Metals Monitoring for Process Control of Laser-Based Coatings Removal

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Introduction

The lead paint abatement market is reportedly $400 billion with applications ranging from civilian infrastructure to hazardous waste sites. Solvent-based and abrasive technologies have long been the preferred tools of the trade for coatings removal but environmental issues have renewed interest in other alternatives including laser-based techniques. Reduced laser cost over the past few years combined with inherent waste volume reduction are key factors contributing to broader applicability of laser-based coatings removal systems. Typically, these technologies act by focusing a pulsed high energy laser beam on the coating to produce a plasma which ablates and combusts the largely organic coating matrix. The combustion of the organic components produces the waste volume reduction which can be two-thirds or more. For industrial applications the laser power needed ranges from a few watts for small jobs to several kW for large tasks.

The presence of the plasma in the laser-based coatings method provides an opportunity to develop a passive feedback control system which can optimize (reduce) the dwell of the laser on a spot, thus improving the economics, which simultaneously serves to minimize substrate damage that results from overexposing the bare substrate. The feedback control system is analogous to the detection scheme employed in laser-based breakdown spectroscopy (LIBS), a new class of
analytical detection and monitoring technologies pioneered by Cremers of Los Alamos National Laboratory\textsuperscript{2,3} and others.\textsuperscript{4-7} In LIBS, specific atomic wavelengths characteristic of the desired analyte are monitored in the highly excited plasma, typically with a spectrometer and multi-channel analyzer.

This paper describes a temporally-resolved bandpass filtered radiometer approach to monitor the lead present in lead-based paint to control the laser cleaning head in a pulsed CO\textsubscript{2} laser-based cleaning system.

**Experimental**

The basis of the feedback control system is a two color radiometer scheme employing a 405.7 nm interference filter centered (1 nm FWHM) on the lead atomic transition line and an off-band filter centered in a region determined to encompass no discrete features, 400 nm.\textsuperscript{8} These filters have been interfaced with two inexpensive, miniature PMT packages with built in voltage transformers and transimpedance amplifiers. A diagram of the complete detector package, composed of fiber optics to view the laser-generated plasma, filtered radiometer to acquire spectrally-specific analog data, and a computer, is shown in Figure 1. The fiber optics, 10 m in length, are interfaced to the laser scanner head such that they view the laser-created plasma. The analog signals output by the radiometer are input into a computer through a 1.2 MHz A/D data acquisition board. The temporal traces are evaluated by routines employing LabWindows CVI\textsuperscript{®} software. The on-line and off-line temporal traces are subtracted to correct for residual plasma emission and integrated within specific time windows. The integrated values are then used to output analog values (0-10 V) for laser scanner head control.
The lasers used to develop and test the feedback control system were pulsed CO$_2$ lasers ranging in energy from 5 to 18 J and operating at repetition rates of 1 to 20 Hz with a typical pulse width of <5 µs. The focused spot size of the laser depends upon the laser energy and has varied from 0.5 to 2 cm$^2$.

The samples have been industrial grade aluminum, steel and concrete obtained from local vendors. These have been coated by brush or with roller with non-lead latex paint and lead-containing red traffic paint (typically 12 to 15 wt% lead) or yellow automotive paint (approximately 4 wt% lead). Several classes of substrates have been used: without coatings, with only a single coating and with alternating stripes of lead and non-lead paint. The prepared samples were mounted in an x-y table and irradiated in fixed position and at a constant velocity.

Results and Discussion

The development of a process control mechanism requires sensitive, unambiguous detection of lead in the paint and residual lead on the substrate surface. To accomplish this requires appropriate temporal processing of the radiometer analog signals to optimize the sensitivity of the lead signal while simultaneously decreasing background and interfering emissions. This is illustrated with LIBS spectra from latex paint spiked with 2 wt% lead nitrate, obtained with a 20 mJ Q-switched Nd:YAG laser operated on the 1.06 µm fundamental and a spectrometer/multichannel analyzer combination, shown in Figure 2 for two delay times after laser firing. At 12 µs delay the spectrum contains a strong plasma continuum plus intense titanium emissions in addition to the lead line at 405.7 nm (the Ti lines result from TiO$_2$ in the paint). At 60 µs delay the plasma has cooled considerably, the titanium lines have disappeared and the predominant feature is Pb emission at 405.7 nm. Figure 2b also shows there to be no atomic
features present at 400 nm at long delays verifying the validity of selecting this wavelength for background subtraction.

With higher powered lasers the temporal behavior changes significantly. Figure 3 shows temporally resolved data from the radiometer for both 405.7 and 400 nm channels (appropriately offset in the figure) for a single shot of 4.59 J pulsed CO$_2$ laser energy focused to a 0.7 x 0.7 cm spot size on an aluminum target coated with lead paint. Both channels exhibit strong emission in the first 500 µs due to the plasma. The emission from 500 to 1500 µs is likely due to an emission continuum from combustion of the organic matrix. This emission increase is observed in both channels but is more pronounced at 405.7 nm. The 405.7 nm lead atomic line persists for times up to 4 ms whereas the 400 nm emission typically decays before 1 ms, often by 0.5 ms. This temporal discrimination permits operation with the 405.7 nm channel only. For this mode of operation the oscilloscope board was typically set to 25 kHz and data integrated over the range 0.8 to 3.8 ms. Thus, lead can be detected using the 405.7 nm channel only and also by taking the difference of the 405.7 and 400 nm channels.

The next step in developing a feedback control system is to use the radiometer to distinguish the level of paint on a substrate surface. This first requires examining the bare substrates with no paint present. Owing to its high infrared reflectivity, aluminum produces no plasma, and hence, no emission in either radiometer channel when irradiated. Bare steel samples will often produce a transient signal on the first one or two shots arising from combustion of organic residue from the manufacturing and rolling process. Concrete produces a temporally broad, prompt signal (< 1 ms) in both channels arising from coupling of the laser energy with the concrete substrate. After several laser shots the concrete surface is discolored.
For painted substrates all three substrates behave similarly until the substrate begins to be exposed (breakthrough). With lead paint, traces similar to Figure 3 result for all three substrates. For non-lead paint both the 405.7 and 400 nm traces exhibit equal magnitude features at 500 µs and contain no intensity observed at times > 1 ms. Thus, when the two channels are subtracted, the features exactly cancel.

During breakthrough, aluminum and steel showed emission signals consistent with consumption of the remaining traces of coating until the edges were fully ablated, at which point the signals disappeared. The traces after complete coating removal corresponded precisely to those observed for the bare material. Concrete was a notable exception, however. During breakthrough the more prompt signals (<500 µs) in the 400 and 405 nm bandpasses do not decrease appreciably and they also persist for many shots after apparent coating removal. During this time the concrete substrate darkens. This behavior is attributed to exchange of residual coating material between laser shots into the porous concrete matrix. The long time (0.5 to 4 ms) behavior in the 405.7 nm bandpass, however, remained well-behaved with the intensity closely tracking substrate ablation.

An example of the radiometer data during complete paint removal is shown in Figure 4. For this experiment the persistent 405.7 nm signal was integrated and monitored as the laser ablated lead paint from a fixed area. The data are shown without averaging and the variability reflects the true variability in the plasma from shot to short. Thus, the change in signal intensity from shot five to shot eight is real as are the signal fluctuations during breakthrough.
Process Control

The final capability demonstration for process control is to distinguish residual paint levels in real time with the scanner head moving and to adjust the X velocity based upon coating thickness. An example of real time coating identification is shown in Figure 5. Here, the fiber optics are viewing the ablation of alternating latex and lead paint stripes on concrete as the X-Y table moves at a constant velocity in the X dimension. The data in Figure 5 show the radiometer is able to distinguish the two types of paint in real time during a scan.

Finally, the radiometer has been integrated with a laser cleaning head and has been demonstrated for real time process control with a 2 kW laser. An schematic of the process is summarized in Figure 6. The figure shows the laser “boot” performing a raster scan across a painted substrate (steel) leaving clean areas behind. A closeup of the boot shows the direction of travel, the coating which is actively being ablated, and the location of co-aligned fiber optics viewing the laser-created plasma. The total integrated intensity (difference between the 405.7 nm and 400 nm channels or 405.7 nm channel alone) is compared to that from pre-determined “clean” signal levels to form the basis of a scan velocity controlling algorithm. The capability to increase the scan velocity in areas of thin lead paint and to slow the scan speed in areas of thicker layers has been demonstrated at 10 to 20 Hz operation with an 18 J laser.

Work in progress includes incorporation of the computer and radiometer into a single package and permanent integration and testing of the feedback control device with a laser-based coatings removal system.
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References


Figure 1. Schematic of the radiometer detection system.
Figure 2. LIBS spectra from lead nitrate-spiked latex paint (2 wt%) at two different delays.
Figure 3. Temporally resolved radiometer data for pulsed CO$_2$ laser irradiation of lead paint on aluminum. The lower plot is the 400 nm channel, the middle plot is the 405.7 nm channel and the uppermost plot is the difference.
Figure 4. 405.7 nm channel data for lead paint ablation from an aluminum substrate at 1 Hz laser repetition rate.
Figure 5. Linear scan of concrete containing alternating stripes of non-lead latex paint and lead traffic paint.
Figure 6. Use of radiometer as process control for laser-based coatings removal.