flowing streams for application to nuclear fuel reprocessing plants. The work carried out by this LDRD project is a natural extension of this previous work. Indirect benefits include: (1) enhancement of the capabilities of portable LIBS instruments making the instruments more commercially attractive due to an increase in the market for such devices and (2) demonstration of continuing LANL expertise in the area of LIBS technology development.

Scientific Approach and Accomplishments

Several useful results have come from this work that help increase the analytical capabilities of the LIBS method making it more useful. These are described in detail below.

Double-Pulse Excitation

LIBS measurements are typically carried out using what are termed single, repetitive laser sparks or repetitive single sparks (RSS). That is, a series of laser sparks are formed on the sample surface such that the pulses are spaced apart in time by more than 100 milliseconds. At these long times, there are no inter-pulse effects because the plasma formed by a laser spark typically decays completely within about 100 microseconds after formation. The use of a double-pulse method in which a pair of laser sparks closely spaced in time (less than 100 microseconds) was investigated as a means to enhance the detection of elements in soils and in metals. At this short inter-pulse spacing, inter-pulse effects are expected. Previous work on the detection of metals under water has shown the enhancement of LIBS signals using a double-pulse method [2]. In our LDRD project, a pair of lasers was used to generate the pair of pulses so the timing between the two pulses could be accurately controlled and the energy of the individual pulses could be adjusted to any desired value. The repetitive double pulses, here termed the repetitive spark pair (RSP), were incident colinearly on the sample surface. The time between the double pulses (Δt) and the energy of the first pulse were varied to study the effect on the analyte signals. A diagram of the experimental set-up is shown in Figure 1(a) and the timing between the two pulses of the RSP and the gate-pulse to the detector is shown in Figure 1(b). The gate-pulse determined when the detector was turned on to record the plasma light. The timing parameters shown in the figure are defined in the caption. As discussed elsewhere, monitoring all the plasma light does not necessarily provide optimum detection capabilities. Samples used were aluminum, brass, clean soil, and soil spiked with a metal at a known concentration.

The enhancement of the analyte signal obtained using two pulses of energy E (the RSP) compared to that recorded using a single laser pulse of energy 2E was dependent on Δt and the lens-to sample distance (LTSD). An enhancement up to 5 was found for some LTSD values for soils and an enhancement factor up to 30 for major elements in a metal. These results are shown in Figure 2 for soil and aluminum metal for different LTSD values. In all cases examined, the signal obtained from a single pulse of energy 2E was equal to or less than that obtained using double pulses each of energy E. The maximum enhancement appeared to occur for Δt values between 1 and 5 microseconds. Although a significant signal enhancement was not observed for all LTSD values, the double-pulse method will be useful for use with fiber optics in those cases where pulses of energy 2E exceed the damage threshold of the fiber but a pulse energy of E can be reliably transmitted. For Mn and Pb, the detection limits obtained using a neutral emission line were about equal using either single or double pulse excitation whereas detection limits obtained for Ba and Be, using an ion line, were 3-4 times higher for the RSP. Measurement precision, however, was similar for the two types of excitation.

The temperature and electron density of the plasmas produced by the RSS and the RSP were measured as functions of Δt, the LTSD, and the energy of the first pulse. The data show that the temperature of the second plasma of the RSP was not significantly greater than that of the first plasma of the RSP or of the RSS, in general agreement with results obtained previously [3]. In addition, the data show no significant changes in the temperature of the second plasma over the range Δt = 1-180 μsec, although the maximum temperature of 9400K was attained at Δt = 5 μsec, somewhat later than the delay at which the maximum analyte signals were observed (see Figure 1). Also, the temperature of the second plasma of the RSP was not a strong function of the LTSD or the energy of the first pulse. Similarly, n_e showed no significant dependence on Δt except at early times where n_e values were about 30% lower than those obtained for Δt > 100 μsec.

As noted above, the temperature of the second plasma of the RSP was not significantly greater than that of the first plasma, indicating that reheating of the plasma cannot account for the observed signal enhancement. However, time-resolved imaging of the laser-material interaction using a gated CCD camera (see Figure 1), in addition to a series of other experiments, indicated a possible mechanism for the enhancement in the element signals observed using double-pulse excitation. Images of the laser plasmas formed on aluminum metal using the RSP show the existence of a "cloud" above the surface that existed for a time period greater than 100 microseconds after formation of the first plasma of the RSP. The top image of Figure 3 shows this "cloud" which only appears when the focal volume is irradiated by the second pulse of the RSP. The nature of this "cloud" was investigated by blowing a strong stream of air across the sample to intercept this "cloud". Comparison of the images obtained with the air flow on and then off showed that (1) the "cloud" disappeared due to the action of the air flow (middle image of Figure 3) and (2) the signal enhancement observed from the second pulse of the RSP also disappeared for longer inter-pulse spacing times when the air flow was on. As the lower image of Figure 3 shows, the "cloud" is not present using the RSS, or single spark excitation.

These results indicate that the "cloud" consisted of fine particles that were blown away by the airflow. The dependence of the Al(I) signal from the second pulse of the RSP is shown in Figure 4 as a function of Δt. Note that with the airflow on, the enhancement dropped significantly for values of Δt > 60 microseconds. Given the velocity of the air flow across the sample surface and the width of the "cloud" as measured from the images (about 2 mm), a simple calculation shows that the "cloud" of particles will be completely removed from the focal volume in about 60 microseconds. Therefore, the enhancement observed by using the RSP on a metal is due to ablation and excitation of the fine particles generated by the first pulse of the RSP. If these particles are blown away, the enhancement disappears. A similar mechanism is operative in the RSP excitation of soils.

LIBS Using Low Laser-Pulse Energies

The dependence of LIBS analytical results (detection limits, precision) on low laser-pulse energies (<100 mJ) and gating parameters used in time-resolved detection was examined using a series of certified synthetic silicate samples. These samples were used as simulants for soils because they contained the major elements commonly found in soils, the concentrations of these major species were constant for all samples in the series, and concentrations of the analytes of interest spanned a wide range. For this study, over 300 calibration curves were prepared and characteristics compared. The effect of low pulse energies (<100 mJ) was investigated because this regime is most important for field-based measurements using compact laser systems.

The results indicate that. in general, low pulse energies will not seriously compromise detection capabilities for soil-like materials. Comparable detection limits and precisions were obtained using pulse energies in the range 10-100 mJ and the relative standard deviation of replicate measurements was independent of analyte concentration and laser pulse energy. On the other hand, for the lowest energies (10 and 25 mJ), spectral interferences may be a problem for some complex samples with a high density of emission lines because of spectral line broadening. In addition, the calibration curves for two analytes (Mn and Cr) were very nonlinear, especially at the two lowest energies used here, whereas for the other elements examined (Ag, Ba, Be, Cu, Pb, Sr, Ti, and Zn) the curves were mainly linear. These differences are related to the characteristics of the upper emitting energy level responsible for the observed emission line. For the elements Mn and Cr, these upper energy levels were low lying (e.g. of low energy) and the emitting transition ended in the atomic ground state. In this case, self-absorption is a strong process that can produce the observed curvature of the calibration curves.

Gated Versus Non-gated Detection

In LIBS measurements, a gated detection system is normally used to monitor the plasma light at certain periods after formation of the laser spark. In some instances, gated detection is necessary to minimize the strong, spectrally broad continuum light that occurs during the first 1-2 microseconds after plasma formation. This strong continuum light is what gives the laser spark its "white light" appearance. Unfortunately, there is little information in this "white light"—the main spectral information occurs after this "white light" has decayed and emissions from atomic species predominate. The detector is gated off during the first few microseconds to prevent detection of this "white light" that can mask the weaker atomic emissions. Although the technology of gated detection is well developed, gated detectors are much more expensive and somewhat more complex and typically larger than a non-gated detector. For this reason, the use of a non-gated detector will be preferred for a field-based LIBS instrument.

Using different values of the timing parameters t_d and t_b (see Fig. 1), calibration curves were constructed for the elements Ag, Be, Cu, and Zn using the synthetic samples and a pulse energy of 50 mJ. The (t_d, t_b) combinations used here were (1,20), (1, 1), (2, 1), (3, 2), (5, 2) and (10, 5) in addition to continuous mode in which all the plasma light was recorded (e.g. non-gated detection). As t_d increased, it was necessary to increase t_b to maintain at useful levels the intensity of the spectral lines observed from the decaying plasma.

From these curves detection limits (C_L) were computed and compared. The values of C_L are shown in Figure 5 as a function of the different timing parameters. As the data show, C_L remained essentially uniform for both the neutral and once-ionized species monitored here for the continuous detection mode, for the combination (1,20) typically used for LIBS measurements, and for the combination (1,1). For the other t_d, t_b combinations, the detection limits were somewhat higher. Replicate measurements of several samples were used to determine the reproducibility or measurement precision represented by the quantity %RSD (percent relative standard deviation). Comparison of the %RSD values obtained for the analytes examined here at the different t_d, t_b combinations shows no distinct trend, that is, the average %RSD values of the ratioed analyte signal were all within the range of 3-10% and the average %RSD of the absolute analyte signals were in the range 8-17%. These results indicate that neither monitoring one particular period of observation after plasma formation, nor monitoring all the plasma light, appear to increase the noise in the measurements.

Publication

1. Chinni, R.C. and Cremers, D.A., "Dependence of Analytical Results on Low Laser Pulse Energies (<100 mJ) and Timing Parameters in Laser-Induced Breakdown Spectroscopy," LANL report LA-UR-97-3421 (to be published in *Applied Spectroscopy*).

References

[1] Radziemski, L.J. and Cremers, D.A., "Spectrochemical Analysis Using Laser Plasma Excitation," in Laser-Induced Plasmas and Applications (Marcel Dekker, New York, 1989), Chapter 7.

[2] Pichahchy, A.E., Cremers, D.A., and Ferris, M.J., "Elemental Analysis of Metals Under Water Using Laser-Induced Breakdown Spectroscopy," *Spectrochimica Acta* **B52**, 25-39 (1997).

[3] Uebbing, J., Brust, J., Sdorra, W., Leis, F.. and Niemax, K., "Reheating of a Laser-Produced Plasma by a Second Pulse Laser," *Applied Spectroscopy*, **45**, 1419 (1991).

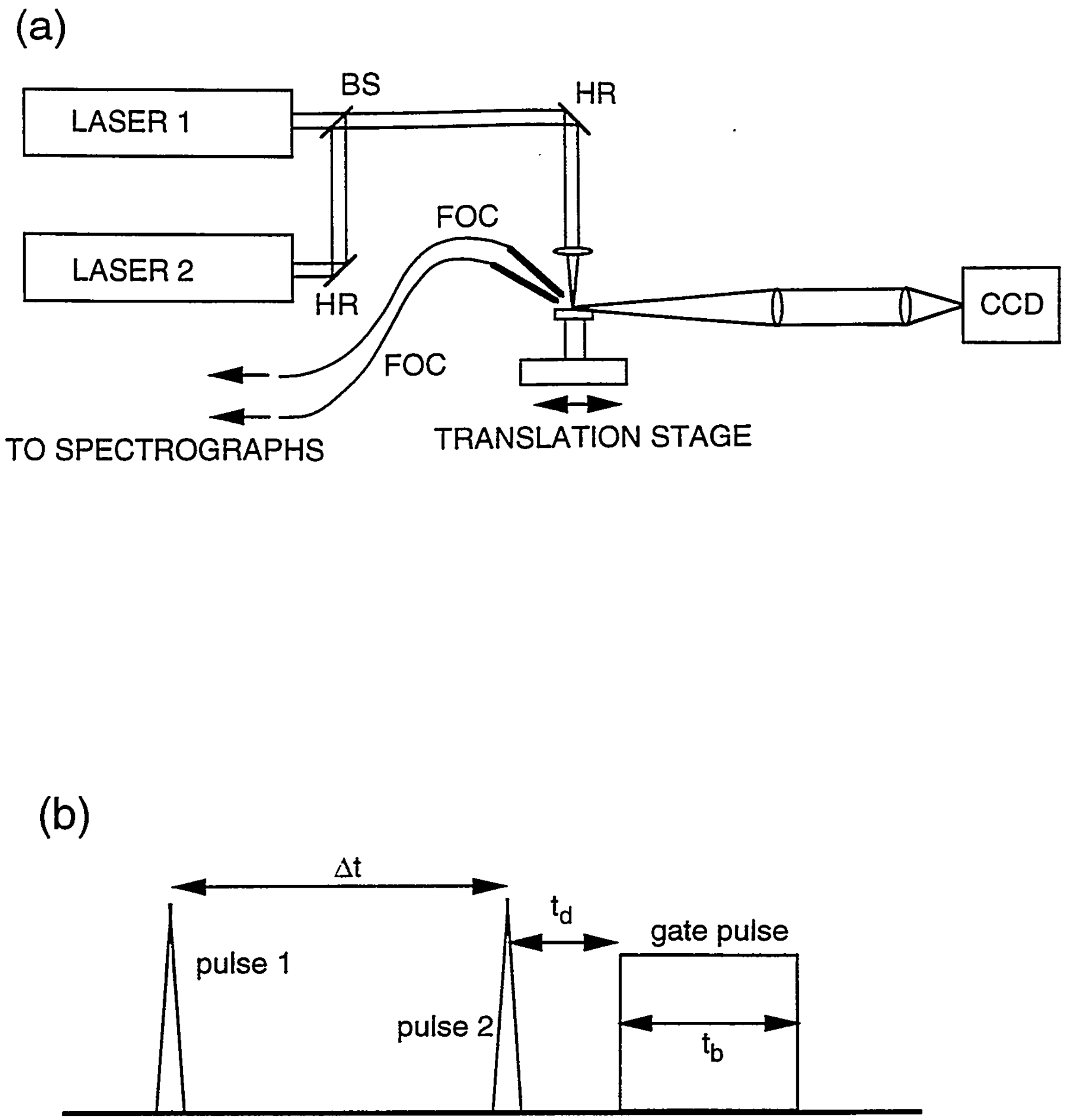


Figure 1. (a) Diagram of the apparatus used for double-pulse excitation of soil and metal samples using two separate lasers. The laser plasmas were examined using spectroscopic methods and by recording time-resolved two-dimensional images of a single plasma. FOC = fiber optic cable; HR = high reflector at 1064 nm; BS = beamsplitter; GT = Galilean telescope. (b) Timing between the two laser pulses and the gate pulse to the detector intensifier. Here t_d is the time after plasma formation at which the detector was gated on to monitor the plasma light and t_b is the length of time the detector was left on to record the plasma light.

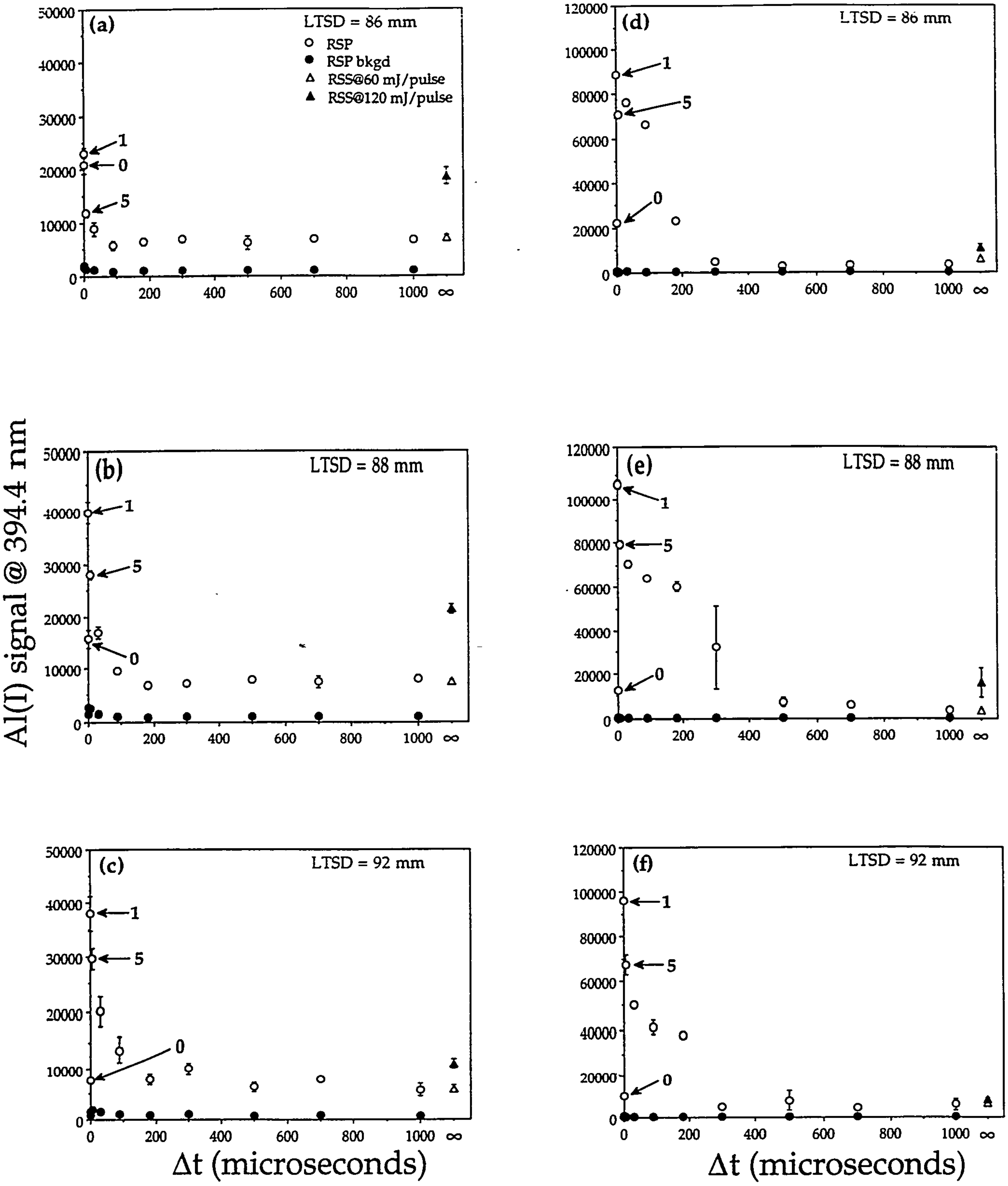
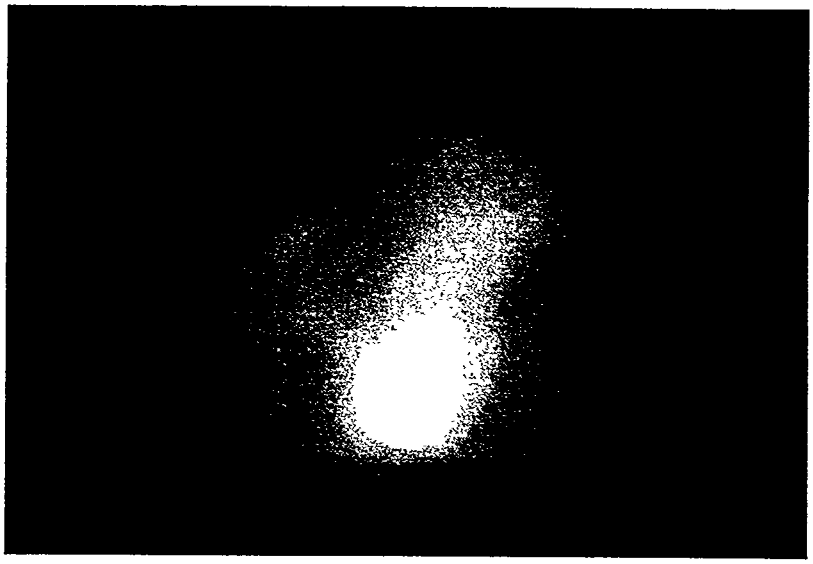
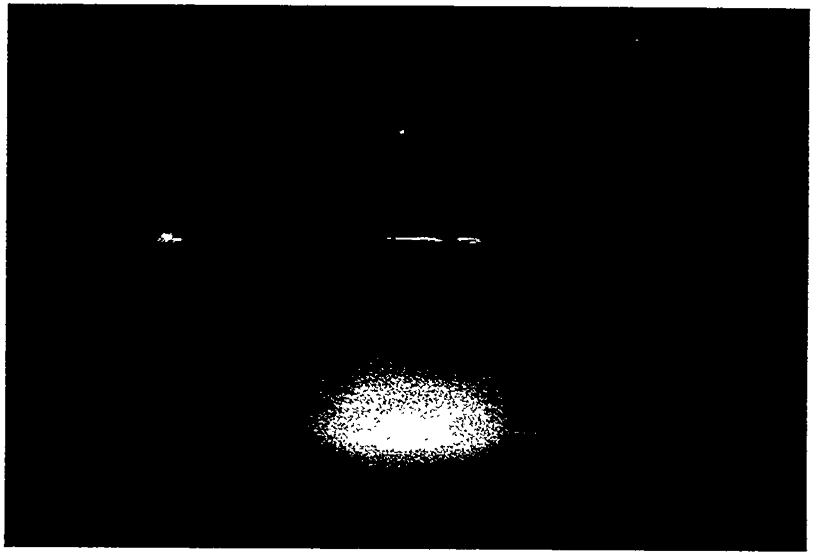


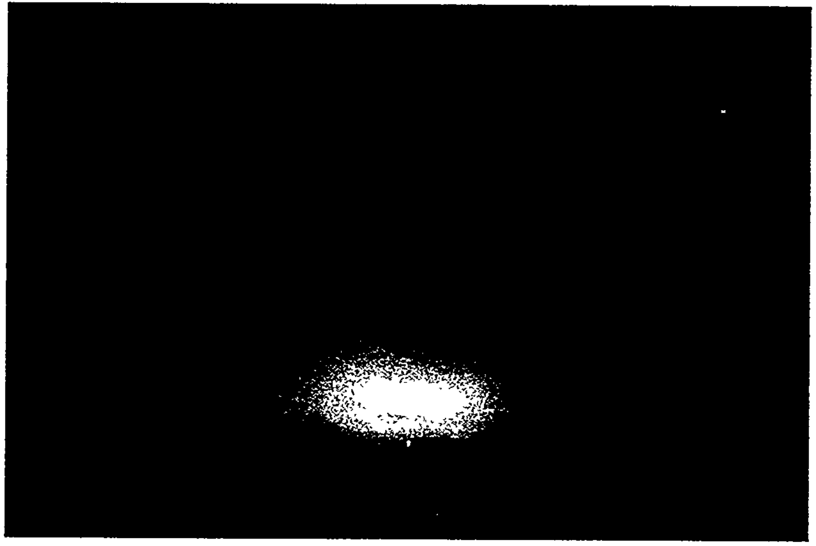
Figure 2. Dependence of the Al(I) emission and the plasma continuum background emission signals on Δt for three values of LTSD using the RSP. Data are shown for soil (a-c) and aluminum metal (d-f). Also shown is the Al(I) signal obtained using the RSS (plotted at Δt = ∞) and pulses of 60 and 120 mJ.



RSP @ Δt = 70 μsec; no airflow



RSP @ Δt = 70 μsec; airflow = 40 L/min



RSS; no airflow

Figure 3. Images of the RSP formed on an aluminum plate with and without air flow (40 L/min.) horizontally across the plate. Also shown is the RSS without air flow.

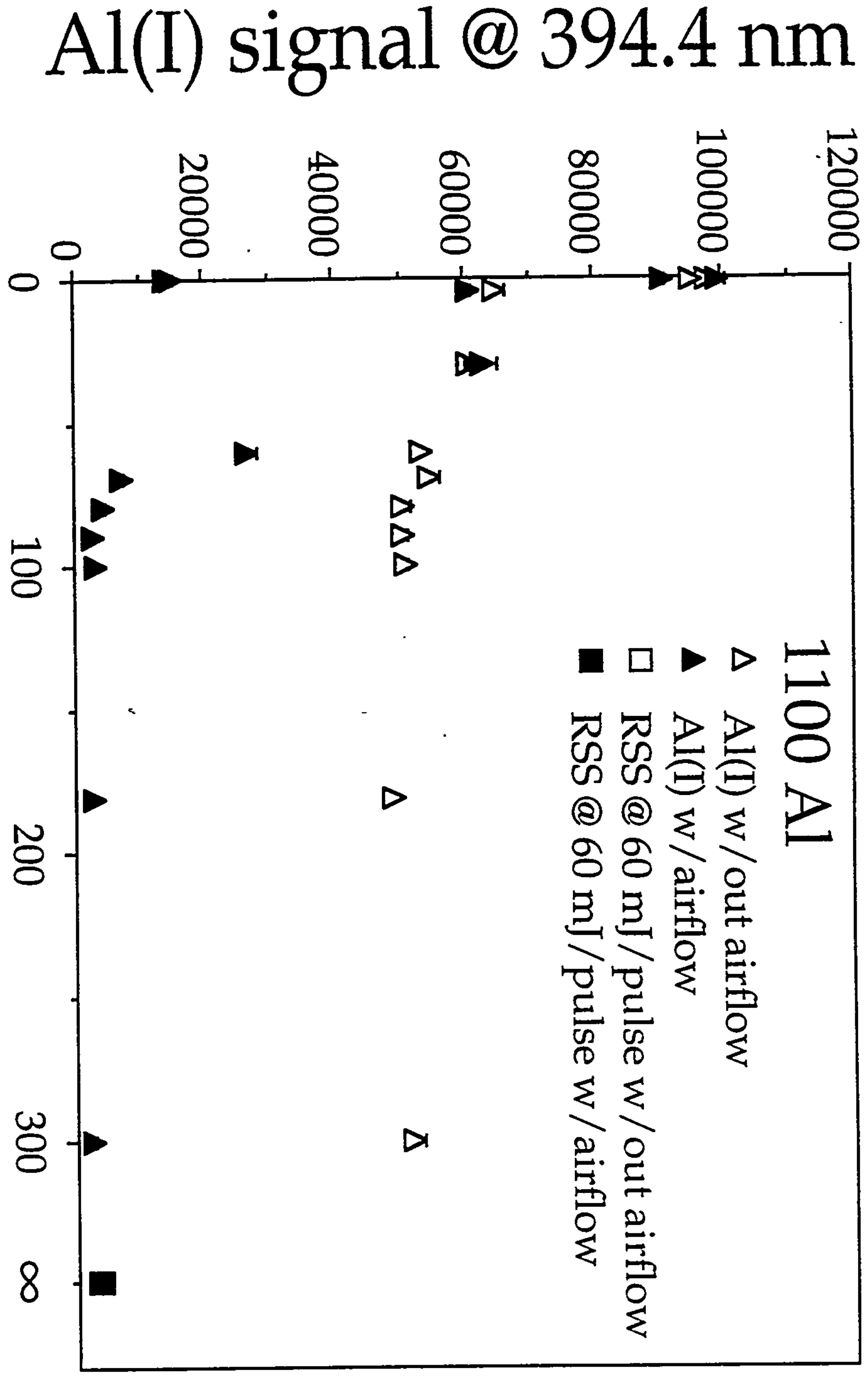


Figure 4. Dependence of Al(I) signal as a function of Δt recorded from aluminum metal sample with and without a stream of air flowing through the plasma volume. Data are shown for the RSP and RSS (plotted at Δt = ∞) under different conditions. The air flow rate was 20 L/min.

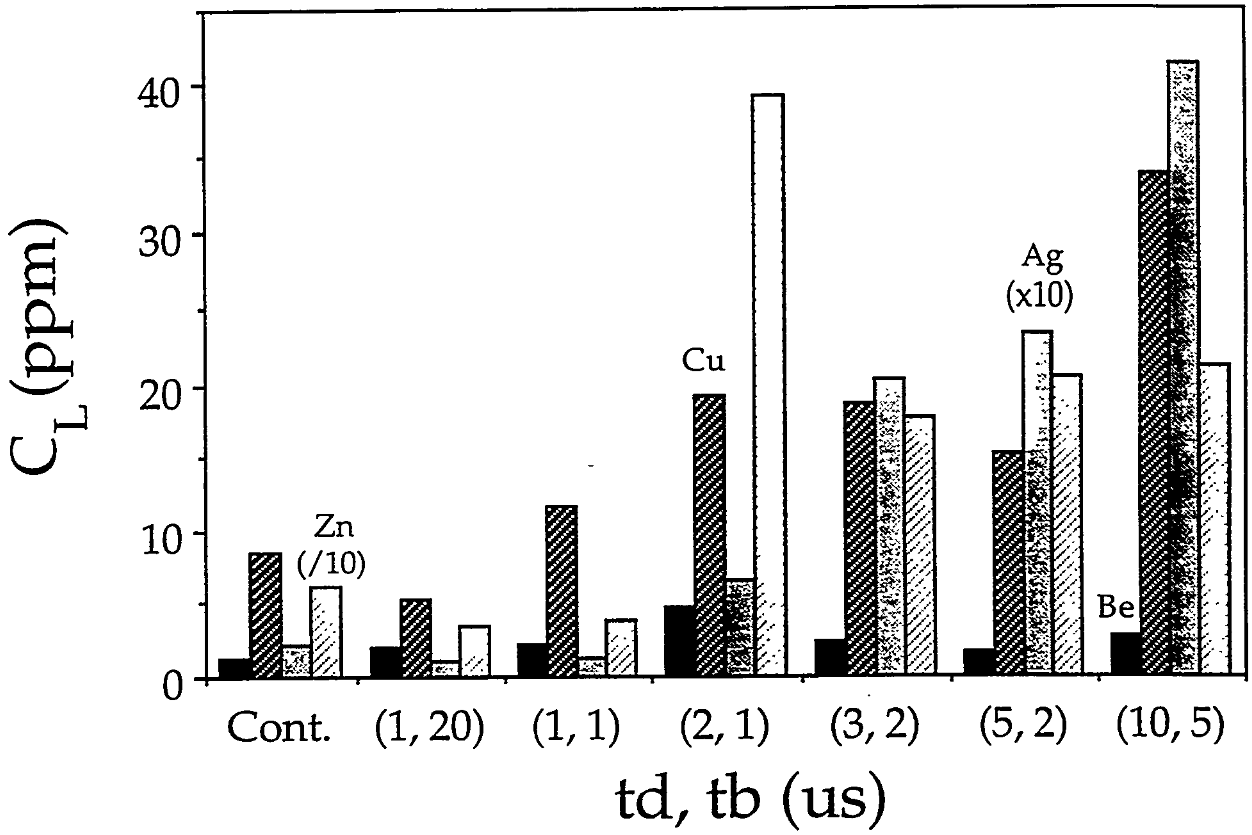


Figure 5. Detection limits determined using the analyte/Fe ratio as a function of the timing parameters t_d, t_b. The detection limits for Zn and Ag have been divided by and multipled by a factors of ten, respectively, for display here.