

Detection of Lead in Soil with Excimer Laser Fragmentation Fluorescence Spectroscopy (ELFFS)

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ABSTRACT

Excimer laser fragmentation fluorescence spectroscopy (ELFFS) is used to monitor lead in soil sample and investigate laser-solid interactions. Pure lead nitrate salt and soil doped with lead nitrate are photolyzed with 193 nm light from an ArF excimer at fluences from 0.4 to 4 J/cm². Lead emission is observed at 357.2, 364.0, 368.3, 373.9 and 405.8 nm. Time-resolved data show the decay time of the lead emission at 405.8 nm grows with increasing fluence, and a plasma is formed above fluences of 2 J/cm², where a strong continuum emission interferes with the analyte signal. Fluences below this threshold allow us to achieve a detection limit of approximately 200 ppm in soil.

INTRODUCTION

Lead (Pb) poisoning from environmental and occupational exposure remains one of the most common and preventable diseases. There are numerous serious and detrimental health effects from inhalation or ingestion of lead, including poisoning or even death in extreme circumstances¹. Various in situ, real-time methods to measure heavy metals in soil have been developed as a replacement for conventional wet-chemistry techniques that require laborious and time consuming processes, such as preparation, dissolution, chelation, and ion exchange^{2,3}. Chemical analysis of soil sample with spectroscopic methods is often achieved with much less sample preparation and time, but there are often difficulties with calibration, matrix effects, and sensitivity⁴.

Here we apply excimer laser fragmentation fluorescence spectroscopy (ELFFS) to pure lead nitrate salts and soils doped with lead nitrate. We and other groups have used

ELFFS to monitor various gaseous hydrocarbons, ammonia, combustion generated metal species, and soot particles from diesel and other combustion exhausts⁵⁻⁹. The main difference between this method and other direct solid ablation analysis techniques, such as laser induced breakdown spectroscopy (LIBS) or laser ablation, is that the surface is photolyzed at laser fluences below the threshold where plasma formation occurs. The method benefits from an increased signal to noise (S/N) ratio compared with LIBS since the lack of a plasma eliminates the strong continuum emission that interferes with the analyte signals. The emission from the sample surface is recorded during the laser pulse without gating, and the emission peak is normally proportional to the concentration of the emitting species¹⁰.

EXPERIMENTAL

A schematic of the experimental apparatus is shown in Fig. 1. 193 nm photons with a pulse duration of 20 ns are emitted from an ArF excimer laser (Lambda Physik LPX 210i). The laser beam is focused with a 3.8 cm diameter, 25 cm focal length UV grade fused silica lens, and a 5 cm diameter mirror redirects the beam onto the solid surface of the sample. Laser fluences range from 0.4 to 4 J/cm². The fluence is varied by changing the voltage of the laser and/or by introducing screens in the beam path. Fluorescence is collected with a 3.8 cm biconvex lens (f# of 1.0) onto the entrance slit of a 0.3 m CGA/McPherson scanning monochromator. The slit width of the monochromator is 0.4 mm, corresponding to a 1.1 nm bandpass. The light from the monochromator is detected

by a Pacific 508 photomultiplier tube, and the signal is digitized by a LeCroy LT 342 digital oscilloscope and transferred to a PC through a GPIB cable for further analysis.

Two different sample plates are used: the first plate is a flat anodized aluminum plate; the second has two wells machined 2 mm into the surface to hold the solid samples. The wells allow us to reproducibly fill the sample to the same level, and contains the solids when ablating at high laser fluences. The sample plate is on a mounting system in the laser interrogation region that includes a magnetic connection and vertical translational stage to insure repeatability of a desired position and the optimal height of the test plate, respectively. The sample plate can be also horizontally translated with a motor or manually to introduce a fresh sample into the laser interrogation region. The aluminum plate was found to have a low scattering background, with no atomic or ionic Al peaks evident at the energy levels used here. Lead nitrate ($\text{Pb}(\text{NO}_3)_2$), (Aldrich, 99+ %) is used pure and in a mixture with soil. Pure lead nitrate is dissolved in water and applied to one of the sample wells. The solution is dried with a heat lamp or gun. Soil is obtained from a residential garden in Berkeley, CA. It is ground using a mortar and pestle and sifted using a coarse screen ($1.5 \times 1.5 \text{ mm}^2$). A measured amount of a known concentration lead nitrate solution is added to the soil to obtain a slurry. The slurry is applied to the other sample well, and then dried.

RESULTS AND DISCUSSION

The emission spectrum from $\text{Pb}(\text{NO}_3)_2$ and the background signal are shown in Fig. 2. The peak value of the emission during a time window of approximately 100 nsec

around the laser pulse is recorded for each single shot. The spectrum presented was collected at a laser fluence of 0.4 J/cm^2 . The monochromator was scanned at a rate corresponding to 5 shots/nm, and a rolling average of 5 shots was used to smooth the data. The background signal is obtained directly from the anodized surface and contains both optical and electrical noise. In the background spectrum the only peak observed is the 2nd harmonic of the laser scattering at 386 nm. The lead emission spectrum also shows 5 distinctive emission lines of lead atoms at 357.2, 364.0, 368.3, 373.9 and 405.8 nm. The 405.8 nm peak, a commonly used emission line for Pb analysis owing to its strong emission, involves electronic transitions from $7s^1 3P$ to $6p^2 3P$. Note that at this fluence there is little broadband emission associated with plasma formation.

The time resolved emission from $\text{Pb}(\text{NO}_3)_2$ at 405.8 nm and the background signal at 415 nm are presented in Fig. 3. The signals are shifted in time to a common scale, as the different laser conditions affect the time where lasing actually occurs. The full width at half maximum for these signals is shown in Table 1.

There are several points to consider in these results. During the first microsecond (Fig. 3a) at the lowest fluence, 0.53 J/cm^2 , the background signal is relatively low (0.05 V), and lasts about as long as the laser pulse. Similar signals are observed at other wavelengths not associated with known transitions. The background is mainly due to 193 nm laser light leaking through the monochromator (its rejection ratio is approximately 4000:1). The signal from lead at these conditions peaks near 0.3 V, and lasts longer. At higher fluences, the peak of the lead emission does not increase, but the emission tail grows. The background signal increases dramatically, reaching the same

peak value as the lead emission at the highest fluence (3.29 J/cm^2). Others and we have previously observed that the peak signal is not a strong function of laser fluence, presumably since the process has a step that can be saturated^{9,11}.

Even more dramatic changes are observed at longer times (Fig. 3b). At fluences below 2 J/cm^2 the signal is a single peak with a near exponential decay. At higher fluences, a second peak emerges at longer times, peaking in the $3 - 5 \text{ } \mu\text{sec}$ range. At the lower fluences, atoms or molecules are released from the matrix through direct photochemical bond-breaking rather than through photothermal processes, since the 193 nm photons are energetic enough to break the most of the molecular bonds. As the fluence increases, more species are liberated and electronically excited, and a larger fraction of species are ionized. Above the threshold, the extent of fragmentation and ionization increases, and the liberated and ionized species absorb the incoming light, forming a plasma. Plasma formation has been widely studied using laser ablation or laser breakdown techniques¹²⁻¹⁴.

Once a plasma plume is formed by accumulation of photon energy at high fluence, incoming light is absorbed and emission is trapped within a plasma so that the plume grows, reaching an elevated temperature ($5,000 \sim 15,000 \text{ K}$) and triggering broadband emission from air, electrons, atomic or ionic species, and ablated fragments. After the plume of the fully grown plasma cools, the analyte emission forms another peak as shown in Fig. 3(b), which is characteristic of Pb emission in LIBS. The lifetime of the signal in this case extends to $10 \text{ } \mu\text{s}$. Note that the magnitude of the background peak linearly increases with the fluence and reaches the same as that from $\text{Pb}(\text{NO}_3)_2$ while

lead signal intensities are almost unchanged. Therefore, it can be expected that if the background is subtracted from the lead emission, the net signal will decrease with increasing fluence. By using lower fluences and avoiding plasma formation, we significantly achieve better signal to noise ratios. The temperature increase in the gas phase and changes in collisional quenching are not significant compared to cases with a plasma. Finally, photon energy transfer to the target material is more efficient and there is no need for signal gating and time-resolved data analysis.

The same measurement procedure is applied to soil samples with lead nitrate salt added, where the sample surface is significantly rougher. The spectrum of lead in soil is shown in Fig. 4. The spectrum of pure soil does not contain any obvious distinct peaks except ones from laser scattering (not shown here). However, the noise level from background soil is often considerably higher than that from anodized Al plate, so the laser energy is reduced to optimize S/N, and the five emission lines of lead are still observed. As with the pure lead nitrate, the lead signal increases with laser fluence, but the background increases at a faster rate.

Direct application of spectroscopic techniques for metal detection in soils without any sample preparation has limits since soil is inherently inhomogeneous in nature. It is not expected that the target species is contained uniformly in soil, so variations could easily occur in different locations from a sample. The surface roughness and material properties of the soil is also not uniform. When focused on a single point, the laser eventually craters the soil surface, which affects both the laser-soil interaction and the detection sensitivity. We minimized the crater effect by introducing a fresh sample into

the probe volume approximately at the translational rate of 0.11 mm/sec. In addition, Eppler et al.¹⁵, Wisbrun et al.¹⁶, Bulatov et al.⁴, and Capitelli et al.³ showed that various types of soil interact differently with photons during laser induced plasma formation, and in turn, the recorded signals have different characteristics.

Fig. 5 shows the relationship between the peak emission amplitude with the lead concentrations in soil. The values shown are the difference in maximum lead emission and background peaks at 405.8 and 345 nm, respectively. The resulting signal is roughly linear with concentration, and indicates that the method could be used to quickly screen samples without significant preparation. The detection limit is lower than the regulatory standards imposed by US EPA for the presence of lead in soil (400 ppm¹⁷). The sensitivity of the system is dominated by optics and sample conditions, such as alignment, laser fluence, sample preparation and the soil matrix. While additional work is needed to ascertain the robustness of the analytical method, the lack of interferences from plasma-type emission is certainly promising.

CONCLUSIONS

Excimer laser fragmentation fluorescence spectroscopy has been successfully applied to the detection of lead in soil samples using a 193 nm ArF excimer laser. The detection method differs from other solid ablation processes in that lower laser fluences are used, and there is no plasma generation and subsequent broadband emission. A fluence threshold of approximately 2 J/cm² is found for plasma formation. The

detection limit for Pb in soil samples is about 200 ppm, achieved with minimal sample preparation and an analysis time on the order of a minute.

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Table 1: Full width at half maximum of the signals produced by photofragmentation fluorescence (* FWHM of the first peak).

Fluence	0.53 J/cm ²	2.05 J/cm ²	3.29 J/cm ²
Lead	42 ns	109 ns	254 ns*
Background	16 ns	22 ns	81 ns

Figure 1: Schematic of the experimental apparatus

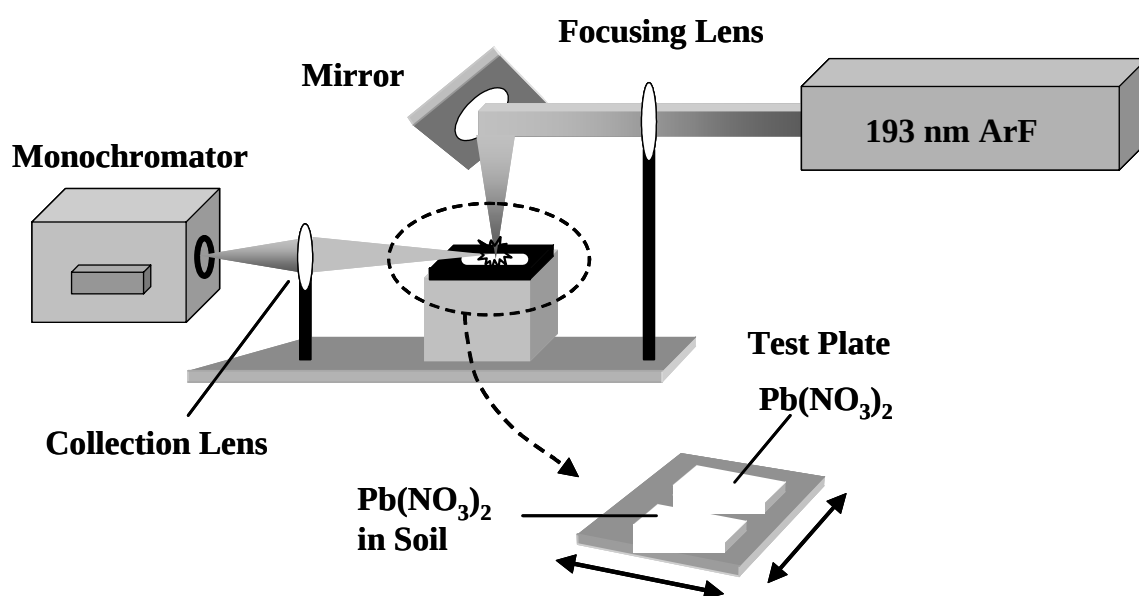


Figure 2: Emission spectra of background from the anodized Al surface and lead from $\text{Pb}(\text{NO}_3)_2$ at the laser fluence of 0.4 J/cm^2 .

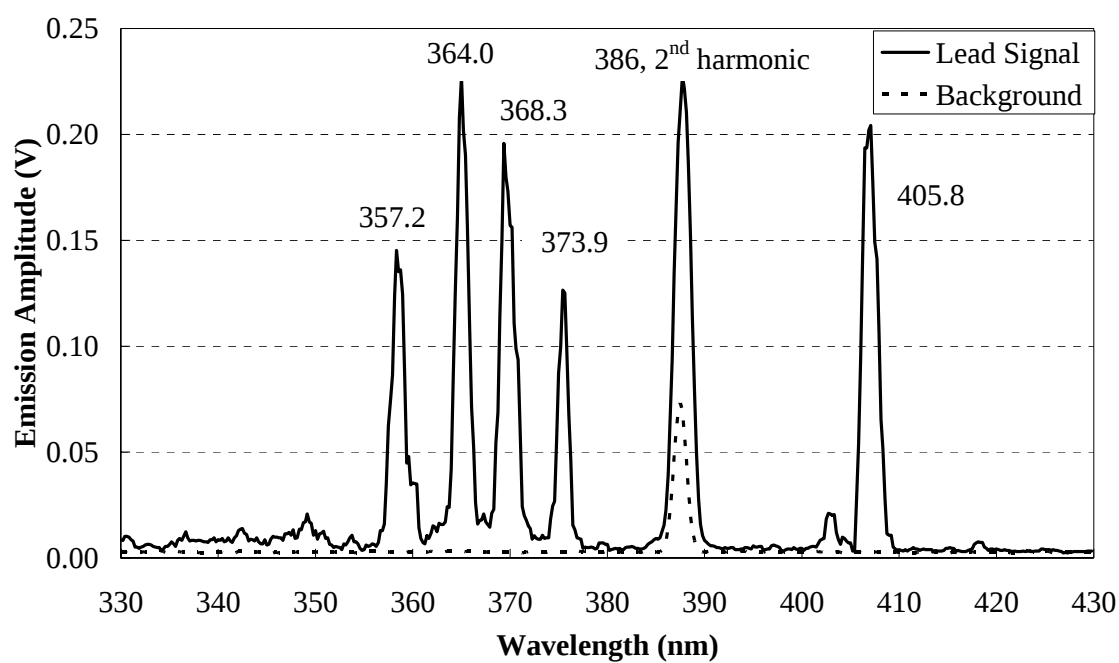
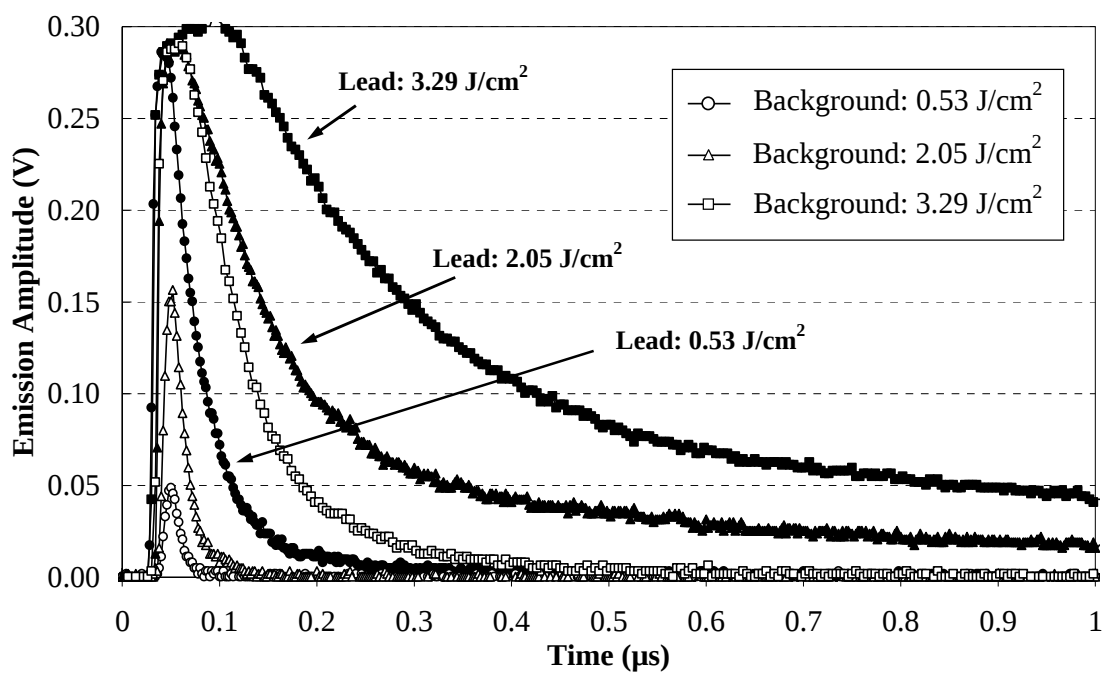


Figure 3: Time resolved emission from $\text{Pb}(\text{NO}_3)_2$ (405.8 nm) and background (415 nm) at various fluence conditions. (a) Emission during the first μsecond .



(b) Lead emission at longer time scales. Note that plasma formation threshold appears approximately 2 J/cm^2 .

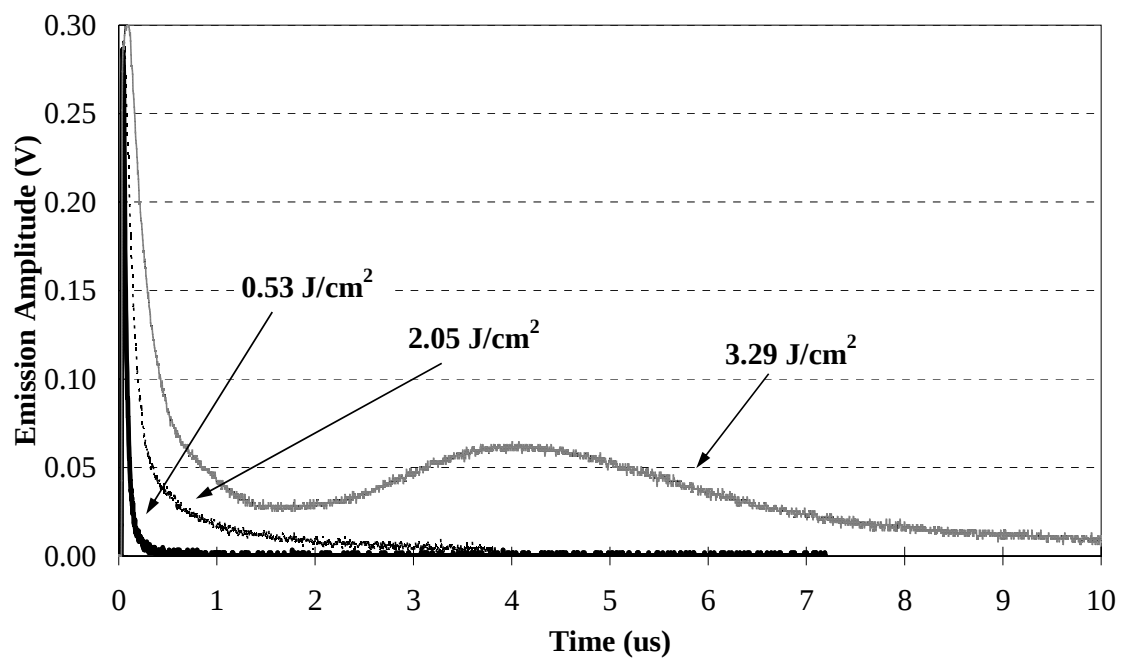


Figure 4: Emission spectrum of Pb in soil for the laser energy of 30 mJ.

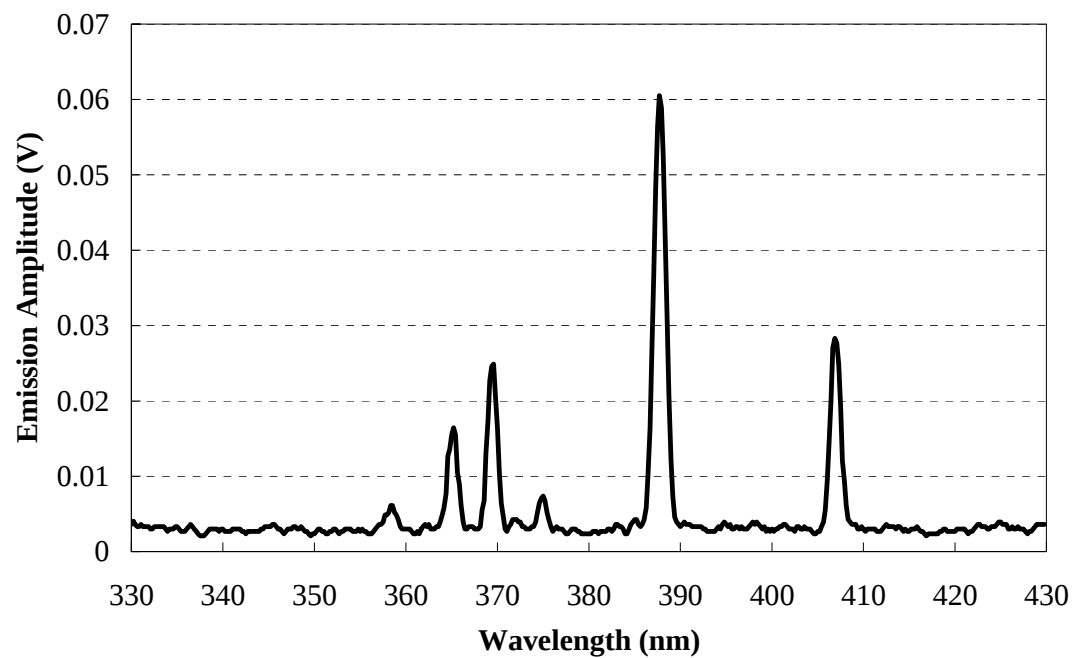


Figure 5: Correlation curve for lead emission and concentration of lead in soil. The presented values are maximum lead emission peaks subtracted by background scattering measured at 415 and 345 nm, respectively.

