SPS Chapter Research Award Proposal

Project Proposal Title	**Identification of Paint Samples using Laser Induced Breakdown Spectroscopy.**
Name of School	Tuskegee University
SPS Chapter Number	**7446**
Total Amount Requested	$1998.41

Abstract

It is proposed to identify paints from different commercial brands using laser induced breakdown spectroscopy (LIBS) based on different in trace elements concentrations and comparison of spectrums. This grant will be able to demonstrate that LIBS method can be used in forensic analysis of paints.

Proposal Statement

Overview of Proposed Project

This project is intended to answer if the LIBS technique could be used to find the difference between identical color paints from different brands. Also this project will be able to answer that how the paints compositions are affected when immersed in solution of different pH.

Motivation of the project comes from the fact that paints are used in artwork paintings, protective coating from the walls. When exposed the environment these paints deteriorate with time when exposed to harsh conditions and environment. Our motivation is to be able to tell the source of an unknown paint that from which company it belongs to and how it is affected by different pH solutions.

This project would start from buying paint sample and lay over the glass slide and let it be dry. The paint coated glass slides would be placed in acidic water solution that would mimic the PH of rain water for various time duration and LIBS spectrum would be recorded to identify the effect acidic water on the paint. The goals of the project would be following:

1. To be able to identify the source of a paint by LIBS analysis.
2. To understand the mechanism of the discoloration in the paint and role of different pH water in its deterioration. This research opportunity would help to strengthen the SPS chapter partnership is scientific research locally and opportunity to meet other students from the chapter from various institutions in conferences. Participation in SPS sponsored conferences would help in exchange of scientific views.

Background for Proposed Project

Laser induced breakdown spectroscopy (LIBS) is a real time measurement technique that has been used for identify the elements in solid, liquid and gas medium[1-7]. This technique has certain advantages over other techniques as minimal or no sample preparation is required. It can remotely measure the elements present in the paint samples. In LIBS technique, a high intensity laser light is focused on the top of sample with help of a lens. At the focal spot the intensity of laser light becomes so high that it ablates the sample material and

generates a plume of plasma (See **Error! Reference source not found.**). The plasma plume contains the ionized elements present in the sample. The optical emission of the plasma in cooling process is collected by a group of focusing lenses on the tip of the optical fiber and finally sent to spectrometer. The Ocean Optics LIBS 2500 plus spectrometer disperses the light of plasma plume consisting of various wavelengths at different angle. The CCD detector finally converts the light spectrum into electronic signal that can be displayed on computer.

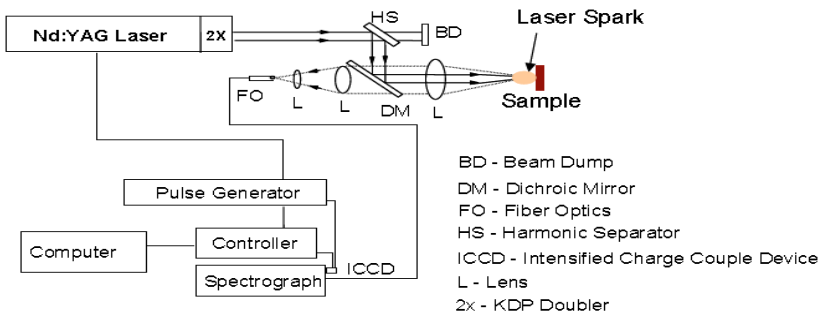

Figure 1: Experimental set-up to obtain the LIBS spectra.

Error! Reference source not found. shows the typical LIBS signal spectrum of a mineral.

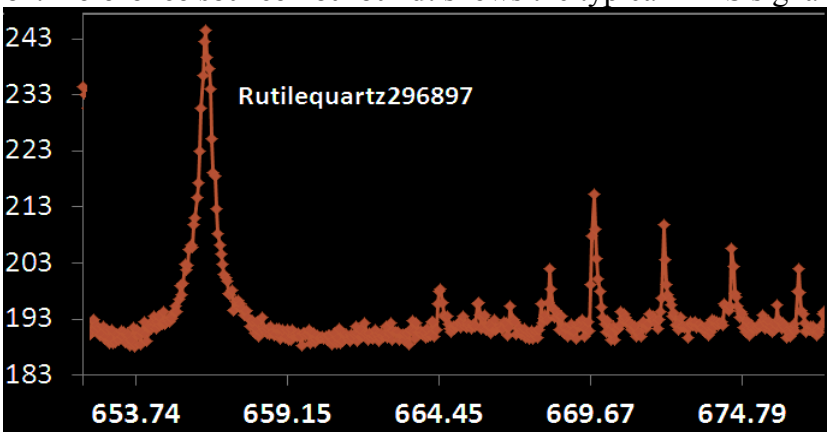

Figure 2: LIBS spectrum of quartz.

Laser induced breakdown spectroscopy is very fast technique. Miniaturized spectrometers and lasers can be easily installed at the preferred locations. Just a spark of laser light is enough to reveal the identity of the samples. The whole operation takes only few seconds. Laser induced breakdown spectroscopy has these entire features. This fixture is suitable for space applications where the size and weight of instrument greatly matters. Another important change is data analysis processes and use of calibration free method of LIBS.

The conventional method is to do the calibration of LIBS instrument is to use known samples to get a calibration curve and then use the unknown sample. Lately, calibration free methods do not need initial calibration. The calibration free method involves following steps.

The following equation is used to correlated the emission intensity with the temperature and energy levels of atoms or ions involved in the LIBS emission,

$$\ln \frac{I_{ul} 4\pi}{A_{ul} h \nu_{ul} g_u} = \ln \frac{N_0 G}{Z} - \frac{E_u}{KT}$$

In above mentioned equations, I_{ul} is LIBS emission line peak intensity, vul is frequency, Aul is spontaneous emission coefficient, h is Planck's constant, Z is partition function at temperature T, g_u is statistical weight of the upper energy level involved in emission, G is instrumental factor, K is Boltzmann's constant and Eu energy of upper level involved in emission of LIBS signal.

The left hand side of equation given below is plotted with respect of energy difference of levels. The slope of the graph gives the temperature of the plasma plume and the intercept of the graph gives N_0 the initial number of emitters. N_0 is also proportional to species weight percent in the sample. This can be achieved by the normalization procedure. $\sum_i w\%_i = x\sum_i N_{0,i}AW_i = 1$

This equation helps to provide the normalization constant. The weight percent of individual species can be calculated using the formula, $w\%_i = xN_{0,i}AW_i$

For this method to be accurate the LTE approximation should be extremely valid.
This method is useful where is usual calibration is not possible, for example in space exploration.
The use of artificial neural network (ANN) partial least square regression (PLS) has been very popular recently.
It is proposed to use the laser induced breakdown spectroscopy method to detect trace elements in paint samples. The purpose of this experiment is to develop a cheaper and real time method to detect trace elements in paint from various commercial brands. It is important to understand the trace elements within the paint samples and identify the commercial brands that can be useful in forensics. This method can be used for screening of paints for the presence of contaminants such lead etc.

Expected Results

The expected results are as follows,

1. Obtaining library of pattern of spectral features from different paint.
2. Obtaining best experimental condition for exaplpe lens to sample distance, time delay between laser pusle and the ICCD detector of spectrometer and laser power to get maxium signal intensity.
3. Getting information of about the trace elements present in different paint.
4. To be able to get a data bank to perform statistical anaylysis.

Description of Proposed Research - Methods, Design, and Procedures

We are proposing to perform the LIBS spectroscopy of paint by just taking a sample of paint on flass slide and placing under the focused laser for the LIBS experiment. The whole process is shown in figure 3.

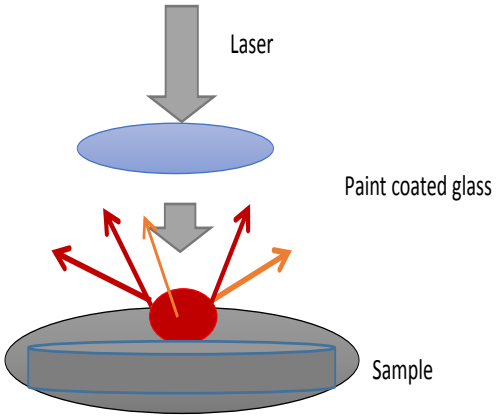

Figure 3: Method of preparing paint samples for the LIBS analvsis.

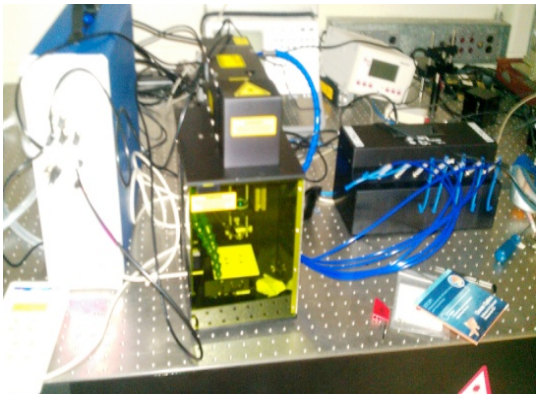

Figure 4: LIBS Setup: Ocean Optics LIBS 2500 plus spectrometer along with LIBS Sample Chamber and laser.

Plan for Carrying Out Proposed Project

Proposed Experimental Plan:

1. To find the effect of intensity of the laser beam on the LIBS signal of the paint sample.
2. To find the effect of delay between the laser pulse and detection device.

3. To find the effect of duration of paint sample immersed on the different pH liquid on the LIBS signal.
4. To find the effect of water content in paint on LIBS signal.
5. To collect paint samples from the various commercial brands and record the LIBS signal.
6. To analyze the recorded LIBS signal.

The proposed work would be done under the faculty advisors Dr. Akshaya Kumar and Dr. Prakash C. Sharma in physics Department Tuskegee university. Department of physics has Ocean Optics LIBS spectrometer along with pulsed YAG laser in the Laser and Optics Laboratory. Faculty members are using LIBS equipment for the research purposes. Taking guidance and working in collaboration with faculty members is planned.
The outcomes of our experimental findings will also be presented in local SPS chapter meetings.

Project Timeline

Time	Jan 1, 2015 to Feb. 28,2015	Feb 1, 2015 to May 31, 2015	June 1, 2015- October 31, 2015	November 1, 2015 to December 31, 2015
Task	Collecting Samples. Learning operations of laser and spectrometer. Reading literature	Recording Spectrum in different experimental conditions Writing interim report.	Analyzing collected data. Identifying the need of changing experimental condition and recording the additional data if required.	Writing final report Writing paper. Preparing presentation for a conference.

Budget Justification

A neutral density filter ($604.07) for varying laser power, an automatic pipette ($179.00) for accurate paint dispense, Laser line mirror($125.00) for alignment of the laser, pH meter($520.00) for measuring pH accurately, Low-form beaker($61.00) for storage of samples, Glass slides($31) for sample holdings, translation stage($288.50) for adjustment of samples, mirror mount($119.84) for mounting mirror, paint samples and lab supplies($70) for research purposes.

Bibliography

[1] Detection of lead in paint samples synthesized locally using-laser-induced breakdown spectroscopy MOHAMMED A.GONDAL, MOHAMED M.NASR, MUBARAK M. AHMED, ZAIN H. YAMANI AND M. S. ALSALHI Journal of Environmental Science and Health Part A Volume 46 (2011)1-8

[2] Application of laser-induced breakdown spectroscopy for total carbon quantification in soil samples. Ayyalasomayajula KK, Yu-Yueh F, Singh JP, McIntyre DL, Jain J. Appl Opt. 2012 Mar 1;51(7):B149-54.

[3] Laser induced breakdown spectroscopy in water, BOUDJEMAI, S; GASMI, T; BOUSHAKI, R; KASBADJI, R; MEDJAHED, F, J. Appl. Sci. Environ. Mgt. (2004) Vol. 8 (1) 13 - 15

[4] AC Pope et al, Lung Cancer, Cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. Journal of American Medical Association, 287 (2002)1132.

[5] Akshaya Kumar, F.Y.Yueh and J.P.Singh " Determination of trace elements in Liquid using Meinhard Nebulizer by Laser Induced Breadown Spctroscopy"Applied Optics Vol. 42 (2003)6040.

[6] F.Y.Yueh, J.P.Singh and H.Zhang "Elemental Analysis with Laser Induced Breakdown Spectroscopy" In Encyclopedia of Analytical Chemistry, John Wiley and Sons. Ltd, Chishester, U.K., 2000.

[7] D.A. Rasak, B.C.Castle, B.W.Smith, and J.D.Winefordner, Critical Reviews in Analytical Chemistry 27(4):257-290(1997)