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In Situ Determination of Lead in Paint by Laser-Induced Breakdown Spectroscopy Using a Fiber-Optic Probe

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On-site determination of leaded paint in houses is important for minimizing the costs of renovations. A simple fiber-optic probe suitable for remote elemental analysis using laser-induced breakdown spectroscopy has been developed for this purpose and is used to determine the lead concentration in samples of dry paint. Optical fibers transport the laser pulse to the sample and transfer the emission signal to the spectrometer. The use of separate excitation and collection fibers allows coupling of the probe to a conventional spectrometer using simple optics. The measurement takes less than 1 min to perform, requires no sample preparation, and can be made through overlayers of non-lead-containing paint. The limit of detection is 0.014% Pb in latex paint, on a dry weight basis, with relative sample standard deviations of 5—10%.

Prior to the 1940s, lead compounds were commonly used as blocking and coloring agents in interior and exterior house paints. However, in more recent years, it was established that exposure to lead in house paint can produce lead poisoning in young children. Subsequently, federal guidelines were established to set abatement limits for lead in paint on existing housing at 0.5% (w/w, dry weight basis).[1] Although the Consumer Products Safety Commission currently regulates lead in paint, with 0.06% (w/w, dry weight basis) Pb being defined as lead-containing paint,[2] leaded paint can still be found in older structures. These old lead-based paints mobilize as dust during renovations, leading to a potential for high exposures. Since abatement of lead-based paint is very expensive, it is desirable to develop techniques that can be used on-site to rapidly identify lead-containing paint on walls and trim.

The instruments most widely used for the analysis of paint in the field are portable X-ray fluorescence (XRF) spectrometers. These instruments use the radiation that accompanies a radioactive decay as an X-ray source. K-shell radiation from lead is excited by instruments with Cobalt-57 sources, and L-shell measurements can be performed using Cadmium-109 or Curium-244 sources. At least one commercial instrument is available that can be used to perform both measurements. Since the penetration depth of portable XRF instruments is usually not known (varying from several centimeters for those that use K-shell X-rays to <0.1

mm for those that use L-shell X-rays),[3] they are typically used for screening and are calibrated to provide a positive indication if lead exceeds 1 mg/cm². XRF analysis is rapid, a typical exposure time being 5 s. However, it does suffer from substrate effects and attenuation of signals from overlayers of non-lead-containing paint. Also, the measurement volume is typically not known. XRF screening is confirmed by independent analysis, typically dissolution followed by ICP emission.[4]

Laser-induced breakdown spectroscopy (LIBS) is a useful method for determining the elemental composition of solids. This method has been recently reviewed, and a number of different applications have been described.[5] In the LIBS technique, a high-power pulsed laser is used to generate a plasma from the sample of interest. For example, a 10-ns pulse from a 100-mJ laser delivers a peak power of 10 MW. Furthermore, when focused to a 100-μm-diameter spot, this pulse produces a peak power density of about 130 GW/cm². At such high power densities, the electric field is strong enough (>10^5 V/cm) to produce dielectric breakdown of any medium. Plasmas consisting of atomic and ionized species can thus be produced from most matrices. This phenomenon was first demonstrated in 1963 using a pulsed ruby laser.[6] The elemental composition of the sample is accomplished by measuring the atomic emission from the atoms and ions in the plasma.

There are many reports of the use of LIBS for measuring metals in solid substrates.[7-11] There have also been LIBS investigations of aerosols,[12] single particles,[13-15] metals in solution,

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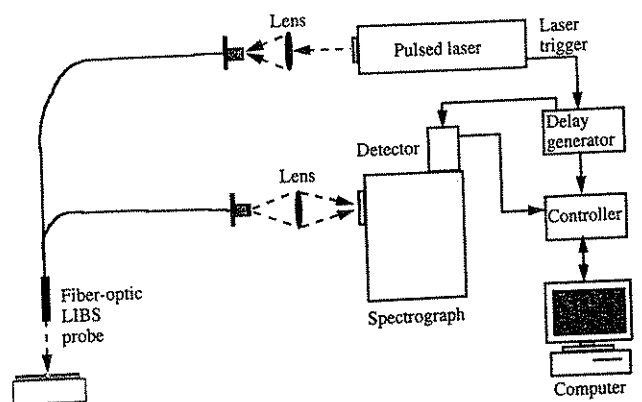
* Author to whom correspondence should be sent. Phone: 803-777-2779. Fax: 803-777-9521. E-mail: ANGEL@PSC.PSC.SC.EDU.
(1) Section 302 of Lead Based Paint Poison Prevention Act (LBPPPA), Federal Housing Act, 1987.
(2) Consumer Product Safety Commission. Lead-containing paint and certain consumer products. *Code of Federal Regulations;* 16CFR Part 1303; U.S. Government Printing Office: Washington, DC, 1995; pp 345—349.

Figure 1. Schematic diagram of LIBS apparatus showing launch and collection optical fibers.

Figure 2. Detail of the fiber-optic LIBS probe. The lens nearest the fibers is a 1-in. diameter $f/2$ plano convex, and the lens nearest the sample is a 1-in. $f/0.56$ aspheric.

including uranium,[16] and even chlorinated species in solution.[17] More recently, LIBS has been used for measuring Ba and Cr in soil using a fiber-optic cable.[18] LIBS is ideally suited for the determination of lead in paint using optical fibers because of the intense visible lead emission and because of the relative ease of forming a plasma on dry paint (as little as 1 mJ of laser energy per pulse). In this paper, we describe a fiber-optic-based LIBS probe that is suitable for determining lead in dry paint at levels well below the currently regulated values.

EXPERIMENTAL SECTION

LIBS System. The LIBS system (see Figure 1) consists of a frequency-doubled Q-switched Nd–YAG laser (Quantel Model YG-580-20 operating at 532 nm, or New Wave Research Model Mini/Lase-20 operating at 1064 nm), a 0.5-m $f/7$ spectrograph (SPEX Model 1870), and a gated, intensified diode array detector (EG&G OMA III). The data shown here were acquired using 50-, or 150-μm slits (0.04- or 0.11-nm spectral bandwidth). A pulse amplifier (EG&G Model 1304) was used to gate the detector, and a digital delay generator (Stanford Research Systems Model DG535) provided timing delays and synchronized gating for the LIBS system. The delay generator was set to allow the background emission to decay (3.0 μs) then to turn on the detector ("gating") for a 12.6-μs exposure for each laser pulse. Data were collected using the OMA2000 software package from EG&G. Most spectra were acquired by averaging 20–100 laser pulses at 2 Hz for a 10–50 s total acquisition time. Laser power at the probe tip was typically 4.2 or 19.0 mJ/pulse, depending on the particular fiber-optic probe used.

Fiber-Optic Probe. All measurements were made using dual-fiber fiber-optic probes. The probes used were simple modifications of existing designs that have been used in our group for Raman spectroscopy.[19] The use of one optical fiber for laser excitation and a separate fiber for light collection greatly simplifies the optical setup. In this work, three different probes were used with excitation and collection fiber diameters of 600 μm/600 μm, 600 μm/1000 μm, and 1000 μm/1000 μm, respectively. Both fibers were about 4 m in length, and all fibers were 0.48 NA (3M Model FT-600, or FT-1.0-URT). The laser light was focused into the
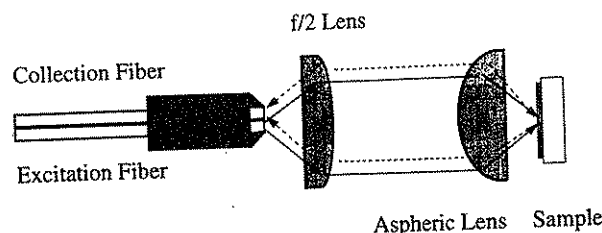
excitation fiber using an 8-in. focal length lens. Care was taken to eliminate damage to the input face of the fiber by placing a pinhole at the fiber tip that was just slightly smaller than the fiber core diameter (560-μm diameter in the case of a 600-μm fiber).

The dual-fiber probes were modified by the addition of two lenses at the probe tip (see Figure 2). This was done by cementing the distal ends of the two optical fibers in a stainless steel barrel and then polishing the end of the barrel flat. Two lenses, $f/2$ (0.25 NA) plano convex and $f/0.56$ (0.9 NA) aspheric, were used to focus light from the excitation fiber onto the sample and also to collect the LIBS signal and transfer it into the collection fiber. The 0.9 NA aspheric lens was used to achieve the smallest possible laser spot on the sample while maintaining a reasonable working distance. The $f/2$ plano convex lens at the fiber tip was not optimal and resulted in some light losses as well as a larger laser spot on the sample. An $f/1.5$ lens was used to image the light from the collection fiber onto the spectrograph slit.

Preparation of Samples. Standard paint samples were prepared by adding $Pb(NO_3)_2$ or PbO (Aldrich Chemical Co.) to latex or oil-based paint (Home Depot "Americas Finest" flat white latex and oil-based wall paint) and mixing thoroughly while wet. $Pb(NO_3)_2$ was used for calibration samples, because it was easier to make homogeneous samples with $Pb(NO_3)_2$. The wet Pb-doped paint was then painted onto smooth copper blocks and allowed to dry. Different thicknesses, ranging from three to 18 layers of paint (about 0.4–2.34-mm thickness), were used. Each layer was allowed to dry thoroughly before subsequent layers were added. All concentrations are percent by weight and refer to the percent of Pb in the dry paint. The thicknesses of the paint layer were estimated by peeling the layers from the sample surfaces and measuring the thickness with a micrometer. The average thickness determined in this way was about 130 μm/layer.

Analysis of Data. Most data is shown without averaging or smoothing other than that obtained as a result of accumulated laser shots. Calculations were performed and all data plotted using Igor version 1.27 data analysis software from Wavemetrics Inc. For all calculations, emission intensity was based on peak height. A best line fit was made of the five replicate spectra, and the detection limit was taken as 3 times the standard deviation of the intercept divided by the slope (e.g., a "3σ" detection limit). The least-squares fit and limit of detection were calculated using Excel 4.0.

RESULTS AND DISCUSSION

One difficulty in using fiber optics to measure LIBS spectra is avoiding damage to the excitation fiber. Focusing the laser to a tight spot on the fiber tip can chip the surface or, in some cases, completely destroy the fiber. Catastrophic damage at the core cladding interface was observed if the power was too high, if the

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fiber was misaligned, or if laser spots were too small. For the paint sample measurements, power levels of 4.2 and 19.0 mJ were typically measured at the probe tip, the end nearest the sample, for the 600- and 1000-μm excitation fibers, respectively. In the case of a 600-μm excitation fiber, power levels as low as 1 mJ were observed to produce a plasma at the sample. To minimize fiber damage, the laser was used at the lowest power possible and was loosely focused using an $f/8$ lens so that the spot was relatively large compared to the fiber tip. The decreased power density, together with the use of a small pinhole in front of the fiber tip, eliminated fiber damage for input powers as high as 200 mJ. This arrangement resulted in 25–50% throughput to the fiber-optic probe tip, depending on the size of the excitation fiber.

The intensity of the LIBS signal for a particular sample depends on measurement parameters such as laser pulse rate, excitation wavelength, laser power, fiber-optic geometry, and detector gate timing. We have not yet investigated all these parameters, but we have determined that a 2-Hz laser pulse rate produced higher LIBS signals than 5- or 10-Hz rates. This phenomenon has been previously reported and shown to result from a persistent amount of aerosol produced above the sample.[20] Lower pulse rates allow time for the plasma to dissipate before arrival of the next pulse. For the paint measurements, we also observed larger LIBS signals using 1064-nm excitation than using 532-nm excitation at the same laser power. Excitation at 1064 nm produced plasmas on the sample that were visually much larger than those produced using 532-nm excitation. However, better reproducibility was usually obtained using lower laser powers and 532-nm excitation. This is not an effect of pulse-to-pulse variations in the laser at the different laser powers. The reason for this power dependence is still being investigated.

Detector gating is critical to obtaining good quality atomic line spectra and thus high sensitivity. The laser pulse width was about 10 ns. The laser first vaporizes the sample and then forms the hot plasma. Immediately following the laser pulse, typically within a few microseconds, the signal is dominated by thermal emission of the hot plasma. This continuum signal quickly decreases as atomic and ionic emissions begin to increase. The optimal time for measuring atomic lines depends on the sample matrix and elements of interest, but it usually starts 5–10 μs after the laser pulse and may last for many tens of microseconds. All of the data presented here were obtained with a 12.6-μs exposure time after waiting 3.0-μs for the background emission to decrease. However, there was always significant background emission during the exposure times, and noise in the background is a major noise source when the lead concentration approaches the detection limit.

The fiber-optic probe used for this work was not optimized for LIBS measurements. However, the design is very easy to make in the laboratory, and because it uses separate excitation and collection fibers, it is easy to interface to any laser spectrometer system using simple lenses. The probe was designed for Raman measurements, where the efficiency is determined by the overlap of the fields of view of the two optical fibers. This geometry may not be optimal for the LIBS measurement because the sample is ejected and vaporized during the process—the best signal region might not correspond exactly to the excitation region. The plasma is not confined to the surface but extends
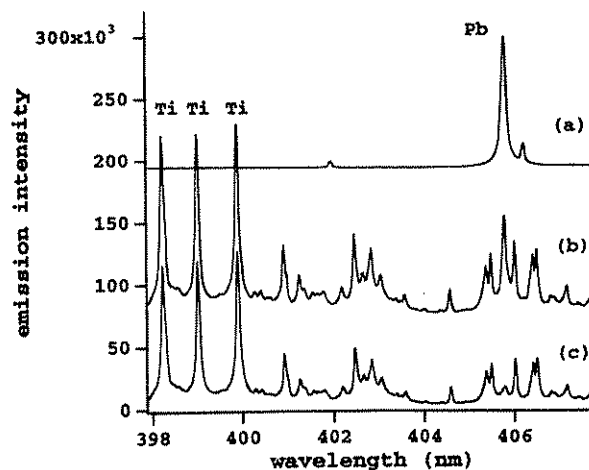
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Figure 3. (a) Pb in solder; (b) 1.10% Pb, added as Pb(NO₃)₂, in latex paint; (c) latex paint with no added lead. Note the three strong Ti lines in both paint samples. Spectrum a was measured using the 600 μm/600 μm probe with 4.2 mJ of 532-nm excitation, 20 laser pulses (10-s acquisition). Spectra b and c were measured with the 1000 μm/1000 μm fiber-optic probe using 19.0 mJ of 1064-nm excitation at the fiber tip, and 20 laser pulses (10-s acquisition). Spectra are offset vertically for clarity.

some distance above it. As indicated above, the reproducibility of a LIBS measurement does not necessarily improve for higher signal levels. It is not known if the fields of view of the two fibers should overlap for best reproducibility in a LIBS measurement. Preliminary observations using a 600-μm excitation fiber show that signal acquired with a 1000-μm collection fiber is more than double that observed with a 600-μm fiber. The use of a larger diameter excitation fiber also increases the LIBS signal. However, in this study, the reproducibility of the measurements did not improve with increased laser power or signal level.

Figure 3a shows the LIBS spectrum of lead from a solder sample containing ~60% lead. The spectrum shown in Figure 3a was measured using the 600 μm/600 μm probe with 4.2 mJ of 532-nm excitation at the probe tip, 100 laser shots, and 150-μm slits. The intense Pb line at 405.78 nm was used for calibration purposes. Figure 3b shows the Pb line for a latex paint sample containing 1.10% lead, added as Pb(NO₃)₂, measured using the 1000 μm/1000 μm probe with 19.0 mJ of 1064-nm excitation at the probe tip, 20 laser shots, and 50-μm slits. The three intense lines below 400 nm are due to Ti in the paint. Figure 3c shows a latex paint base sample (no added lead) for comparison measured in the same way. The small peak at ~405.7 nm is due to a Ti peak at 405.6 nm and a small amount of residual lead that is found in most commercial paint.

The intensity of the accumulated LIBS signal does not change in direct proportion to the number of laser shots, as shown in Figure 4a, possibly as a result of sample ablation. For this reason, better reproducibility results from moving the sample between laser shots. During the measurement process, the laser vaporizes the sample, with each pulse forming a small "crater" approximately 50 μm in diameter in the case of a 600-μm excitation fiber. There are several possible reasons that each pulse shows a decreased LIBS signal. First, the aspheric lens in the probe has a very high NA and a tight focal point. As a result of sample ablation, the surface "moves" and is no longer at the optimal focus. This effect results in a decrease in signal with each laser pulse, as is shown quantitatively in Figure 4, traces a and b. In this experiment,
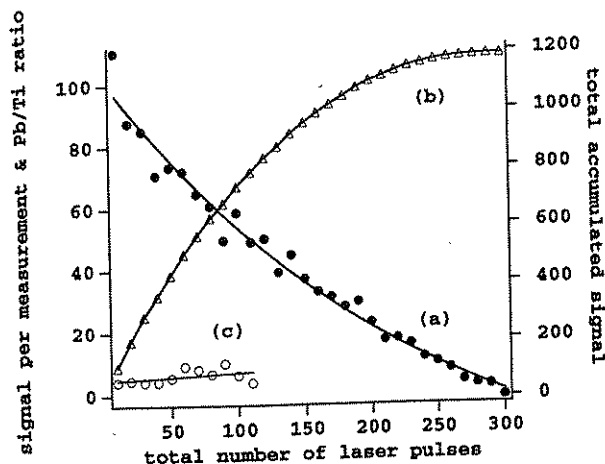
Figure 4. LIBS signal versus number of laser pulses for a latex paint sample using the 600 μm/600 μm fiber-optic probe and 4.2 mJ of 532-nm excitation. (a, left axis, ●) Change in the intensity of the 405.78-nm Pb line for 30 consecutive spectra, each the sum of 10 laser pulses. (b, right axis, △) Integrated Pb signal. (c, left axis, ○) Ratio of the Pb line at 405.78 nm and the Ti line at 399.91 nm. The sample was not moved during the measurement.

30 consecutive spectra were acquired without moving the sample, each an average of 10 laser shots. Interestingly, the decrease is exponential except for the first point.

We believe that this decrease in LIBS signal is due to a decrease in the mass ablated by each laser pulse because the ratios of intensities of the Pb and Ti signals are constant, as shown in Figure 4c. Only the first 110 pulses are shown because the Ti signal is too weak for later measurements. Titanium is present as TiO_2, with a boiling point in excess of 2500 °C. Lead is present as lead nitrate, which decomposes at 470 °C. The fact that the ratio of the volatile and nonvolatile substances is constant indicates a lack of matrix effects in the excitation process. This experiment also indicates that the sample is homogeneous and that the particulate nature of the TiO_2 in the paint does not cause analytical errors.

The intensity of the 405.78-nm Pb line is directly proportional to concentration in the 0–0.1% region. Above about 1% Pb, the slope of the response curve decreases rapidly with increasing Pb concentration. Figure 5 shows the Pb response, added as Pb-$(NO_3)_2$, in latex paint samples versus concentration below about 0.11% measured with the 600 μm/600 μm probe and using 4.2 mJ of 532 nm excitation. In this figure, the intensity value for each concentration is taken as the average intensity for five separate measurements after subtracting the intensity of the baseline. Each measurement was made using 100 laser shots with 150-μm slits. The laser pulse rate was 2 Hz, for a 50-s total measurement time, and the sample was moved so that a different spot on the sample was measured after every fourth pulse. Moving the sample improved the reproducibility significantly. The error bars show ±1 sample standard deviation for the five replicate spectra. The fitted line shown in Figure 5 was determined by linear least squares. As shown in Figure 5, the precision of these measurements, as measured by ±1 sample standard deviation, was 5–10%.

The limit of detection, 0.014% Pb (w/w dry weight) is calculated from the calibration plot. This is the concentration that produces a signal equal to three times the standard deviation of the blank. Since lead-containing paint is defined as paint that contains Pb at a concentration of 0.06% or higher,[2] this method is sufficient to quantitate lead at regulated levels.
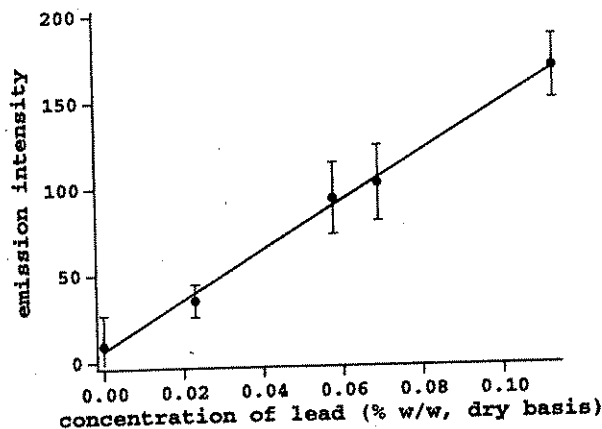
Figure 5. LIBS calibration curve showing the intensity of the 405.78-nm Pb line versus dry weight concentration (w/w %) of Pb, added as Pb$(NO_3)_2$, in latex paint. A 600 μm/600 μm probe was used with 4.2 mJ of 532-nm excitation and 150 μm slits. Each point is the average of five separate measurements, each taken with 100 laser pulses (e.g., 50 s acquisition). The error bars show ±1 sample standard deviation.
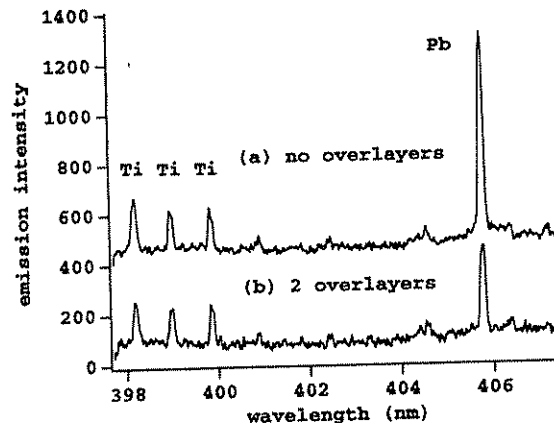

Figure 6. LIBS spectra of 3.05% Pb, added as Pb$(NO_3)_2$, in latex paint with the 600 μm/600 μm fiber-optic probe using 4.2 mJ of 532-nm excitation at the sample. Both spectra were measured with 100 laser pulses (e.g., 50 s acquisition). (a) Leaded paint. (b) Leaded paint with two overlayers of non-lead-containing paint approximately 0.26 mm thick.

An important consideration in implementing an analytical method for lead in paint is the effect of overlayers of non-lead-containing paint. This need arises because older building walls may have layers of lead-containing paint covered by newer paint. XRF cannot detect the presence of overlayers of non-lead-containing paint. In the case of LIBS, the laser pulse ablates material during the measurement, and the fiber-optic probe can be used to measure lead in paint that is covered by layers of newer paint. It can also be used to easily differentiate overlayers from underlying layers of lead-containing paint. Figure 6a was obtained from a latex paint sample containing 3.05% Pb, added as Pb$(NO_3)_2$, with a 600 μm/600 μm probe using 532-nm excitation, 100 laser pulses, with 4.2 mJ at the probe tip. Figure 6b was measured under the same experimental conditions for an identical sample covered with two layers (~0.26 mm) of latex paint with no added lead. The Pb line is clearly visible through the overlayers. There is about 60% attenuation of the Pb signal because the signal was integrated during the entire experiment.

Figure 7a shows a LIBS spectrum of ~3.3% Pb, added as Pb-$(NO_3)_2$, in an oil-based paint. The intensity of the 405.7-nm lead

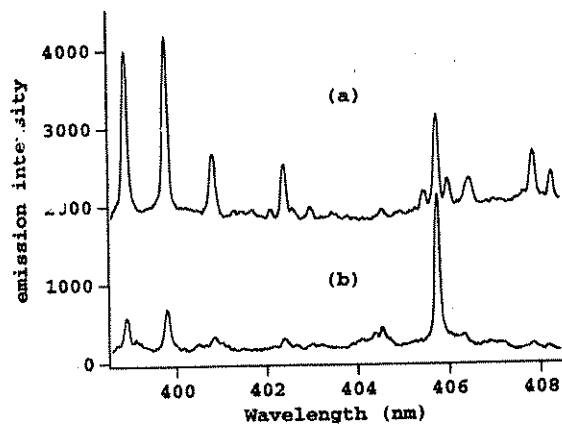**Figure 7.** LIBS spectra of 3.3% Pb, added as $Pb(NO_3)_2$, in oil-based enamel (a) and 3.0% Pb, added as $Pb(NO_3)_2$, in latex paint (b). Both spectra were taken under identical conditions: 100 laser pulses at 2 pulses/s, 4.2 mJ/pulse at the probe tip, 532-nm excitation, and 150-μm slits.

line is 65% as intense in the oil-based paint as in the latex paint sample spectrum shown in Figure 7b. However, there is considerable error in this value because of the different paint thicknesses and colors as well as the difficulty of making a homogeneous sample using oil-based paint. The TiO_2 intensities in spectrum a are much higher than in spectrum b; however, the TiO_2 concentrations are not known in these paints. Although the intensity of the 405.7 nm lead emission line is slightly lower ($\sim$35%) in the oil-based paint, the sensitivity is still sufficient to measure lead in dry paint at levels well below the currently regulated values. We have also measured lead in latex paint, added as PbO, and see results very similar to those observed for lead added as $Pb(NO_3)_2$ to latex paint.

POTENTIAL APPLICATIONS

An advantage of the XRF technique is the speed of the analysis. In one recent study, the Texas State Capitol building was surveyed by performing 2000 XRF measurements in a single week.[21] Exposure times of 5 s were used, and lead levels of 0–8.0 mg/cm^2 were reported with a precision of ± 0.06 mg/cm^2. A disadvantage of XRF analysis is that it is somewhat matrix dependent, with highly penetrating K-shell X-rays requiring substrate correction. In the study mentioned above, the magnitude of the correction varied from -0.7 mg/cm^2 for 4-in. concrete to $+4.4$ mg/cm^2 for 4-in. cinderblock,[21] independent of lead concentration.

In another recent study, corrections varied from -0.03 mg/cm^2 on plasterboard to $+1.1$ mg/cm^2 on concrete, the exact bias

(21) Piorek, S.; Pasmore, J. R.; Lass, B. D.; Koskinen, J.; Sipila, H. In *Lead Poisoning*; Breen, J., Stroup, C., Eds.; Lewis Publishers, CRC Press, Inc.: Boca Raton, FL, 1995; pp 127–134.
(22) Harper, S.; Gutknecht, W.; Beard, M. In *Lead in Paint, Soil, and Dust*; Beard, E., Iske, S., Eds.; ASTM: Ann Arbor, MI, 1995; pp 191–206.

depending on the lead concentration.[22] These corrections are on the same order of magnitude as the lead concentrations measured. While L-shell X-rays do not require substrate correction, they also do not detect lead-containing paint that has been covered by an overcoat. The lead signal decreased by 100% for L-shell and by 50% for K-shell instruments when a lead-paint film was covered by three thick coats of a modern paint formulated without lead. This thickness corresponds to 5–9 coats of old paint.

With appropriate probe modifications and using a fieldable pulsed laser system, the technique described here is suitable for measuring lead in paint directly on a variety of structures, including walls, bridges, and ship hulls, as well as for determining lead in soils. The 1064-nm laser used in this work is made for field use and has a footprint of only 2.0 in. × 3.0 in. × 8.5 in. for the laser head and 7.8 in. × 16 in. × 14 in. for the power supply/chiller. The total weight of the completely self-contained system is $\sim$35 pounds, and it uses 115VAC. Small footprint fieldable spectrographs are also available with resolution equal to or better than that used for this work. The LIBS technique offers another advantage over XRF screening of lead in painted surfaces, since it can distinguish between lead at a surface and lead that has been overcoated or encapsulated. Surface lead is a much greater health hazard and would rate a higher priority in an abatement program than would lead paint that has been overcoated. The ruggedized probe could also be used to measure lead and other heavy metal environmental contaminants such as Cr, U, Hg, and others that pose potential health risks. There also might be industrial applications for monitoring the levels of specific elements such as carbon in steel to differentiate high-carbon and low-carbon steel.

CONCLUSIONS

In-situ LIBS using a fiber-optic probe is a feasible technique for quickly determining the lead content of dry paint. This technique has some potential advantages over XRF including improved sensitivity and the ability to identify overlayers of non-lead-containing paint. The use of a PMT detector, a compact spectrograph, and a small low-power flash lamp-pumped Nd–YAG laser could make this system cost-competitive with high-end fieldable XRF systems. The detection limit in these applications is limited by poor reproducibility. To further improve the sensitivity of the technique, factors that affect the reproducibility need to be better understood.