Detection of Lead Contamination in Soil

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Introduction

Lead (Pb) is a toxic element with severe physiological effects including damage to the human gastrointestinal, neurological, and hematological systems.

WSU's Department of Civil and Environmental Engineering has initiated a study of lead (Pb) contamination in soil obtained from Hamtramck, MI (inside Detroit) and Venezuela. Hamtramck soil contamination is a result of car exhaust (located along Interstate-75), improper battery disposal, building demolition, as well as local ore smelters. Using laboratory-based Atomic Absorption Spectroscopy (AAS) and portable X-Ray Fluorescence Spectroscopy (XRF) the Engineering Dept. has measured contamination ranging from near 0 ppm to nearly 1000 ppm in five separate Detroit soil samples, as well as three Venezuelan samples.

AAS measurements of total Pb contamination were confirmed by LIBS analysis of the five soil samples. LIBS has been used in the past to monitor Pb contamination of soil,[1,2,3,4] and was found to be useful for Pb monitoring down to the 1-100 ppm level.

In this study, no attempt was made to perform an on-site *in* situ, investigation using LIBS. Lab samples only were tested. Two experimental LIBS configurations were studied.[2]

Sample Preparation

LIBS has a significant advantage over AAS in sample preparation time. One method used by AAS required 40 hours of preparation to chemically separate the Pb from its various fractions in the soil. Once dried and crushed for AAS, LIBS soil preparation required only an additional 2 minutes.

- 0.3 g of oven-dried, crushed, sifted soil
- placed into a stainless steel cylindrical dye, then capped
- compressed with a 20 ton hydraulic press for 10 seconds

Compression pelletized and partially solidified the sample, allowing efficient laser ablation as well as causing minimal (or no) cratering, pitting, or scattering of the soil.

Experimental Details

Laser

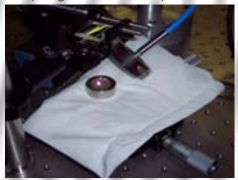
Spectra-Physics LAB 150-10
- 650 mJ/Pulse max
- 1064 nm
- Repetition freq. = 10 Hz
- Pulse duration = 9 ns

LIBS Parameters

- Two accumulated laser pulses per location
- Averaged among 10 target locations = a single measurement.
- 10 averaged measurement = 1 data point.
- Laser Energy = 15 mJ/pulse
- Delay = 2 μs, gate width = 4 μs

Spectrometer

LLA ESA 3000 Echelle spectrometer
- Fiber-coupled input
- Detection with a 1024 x 1024 pixel Intensified CCD-array (24 x 24 μm² pixel size).
- Spectral range = 200 – 834 nm
- 0.005 nm resolution (in the UV)



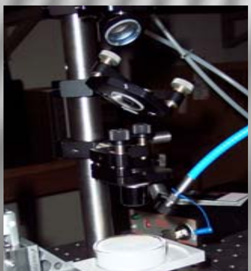
Focusing Optics

Microscope Objective

- 5x high-damage threshold infinite-Conjugate microscope objective
- Spot diameter at target ~ 100 μm.
- Energy at substrate = 15 mJ/pulse.
- Fluence = 190 J/cm²

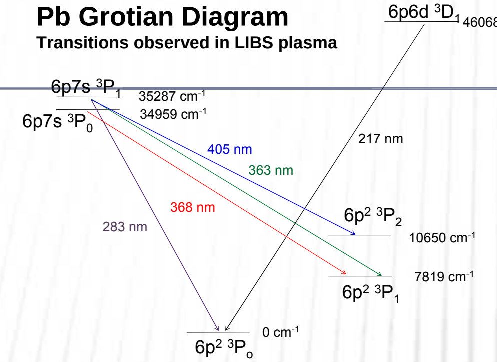
Crossed Cylindrical Lenses

- Cylindrical lens (top), f = 75.6 mm
- Cylindrical lens (bottom), f = 40 mm
- Spot size at target ~ 1mm x 100 μm
- Energy at substrate = 75 mJ/pulse
- Fluence = 75 J/cm²



Pb Grotian Diagram

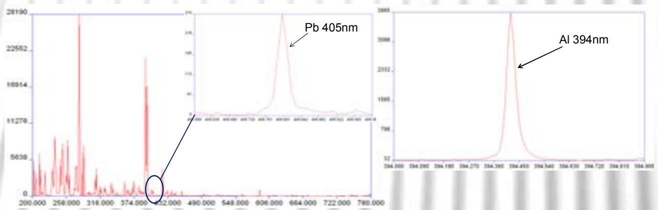
Transitions observed in LIBS plasma



Spectrum

A typical spectrum of a Detroit soil sample is shown below, along with the Pb emission line at 405.78 nm which was the largest emission line and was utilized for all measurements in this study. The Al emission line at 394.40 nm, used for normalization, is shown on the right.

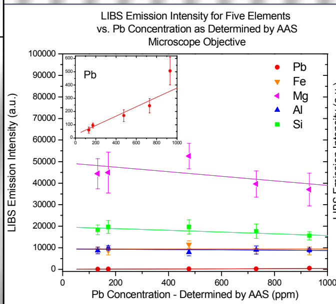
Energy = 15 mJ/pulse, Delay time = 2 μs, Gate width = 4 μs, 20 pulses.

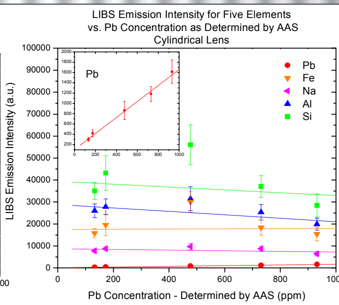


Cylindrical Lenses vs. Microscope Objective

Two crossed cylindrical lenses were used to study the effects of a larger sampling area in contrast to the smaller area from the microscope objective. Emission from six elements was observed: Pb, Fe, Al, Si, Na, and Mg. Only Pb showed any increase in concentration.

Left: (Objective) Emission from 5 elements in five samples. Fluence = 190 J/cm²
Right: (Cylindrical lenses) Emission from 5 elements in five samples. Fluence = 75 J/cm² The graph displays smaller relative standard deviation in Pb, Al, Fe, and Si resulting from the larger sampling area.





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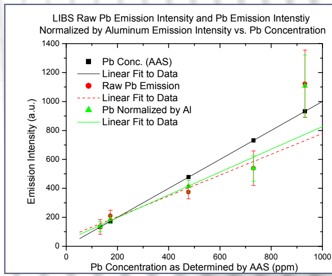
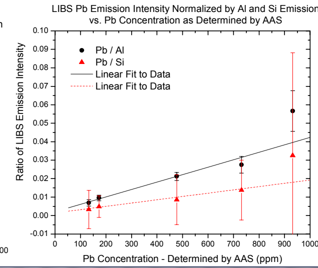
Normalizing Pb

Normalizing the Pb emission intensity at 405 nm by a second "matrix" emission line is recommended.[5,6] Lines from all observed matrix elements were studied. Normalization is in general useful for reducing undesired fluctuations in analyte line emission intensity.



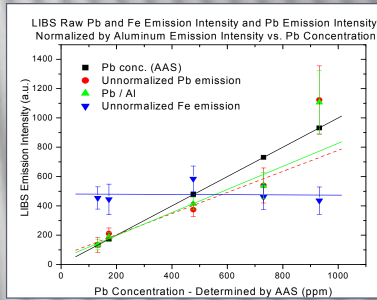
Above: (Objective) Comparison of best normalization line to raw Pb along with AAS concentration.



Above: (Objective) Plot of the 2 best normalization lines. Note: Smaller st. dev. in Pb/Al

Fe Correlation

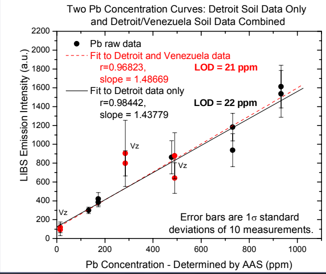
The solution that extracts Pb from the organically bound fraction during AAS sample preparation also extracts Pb from the iron-oxide fraction. A measurement of the possibility of correlation between quantities of Pb and Fe observed via LIBS was conducted. The linear correlation coefficient between Pb and Fe in the five samples was *r* = 0.07. We conclude that there was a 90% chance for no correlation between measured quantities of Fe and Pb, as suggested in the graph displayed on the right.

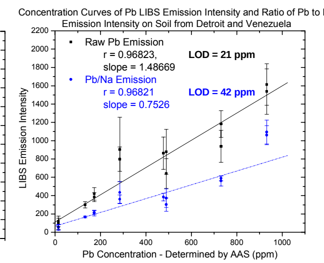


Concentration Curve

Left: Linear concentration curves fit to unnormalized Pb 405 nm emission in 5 Detroit and 3 Venezuelan soils (**Red**), as well as Detroit soils only (**Black**).

Right: Concentration curves comparing unnormalized Pb emissions (**Black**) to Pb emissions normalized by Na (**Blue**).





Comparing Pb concentrations determined by Atomic Absorption Spectroscopy (AAS), X-Ray Fluorescence (XRF), and LIBS.
- **Left**: LIBS Concentration of Pb – 405 nm, Unnormalized (black line above).
- **Right**: LIBS Concentration of Pb – 405 nm, Normalized by Na (blue line above).

soil #	AAS results (ppm)	XRF (ppm)	LIBS (ppm)	LIBS (ppm)
Det 1	477.2	450	505 +/- 126	422 +/- 60
Det 2	730.8	500	638 +/- 121	675 +/- 66
Det 3	932	600	984 +/- 179	1342 +/- 170
Det 4	172.5		195 +/- 46	193 +/- 38
Det 5	132.5		126 +/- 32	134 +/- 20
Vz1	14.5		0	0
Vz2	489.8		436 +/- 142	359 +/- 116
Vz3	284.7		497 +/- 169	440 +/- 113