

To be published in Applied Optics:

Title: [LIBS] Commercialization of LIBS for Lead-in-Paint Inspection

Authors: Richard Myers, Noah Kolodziejski, and Michael Squillante

Accepted: 26 June 2008

Posted: 30 June 2008

Doc. ID: 94508

Published by

OSA

Commercialization of LIBS for Lead-in-Paint Inspection

Richard A. Myers*, Noah J. Kolodziejski and Michael R. Squillante

Radiation Monitoring Devices, Inc., 44 Hunt Street, Watertown, MA 02472-4699, USA

*Corresponding author: rmyers@rmdinc.com

Abstract: A study was undertaken to determine if laser-induced breakdown spectroscopy (LIBS) can be a practical and competitive alternative to X-ray fluorescence (XRF) methods for lead-in-paint inspection. Experiments in the laboratory confirmed that LIBS is suitable for detecting lead in paint at the hazard levels defined by federal agencies. Although we compared speed, function and cost, fundamental differences between the XRF and LIBS measurements limited our ability to make a quantitative performance comparison. While the LIBS method can achieve the required sensitivity and offers a way to obtain unique information during inspection, the current component costs will likely restrict interest in the method to niche applications. ©

2008 Optical Society of America

OCIS codes: (140.3440) laser-induced breakdown; (300.2140) Emission spectroscopy; (280.1545) Chemical analysis

1. Background

A. On-site Lead-in-Paint Inspection

Since 1977, the United States Environment Protection Agency (EPA) and department of Housing and Urban Development (HUD) have prohibited the manufacture and use of commercial paint

containing > 0.06 dry weight percent (wt. %) of lead (Pb) (equivalent to 600 ppm) [1, 2]. However, prior to that time, some paints contained up to 50 dry wt. % of Pb [3, 4]. Older homes with Pb paint are now considered environmental hazards, especially if the paint is accessible to the young. In 2004, the National Safety Council estimated that there are 38 million US homes still containing Pb-based paints above the abatement levels [5]. Although the exact values defining this level varies based on regional laws, HUD defines Pb-based paint hazards to be dry paint with a Pb content greater or equal to 1.0 mg/cm^2 or 0.5 wt. % [6]. Therefore, special procedures are needed when remodeling or rebuilding a structure that has Pb content above these levels. This implies that the measurement accuracy at the hazard level is a critical factor, especially to the owner whom has to pay for the extra precautions required when a positive reading is found. Although this work focuses on the US, which was one of the last industrialized countries to take action to eliminate Pb-based paints, other countries are also dealing with this problem and are instituting more rigorous policies towards paint inspections [7].

The most common method for Pb-in-paint inspection relies upon removing paint chips and sending them to the laboratory for analysis, where methods such as inductively couple plasma (ICP) spectroscopy are employed. While the accuracy of these methods can be very high, they are destructive, require several days of waiting for results and greatly depend on the sample collection method. The primary alternative to laboratory analysis is X-ray fluorescence (XRF) using instruments such as the LPA-1 manufactured by Radiation Monitoring Devices (Watertown, MA). These instruments are considered the gold standard for real-time Pb-based paint inspection, providing reliable sensitivity to Pb in paint at levels below 0.3 mg/cm^2 with an accuracy of $\pm 0.05 \text{ mg/cm}^2$ [6, 8]. Because XRF monitors the fluorescence return signal from a

^{57}Co or ^{109}Cd gamma ray source, the most attractive aspect of the measurement is that it does not mark or damage the painted surface. However, one of the disadvantages of these instruments is the reduced accuracy ($\pm 0.1 \text{ mg/cm}^2$) when analyzing paint on metal or concrete substrates. In addition, proper disposal, costly training and extensive record keeping is required when working with both the real and perceived hazards of radioactive sources. Eliminating the use of the source and its additional costs would be a favorable market factor for any new instrument trying to replace those using XRF.

B. LIBS Technology

Matured over the past decade, laser induced breakdown spectroscopy (LIBS) has been used as an elegant method for material analysis [9-13]. In brief, a basic LIBS system consists of high power pulsed laser, collection optics and a spectrometer. When the laser is discharged it ablates a very small amount of material, which instantaneously superheats, generating a plasma plume that dissociates the ablated material into excited ionic and atomic species. Initially, the plasma emits a continuum of radiation, but as the plasma expands and cools (0.1 to 10 μs), the characteristic atomic emission lines of the elements can be observed. These spectral signatures can be recorded and rapidly processed for material analysis. This is particularly useful for on-site inspections, high volume analyses or on-line industrial monitoring. However, despite the compelling performance in the laboratory, few commercially successful LIBS systems have appeared on the market that can compete with established analytical methods.

Complex matrix interactions between atomic species as well as the plasma and the sample surface makes the use of LIBS for simultaneous multi-element analysis difficult.

However, portable LIBS is possible if the sample set is controlled and the analysis is limited to one or two elements. Consequently, because of its strong and isolated emission line, the detection of Pb-in-paint was one of the early target applications for LIBS analysis [14, 15]. Early research established the ability to measure very low concentrations of Pb in paint with a custom probe with a mainframe laser but no additional work was performed to develop a portable instrument or fully assess its market potential [14]. In another effort, a portable system was developed using the Kigre MK-367 (Kigre Inc., Hilton Head Island, SC) compact neodymium doped yttrium aluminum garnet (Nd:YAG) laser and S2000 (Ocean Optics, Dunedin, FL) compact spectrometer [15]. While this system showed encouraging results, only preliminary work was reported and, as far as we are aware, further studies to assess the performance of the portable system as a commercial tool for Pb-in-paint inspection were not fully explored. Despite the further development of LIBS instrumentation over the past decade, no federally approved LIBS instruments for Pb-in-paint inspection have appeared on the market.

2. Experimental Studies

A. Experimental Setup

To assess the technical performance of LIBS for Pb-paint inspection, we used a Q-switched Nd:YAG solid state laser operating at 1064 nm. The laser had a pulse width of 10 ns, a maximum repetition rate of 10 Hz and a maximum output energy of ~ 200 mJ per pulse. Although a portable laser was not available during this study, the mainframe laser provided a high degree of control over its repetition rate, pulse energy and provided both internal and external triggering capabilities. This control allowed us to simulate the laser output for a range

of portable lasers and synchronize the timing of the laser plasma with the spectrometer. Beamsplitters and a spatial filter were used to reduce the laser energy to < 15 mJ per pulse, consistent with the laser pulse energies of compact Nd:YAG lasers viable for portable LIBS systems. Off-the-shelf optics were used in a collinear backscatter collection geometry. The principle optics included a 35-mm focal length lens for both focusing the laser excitation and collecting the backscattered emission. The 35 mm focal length maintained (1) an appropriate separation from the target, preventing the ejected sample from coating the lens, (2) a focal spot size as small as $100\ \mu\text{m}$ and (3) a depth-of-focus over 1 mm, which reduced the sampling uncertainty due to surface imperfections and provided consonant intensities as the laser “drilled” through the sample.

Using a lens, the backscattered plasma emission was imaged into an optical fiber with a 600 nm diameter whose opposite end was coupled to a $\frac{1}{4}$ -m monochromator. After confirming that the primary Pb emission line at 405.78 nm could be used to monitor the level of Pb in paint, we set the resolution of our spectrometer to 0.01 nm and used a cooled 256×1024 element CCD from Princeton Instruments (Trenton, NJ). Our cooled CCD did not allow temporal separation of the initial plasma signal from the emission signal. We also utilized an Ocean Optics HR2000 spectrometer with a grating centered at ~ 440 nm and a 120 nm bandwidth that provided a spectral resolution of ~ 0.1 nm. While this unit operated at room temperature, it used a CCD that has a high-speed gating feature for reducing the initial plasma signal. Software from Ocean Optics allowed us to externally trigger the laser and adjust the delay between the plasma formation and the start of the signal collection. The delay following the laser trigger pulse was typically set to $2.5\ \mu\text{s}$.

We compensated for the shot-to-shot signal variation (as much as 20%) by subtracting the background signal within 0.5 nm of the Pb emission signal. The only element with a strong spectral emission line within 0.1 nm of the Pb emission is from Gd but it was never observed during our studies [16]. Figure 1 shows our setup and spectra of a latex-based paint with and without added Pb. Because the Nd:YAG laser radiation is not visible, a 632 nm He:Ne laser was used for system alignment.

B. Sample Preparation

We monitored the LIBS signal from solid Pb, aluminum and stainless steel. We also tested NIST-traceable Pb-paint calibration samples designed for use with XRF instruments along with various Pb-containing paint samples from old homes. For a set of samples with a known range of Pb concentrations, we produced paints by mixing commercial water or oil-based paints with either lead oxide (PbO) or lead carbonate (PbCO₃) [14]. We used several different paint bases with varying color tints as well as amounts of Ti. The dry weight of the paints were determined by consulting the manufacture data sheet and confirmed in the laboratory. Paint samples were applied to a substrate with a brush, resulting in a single layer thickness ranging from 20 to 40 μm. Multiple layers were created following appropriate drying times. To simulate years of drying, some samples were placed in a laboratory oven for 24 to 48 hours at an elevated temperature of ~ 90 °C. Plastic, metal wood and glass substrates were used.

Paint sample thickness was measured using a thickness gauge with ~ 3 μm accuracy. To determine the laser removal rate, paint was applied to glass slides and the thickness was

measured. By illuminating the opposite side of the glass slide and viewing the sample through a microscope, we were able to determine the number of laser shots required to penetrate through the paint as a function of laser energy and focal spot size.

C. Experimental Results

Laboratory prepared paint samples containing equivalent Pb concentrations displayed Pb emission strengths that were within experimental error of each other, independent of the color tint, the amount of Ti or the paint-base. This was important since it indicates that a reliable set of calibration standards can be created.

To assess LIBS as an alternative to XRF for rapid, on-site paint inspection, we optimized the amount of material removed during each laser pulse. As seen in Figure 2, while the signal to background ratio increased with laser energy it began to saturate when the pulse energy exceeded 15 mJ and the penetration depth of each laser shot decreased. This phenomenon was observed in all of the paints tested and the decrease in penetration depth with laser energy was attributed plasma screening [17, 18]. This occurs when the intense plasma spark prevents the tail end of the laser pulse from interacting with the target. In addition, the plasma ablation formed craters with diameters from $<100\ \mu\text{m}$ to over $500\ \mu\text{m}$ as the laser pulse energy was increased across the tested range. Using this data, we determined that a pulse energy between 6 and 8 mJ provided the best trade-off between the strength of signal and removal rate.

Figure 3 shows the measured Pb emission signal arising from LIBS experiment using paint samples with PbCO_3 concentrations ranging from 0.1 wt. % to 10 wt. %. The strength of

the emission signal from Pb was recorded by averaging the signal generated with six laser shots and laser pulse energy of 7 mJ. Several random sampling locations were selected for each measurement to determine the signal uniformity and measurement error across each sample. The figure indicates that, at the HUD federal abatement level of 0.5 wt. % Pb, at least a 10:1 signal-to-background ratio can be achieved. The response was linear at this federal action level, which is important for achieving accurate measurements. We measured these samples with RMD's XRF instrument but a comprehensive comparison was not realized because the relatively thin paint layers resulted in readings below the maximum reliable sensitivity of the instrument (0.3 mg/cm²). A separate measurement of the Pb sample using a more sensitive XRF instrument showed that our estimates were accurate for the purpose of our study with error towards overestimating the concentrations.

Once the laser penetrated through the paint, the spectrum also included elements from the substrate. The plasma created at the substrate surface encompassed the surrounding paint layers, resulting in a convolution of the emission signals from both materials. During our test, if the substrate was metal such as Al, which has strong emission lines within our spectral range, the location of the substrate was readily resolved. Although we did not test for it in this study, it may be possible to monitor calcium's emission at 396.8 nm when paint is on drywall or plaster. However, painted wood lack a dominant reference emission line, making it difficult to determine when substrate was reached. Alternatively, there are low-cost instruments, which can measure paint thickness on metal, drywall, wood or concrete (e.g. the PosiTector gauges from DeFelsko Corporation of Ogdensburg, NY). Typically utilizing ultrasonic methods, these instruments are

handheld, non-destructive, rapid (< 2 seconds/reading) and can potentially be integrated into a LIBS analysis inspection tool.

To demonstrate portability, we made measurements with the compact Ocean Optics HR2000 spectrometer. The same set of calibration samples that were used to test the bench-top system, were used to calibrate the signal from the HR2000 unit. We found that the signal-to-background ratio reduced by 25% relative to the cooled CCD spectrometer but it was still easy to detect Pb concentrations below the 0.5 wt. % abatement level. A spectrometer unit with higher resolution and efficiency at the Pb emission line would further improve the performance.

Paint boundaries between layers of Pb-paint and Pb-free paint were difficult to distinguish without significant drying times between layer applications, especially if the Pb-paint was applied over the Pb-free paint. To circumvent this problem we characterized a sample of painted wood trim from a home built in 1880 with both the LIBS setup and portable XRF instrument. Multiple paint layers (more than six different colors) were readily visible. The total thickness ranged from 400 to 600 μm depending on the spot and wood surface contour.

We compared the XRF and the LIBS measurements of our painted trim to show that the LIBS method had an advantage for detecting the Pb as a function of depth and providing historic information about the home. RMD's LPA-1 took several seconds to give a reading of $> 10 \text{ mg/cm}^2$, indicating that there was a high concentration of Pb paint present within the sample. The LPA-1 is not required to provide a more exact number when the Pb concentrations reach these high levels. The comparable LIBS data was recorded using our experimental setup with an

8 mJ laser pulse and the HR2000 spectrometer. Three laser pulses were averaged per data point through $\sim 550 \mu\text{m}$ of paint and $\sim 300 \mu\text{m}$ of substrate. At a 10 Hz rate, the data collection took ~ 10 seconds. Figure 4 gives the LIBS emission data from a representative paint chip as a function of the laser penetration depth. The y-axis represents the raw emission signal above background as well as the corresponding Pb concentration. The calibration of the HR2000 was determined from a fit of emission signals obtained from the same series Pb-paint samples used to generate Figure 3.

It is readily apparent from Figure 4 that the Pb concentrations above federal abatement levels were detected. While the first few paint layers (up to $50 \mu\text{m}$) of the paint chip is free from appreciable Pb, there were intermediate layers at approximately $100 \mu\text{m}$ that had a Pb-emission signal consistent with a ~ 1 wt. % Pb concentration. Paint with this Pb concentration was commonly used between 1940 and 1970 [4]. Although the Pb emission signal decreased again, there was a dramatic increase in signal consistent with Pb concentrations above 10% at a depth of $300 \mu\text{m}$. This is not surprising, especially if the Pb was in the primer, which was common between 1900 and 1940. The signal variation at depths beyond $300 \mu\text{m}$ could be due to further paint layers with various Pb concentrations or the error introduced as the plasma interacts with the already exposed layers. Several locations on different parts of the wood trim were tested and showed a similar profile.

The lack of distinct emission lines from wood made it difficult to determine when the end of the paint was reached. Although there was still an emission signal from Pb at locations deeper than the estimated paint thickness of $500 \mu\text{m}$, it would be expected that the paint and primer

would have absorbed into the wood. This theory was supported when Pb-emission signals consistent with those given in Figure 4 were observed following the removal of paint from an area of wood much larger than the laser spot size. In other words, only paint that had soaked into the wood was sampled. The backside of the wood did not show any measurable Pb.

3. Comparison of LIBS and XRF for Pb-Paint Inspection

A. Methodology

The primary advantage of the XRF instrument is its ability to determine the Pb concentration in a single, non-destructive measurement, independent of the paint thickness. These instruments are designed to accurately determine if a property contains Pb-in-paint above or below the required action level. However, because of this integrated measurement, the substrate material affects the accuracy, particularly if it is metal. While the LIBS measurement makes it easier to isolate the sample from the substrate, it requires “drilling” through the paint and, although the majority old paint chips have a thickness of no more than 0.5 μm , the measurement accuracy and sampling time must be investigated.

A quantitative comparison between XRF and LIBS is difficult. While LIBS measures the Pb concentration per unit volume, a XRF measurement is weight per unit area (or loading). The HUD guidelines permits either type of measurement (1 mg/cm^2 or 0.5 wt. %) but the measurement of one cannot be related to the other without knowledge of the paint density and thickness. This difference can be illustrated by considering a NIST traceable sample used for calibration of portable XRF instruments. These calibration samples consist of a $\sim 40 \mu\text{m}$ layer of Pb-doped paint on a polyester sheet, covered with a laminate. While the commercial XRF

instrument is near its detection limits when measuring a sample with 0.5 mg/cm^2 Pb loading, the LIBS method produces a signal that is nearly thirty times above the background. For a $40 \text{ }\mu\text{m}$ layer of household paint, between 10% and 15% of the total dry weight must be Pb to achieve 0.5 mg/cm^2 . This makes LIBS potentially useful for post-abatement inspection, where limited quantities of material are collected. On the other hand, for samples with a thickness of 1-mm and a XRF reading of 0.5 mg/cm^2 , the average concentration of Pb will be < 0.5 dry wt. %, significantly reducing the LIBS signal per sample depth.

B. Sensitivity

Using a LIBS arrangement consistent with what can be achieved with a portable system, it is possible to determine if paint is above or below the abatement level with an accuracy better than 5%, comparable to current XRF instruments. With additional calibration effort, an integrated measurement could be made for a sample of known thickness.

C. Sampling Time

The time it takes to make a measurement is critical for the inspector who wants to perform as many measurements as possible in the shortest time possible. The average two to three bedroom home inspection requires up to 350 interior and exterior sampling locations. If the inspection method reduces the total number of inspections that the inspector can perform in one day, then the interest in the alternative method will diminish.

Most XRF measurements are performed in two to three seconds, although for more accurate readings or if the source is old, integration times of 30 seconds are not uncommon. The

speed of the LIBS method is determined by time that it takes to “drill” through the paint. Most modern paints have a thickness of 30 to 50 μm , while older paints tended to be thicker but require fewer coats. Assuming an average removal rate of 10 $\mu\text{m}/\text{pulse}$ and a laser operating at a repetition rate of 10 Hz, it would require ~ 5 s of sampling time to interrogate a paint sample with a thickness of 500 μm . For the extreme case of inspecting paint with a thickness of 1.5 mm, or if the thickness is unknown, the LIBS method would take three to four times longer than the XRF method. .

Our research indicates that there are very few instances where the paint would be prohibitively thick across an entire surface. A greater concern is the presence of a barrier such as wallpaper or a thick sealing layer, which is also used as a means of Pb-paint abatement. While the vast majority of Pb paint was used on trims and exterior coating, which would be less likely to have these barrier layers, this concern would require further consideration.

D. Cosmetic Damage

The XRF measurement is non-destructive and non-marking, making it attractive for many Pb-paint inspection needs, especially for home sale surveys. In an effort to anticipate the consumer response to the more destructive LIBS method, we evaluated the laser damage spot following sampling. For nearly all of our test cases, the damage area was no larger than 0.5 mm in diameter and typically closer to 100 μm . The visual impact of the damage site increases when the laser penetrated deep into the substrates resulting in slight darkening around the crater perimeter. Figure 5 shows a picture of a test sample following sampling with various laser intensities used to penetrate a layer of paint. It is apparent that the LIBS method may be

controlled to prevent damage beyond the many common surface imperfections also seen in the image. In addition, it is much less destructive than sampling for laboratory analysis. Finally, because paints have a high degree of homogeneity, a LIBS-based instrument is not expected to require a greater number of sample locations than XRF despite its small sampling volume.

E. Portability

From a marketing point-of-view, the portability of a LIBS inspection tool is a critical factor if it is to compete against the existing XRF instruments. As a reference, the entire RMD's LPA-1 consists of a single hand-held unit with dimensions of 13 x 28 x 23 cm and weight of 1.4 kg [19]. Although less inviting than a complete hand-held unit, until technology evolves, a LIBS Pb-paint inspection unit would likely be too bulky to fit into a single assembly. Therefore, the majority of the weight, including batteries, can be placed on a belt or shoulder mounted pack. Fiber optic coupling also makes it possible to separate a hand-held probe from the bulk of the electronics, which can be advantageous for difficult to access locations.

Along with our current research, previous work has demonstrated that the Ocean Optics spectrometer is sufficient for use in a portable system [15]. The HR2000 measures ~ 15 x 10 x 5 cm and weighs 0.54 kg [20]. However, while still available, the manufacturer has discontinued the currently employed detector array [21]. Although further investigation is required, it is hoped that similar instrumentation performance at comparable price and size can be realized.

Available compact lasers for portable LIBS system include those from Kigre, Inc. Table 1 lists some of the attributes of the Kigre lasers [22]. While some models have repetition rates

that would be too low for lead-paint inspection, models with 10 to 20 Hz rates are in development. Commercially available lasers with energies from 10 to 100 mJ and repetition-rates around 100 kHz are have also been used for LIBS but would require further investigation for use in Pb-paint inspection.

For a LIBS system, the laser is the primary drain on the battery life. As a reference, RMDs LPA-1 uses a battery with 3300 mAh at 7.2 V and will operate for 8 hours. Based on specifications for the Kigre MK-88 laser [22], we estimated that a hand-held camcorder battery would allow operation for > 15,000 laser shots. This is a sufficient number of laser pulses for inspection of one complete household. Battery costs of < \$50/unit makes it reasonable for inspectors to keep several on hand for multiple inspections throughout the day. In addition, consumer battery technology is rapidly advancing further suggesting that this factor would not be a barrier to the market. Because the lifetime of the MK-88 has been reported to be > 40,000,000 shots depending on the operating current and environment, assuming an upper average of 15,000 shots/inspection and 1000 inspections/year (5 per day for 200 days) the laser would last over 2.5 years.

F. Cost

The biggest barrier for a LIBS inspection tool for Pb-paint that can compete with existing XRF instruments is the availability and initial cost of the appropriate components and the compact laser in particular. To be competitive, we estimate that the total bill of materials must be less than ~ \$5000. Assuming a discount for large volume purchases, the spectrometer and the optics alone might be several thousand dollars. Beyond that, existing laser sources that can meet the

necessary performance specifications range in cost from \$5,000 to \$10,000. Until these cost reduce, it will be extremely challenging to manufacture a competitive instrument that would be an attractive replacement the existing lead inspection units.

Even if it is difficult to promote LIBS as a direct replacement for in-home Pb-in-paint inspection methods, some of its advantages could be exploited in complementary applications. For example, alternative methods for Pb-paint inspection are needed for post-abatement screening where the sample size is too small for XRF and laboratory analysis is too slow. The unique aspect of depth profiling also offers a useful alternative inspection tool. While it may not be critical in the majority of inspections, the location of the Pb paint layer can offer a homeowner additional information regarding abatement decisions. Other advantages of the LIBS system include the ability to reach difficult to access locations using fiber coupling and substrate-independent measurements, especially on metal structures such as boats and housing exteriors.

G. Regulatory Concerns

Presently, inspectors that use XRF instruments must be trained to work with the radioactive sources. In addition, the units must be returned to the manufacturer every year or two for source replacement. The manufacturer must then store and dispose of these sources according to government regulations.

The use of a laser is also a safety concern since eye- and skin-protection must be addressed. However, most US states would relieve the inspector from undergoing special licensing as long as appropriate manufacturer safety precautions are incorporated to prevent

unintentional access to the full laser energy. Such precautions as an optical sensor that would only allow laser emission when the unit is against a flat, opaque, surface can be readily implemented. If an eye-safe Class I laser (e.g. 1.54 μm , < 7mJ) can be utilized, it would all licensing requirements for both user and manufacturer [23].

4. Conclusions

It is apparent that a LIBS-based unit offers several advantages over handheld XRF instruments for Pb-paint inspection. In particular, the ability to detect the Pb concentration as a function of depth adds a capability not found in other inspection methods. In addition, a portable unit can have sufficient sensitivity to readily determine the federal abatement levels. By promoting these advantages the technology will be more readily accepted by both the user and federal agencies. However, until federal regulations change or component cost are reduced, LIBS instrument manufacturers will likely be compelled to seek niche markets offering non-competitive solutions to Pb-paint inspection challenges.

Acknowledgements

The authors wish to thank from Michael J. Myers from Kigre, Inc. for helpful discussions. This research work reported in this paper was supported by the US Department of Homeland Security (contract #HBCHC060150).

5. References

1. “CPSC Announces Final Ban On Lead-Containing Paint” Office of Information and Public Affairs, Washington, DC September 2, 1977.

2. "Residential Lead-Based Paint Hazard Reduction Act of 1992," EPA Public Law 102-550, 102nd Congress -- 2nd Session, enacted OCT. 28, 1992.
3. G Markowitz and D Rosner, "Cater to the children: the role of the lead industry in a public health tragedy, 1900-1955," *Am J Public Health*, **90**, 36–46, 2000.
4. "The History of the Use of Lead Pigments in House Paint"
<http://www.leadlawsuits.com/index.php?s=community>, retrieved on March 24, 2008.
5. This information can be found at the National Safety Council web site,
<http://www.nsc.org/issues/lead/>, retrieved on 3/24/08.
6. D. E. Jacobs, "Lead-based paint inspection," in *Guidelines for the Evaluation & Control of Lead-Based Paint Hazards in Housing, Chapter 7*, (Daine Publishing 1995).
7. A. Mathee, H. Rollin, J. Levin and I. Naik, "Lead in Paint: Three Decades Later and Still a Hazard for African Children?" *Environ Health Perspect.*, **115**, 321–322, 2007.
8. R. Jenkins, *X-Ray Fluorescence Spectrometry (Chemical Analysis: A Series of Monographs on Analytical Chemistry and Its Applications)*, 2nd ed., (John Wiley & Sons Inc., 1999).
9. *Laser-Induced Plasmas and Applications*, L. J. Radziemski and D. A. Cremers, eds., (Marcel Dekker 1989).
10. *Handbook of Laser-Induced Breakdown Spectroscopy*, D. A. Cremers and L. J. Radziemski eds., (John Wiley & Sons, 2006).
11. *Laser Induced Breakdown Spectroscopy*, A. W. Miziolek, V. Palleschi and I. Schechter eds., (Cambridge University Press, 2006).
12. Lee W. B., Wu J. Y., Lee Y. I., Sneddon J. (2004). "Recent applications of laser-induced breakdown spectrometry: A review of material approaches". *Appl. Spectrosc. Rev.*, **39**, 27-97.

13. D. W. Hahn, W. L. Flower and K. R. Hencken, "Discrete Particle Detection and Metal Emissions Monitoring Using Laser-Induced Breakdown Spectroscopy," *Appl. Spectrosc.*, **51**, 1836-1844 (1997).
14. B. J. Marquardt, S. R. Goode and S. M. Angel, "In situ determination of lead in paint by laser-induced breakdown spectroscopy using a fiber-optic probe," *Anal. Chem.*, **68**, 997-981, 1996.
15. B. C. Castle, A. K. Knight, K. Visser, B. W. Smith, and J. D. Winefordner, "Battery powered laser-induced plasma spectrometer for elemental determination," *J. Anal. At. Spectrom.*, **13**, 589-595, 1998.
16. *CRC Handbook of Chemistry and Physics*, 67th ed., R. C. Weast, M J. Astle and W. H. Beyer, eds., (CRC Press, 1986).
17. M Corsi, G. Cristoforetti, M. Hidalgo, D. Iriarte, S. Legnaioli, V. Palleschi, A. Salvetti and E. Tognoni, "Effect of laser-induced crater depth in laser-induced breakdown spectroscopy emission features," *Appl. Spectrosc.*, **59**, 853-860, 2005.
18. J. M. Vadillo, J. M. Fernandez Romero, C. Rodriguez and J. J. Laserna, "Effect of plasma shielding on laser ablation rate of pure metals at reduced pressure," *Surf. Interface Anal.*, **27**, 1009-1015, 1999.
19. This information can be found at: <http://www.rmd-lpa1.com/>, retrieved on March 24, 2008.
20. This information can be found at: <http://www.oceanoptics.com/products/hr2000.asp>.
21. "Sony ILX511 to Toshiba TCD1304AP Detector FAQ,"
<http://www.oceanoptics.com/products/detectorfaq.asp>, retrieved on 3/24/08.
22. This information can be found at: <http://www.kigre.com/>, retrieved on March 24, 2008.

23. *American National Standard on the Safe use of Lasers, ANSI Z136.1-2000*, (American National Standards Institute, 2000).

Published by

OSA

Tables

Table 1. Specifications of compact lasers available from Kigre, Inc.

Specification	MK-367	MK-88	MK-81
Wavelength	1064 nm	1540 nm	1540 nm
Laser Energy	25 mJ	3 to 4 mJ	3 mJ
Laser Head (cm)	1.5 x 2 x 10	2 x 5 x 7.6	1.6 x 3 x 1
Power supply (cm)	15 x 10 x 3.8	3 x 5 x 10	3 x 5 x 10
Repetition Rate	1 Hz	10 Hz	1 Hz

Published by

OSA

Figure Captions

Figure 1. Diagram showing the LIBS experimental setup used during our studies. The He:Ne laser was used for alignment. Typical laser energies ranged from 5 to 7 mJ and both a bench top and compact spectrometer were used during our studies. The inset shows the spectrum from latex paint with and without Pb. The Pb-emission at 405.8 nm is noted with an arrow.

Figure 2. The Pb emission signal to background ratio of paint increases as a function of laser energy, but the penetration depth per laser pulse decreases with increasing energy. This decrease is likely due to plasma screening. Data was collected using the cooled CCD and ¼-m spectrometer.

Figure 3. Signal to noise ratio as a function of the dry wt. % of PbCO_3 added to a commercial latex paint. The measurements were performed at 7 mJ with a cooled CCD detector. Data was recorded following averaging of six laser shots. The federal guideline of 0.05 dry wt. % of Pb (5000 ppm) is noted with a dashed line. Concentration errors result from sample preparation and achieving homogeneous blending. Data was collected using the cooled CCD and ¼-m spectrometer.

Figure 4. Pb signal with background subtracted as a function of depth for a sample that came from a house built in ~ 1880 and contained several layers of paint. The dashed line indicates the approximate boundary between the paint and the wood substrate. The Pb emission signal beyond the boundary layer is likely due to absorption of the primer into the

wood substrate as well as the continued sampling of the Pb-paint. Data was recorded with the HR2000 spectrometer from Ocean Optics.

Figure 5. Picture of the paint crater created by the LIBS process. Each was formed with four laser shots. The laser energies range from 28.4 mJ (indicated with an arrow on the left) to 2.2 mJ (indicated with an arrow on the right). The smallest crater has a diameter of $\sim 75 \mu\text{m}$. The paint was applied to an Al substrate and typical paint imperfections can be seen. The region above the arrow on the left was formed with over 100 laser pulses and has a dark ring from ablation of the Al.

Published by
OSSA

Figure 1

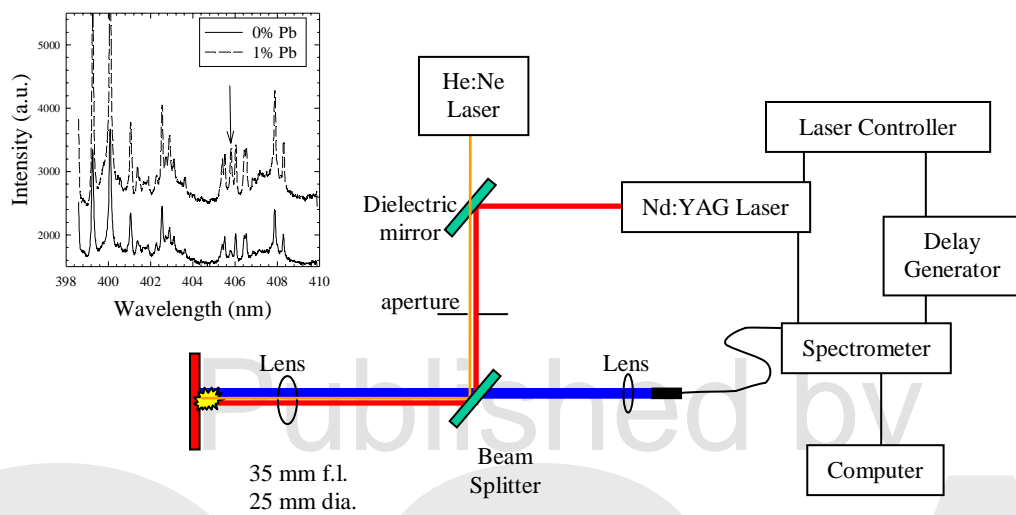


Figure 2

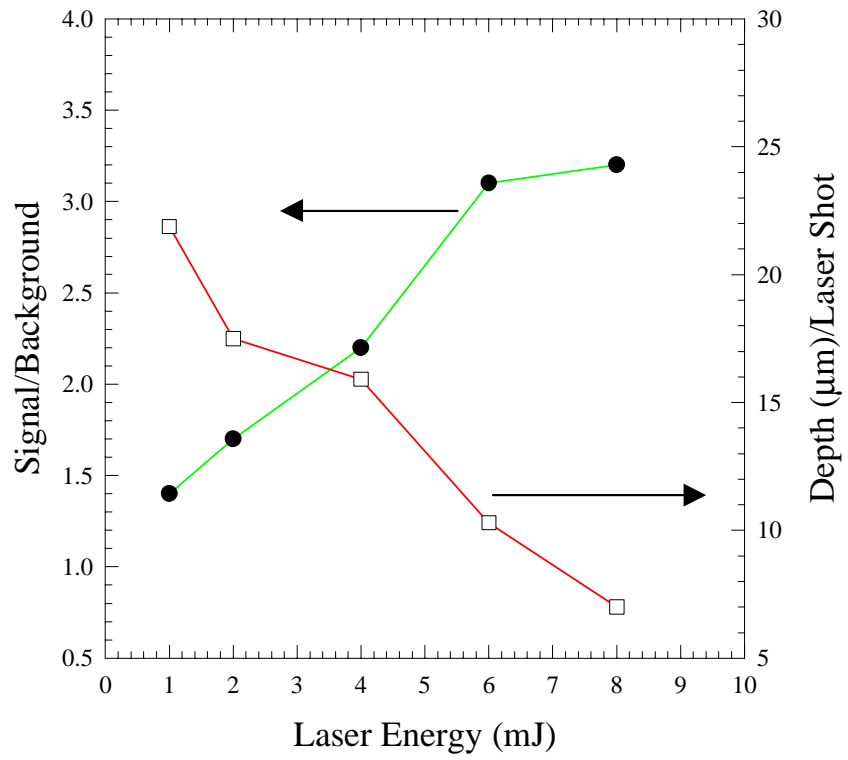


Figure 3

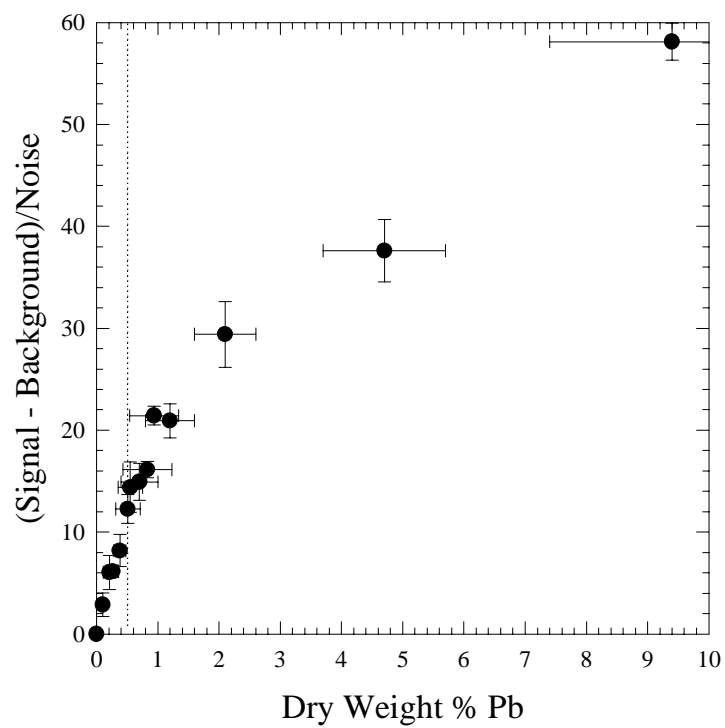


Figure 4

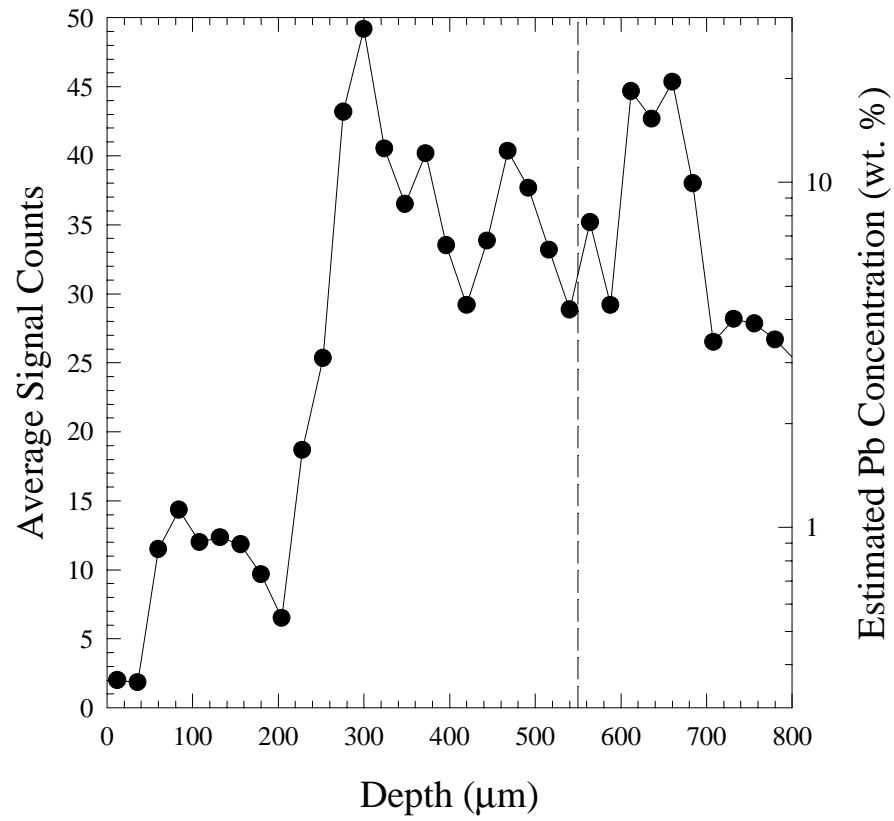


Figure 5

