

Elements Tracing of Lipsticks Using Laser Induced Breakdown Spectroscopy

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ABSTRACT

In this work different samples of lipsticks were examined using (LIBS) to trace elements in them.

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1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is a technique that uses a high peak power laser to disintegrate a sample of a desired material into excited atoms, ions and electrons resulting in plasma formation. When a high power laser is focused on to a target material, plasma can be achieved due to several processes. Emission of radiation from the plasma is the main parameter depending on the target conditions and the intensity of the laser. Liquid, gas and solid materials have different radiation emission characteristics. The structure of the plasma is highly complex to analyze. Several studies have been done on this issue [1]. We have focused mostly on the emission from plasmas which gives information of the species that are involved. Intensity of the emission can be analyzed to understand the characteristics of the individual elements that are present. Spectra recorded for different samples show the proportions to their elemental concentrations. Calibration curves drawn for known samples help to analyze unknown concentrations under similar laboratory conditions. Fluctuations in emission are the basic discrepancies while taking data. It can be avoided by choosing a standard line which is common in both unknown and known samples. Hence fluctuations do not affect the relative intensities. The plasma depends on the size of the focal spot, the media pressure and composition, the wavelength and intensity of the laser and, the target vapor composition. When a plasma condition is achieved, hot plasma on the edge of the target is created due to the expansion waves in what is called the absorption zone. Plasma plume reduces through several modes from hot high density to cold low density (Figure 1). The plasma pushes the surrounding media and forms a shock wave. Laser absorption results in bremsstrahlung which is continuum radiation from free-free electron transitions.

Due to the interaction between positive charge ions and electrons plasma is closest to the sample.

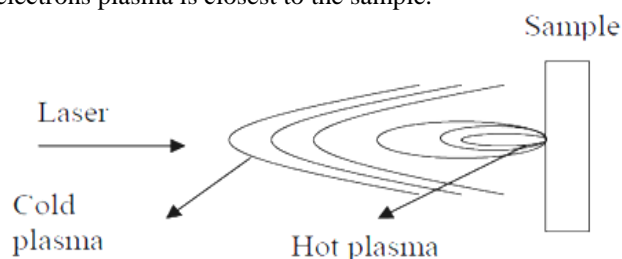


Figure 1. Schematic of plasma formation by laser beam.

The first emission from the plasma is blackbody continuum radiation. It decays faster than the line emission. When it starts to cool down, the characteristic emission of spectral lines can be detected. The ionized atoms are mostly located near the surface, while the neutral atoms are mostly away from the plasma. Singly ionized and neutral atoms are observed near 500ns after plasma initiation.

2. LIBS advantages and disadvantages

LIBS, like other methods of AES, are able to detect all elements and have the ability to provide simultaneous multi-element detection capability with low absolute detection limits. In addition, because the laser spark uses focused optical radiation to form the plasma, LIBS exhibits numerous appealing features that distinguish it from more conventional AES-based analytical techniques like inductively coupled plasma mass spectroscopy. These are: simple and rapid or real time analysis, the ablation and excitation processes are carried out in a single step; little-to-no sample preparation, which results in increased throughput and reduction of tedious and time-consuming sample digestion and preparation procedures (this, however, can lead to a loss of accuracy through contamination). LIBS allow in situ analysis requiring only optical access to the sample.

It can also be performed over a great distance, a technique referred to as *remote* sensing. Unlike remote analysis, in which some part of the LIBS system is close to the sample is the method of *stand-off* analysis. Here, the laser pulse is focused on to the sample at a distance using a long focal length optical system [2]. Virtually any kind of sample can be analyzed: solids, liquids, aerosols, or gases. LIBS have the ability to analyze extremely hard materials which are difficult to digest such as ceramics, glasses and superconductors [3,4]. It is a non-destructive method, very small amount of sample (0.1 μg – 0.1 mg) is vaporized. It provides good sensitivity for some elements (e.g. Cl, F) difficult to monitor with conventional AES methods. In addition, LIBS has adaptability to a variety of different measurement scenarios, e.g. underwater analysis, direct and remote analysis, compact probe with the use of miniature solid state lasers, stand-off analysis. We can summarize LIBS advantages and disadvantages in the following table:

Table 1. Advantages and disadvantages of LIBS technique.

Advantages	Disadvantages
1- Minimal (no) sample Preparation.	1- Variation in the mass ablated Caused by changes in the bulk matrix.
2- All states of matter can be analyzed, as well as conductive And nonconductive samples.	2- Difficulty in obtaining matrix Matching standards.
3- Very small amount of material isaporized(around 10 of ng)	3- Detection limits higher (poorer) than standard solution techniques (i.e. ICP-OES)
4- Easy analysis of refractory materials such as ceramics	4- poor precision, typically 5 – 10 %
5- Micro analysis is possible with spatial resolution of 1 – 10 μm	5- Standard emission isadvantages, such as spectral interference and Self absorption.
6- Capability of remote analysis in Harsh environments.	6- possibility of optical component damage from high energy density lasers
7- Atomization and ionization are In one step.	7- Complexity.
8- Capability of simultaneous multi- Element analysis.	

3. LIBS applications

LIBS are an emerging technique for elemental composition analysis. It can analyze and identify solid, liquid, and gas samples with little-to-low sample preparation. Figure 2 shows some examples.



Figure 2. LIBS can analyze and identify samples in solid, liquid, and gas forms.

A benefit of LIBS technology is rapid, direct chemical characterization of solid samples without laborious dissolution procedures. Furthermore, LIBS can be stand-off and used in hostile environments. LIBS have been used in a lot of areas. LIBS are well suited for the detection of nuclear and hazardous elements because it can be remote and

standoff. For example, it has been used in the material composition analysis of nuclear power station steam generator tubes [4], remote composition analysis of spent-fuel residuals [5], remote analysis of nuclear materials [6, in-situ analysis in the nuclear industry [7,8], and detection of toxic and radioactive elements in sea water and ice [9]. In order to perform remote and stand-off analysis, fiber optic probe LIBS instruments and Figure 2 LIBS can analyze and identify samples in solid, liquid, and gas forms. Telescope LIBS instruments have been developed. The first reported industrial use of a fiber optic probe LIBS instrument was undertaken within the UK nuclear power generation industry in 1993 [10]. Because of the unique point sampling nature of the laser-induced plasma, LIBS can be applied for analysis of aerosols [11]. An aerosol is a suspension of fine solid particles or liquid droplets with characteristic dimensions in the nanometer to micrometer range in a gas. The analysis of aerosols is very important for industrial hygiene and clean room technology. Conventional laboratory-based techniques such as atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES), and inductively coupled plasma mass spectroscopy (ICP-MS) can determine the chemical composition of aerosols after filter collections. However, these techniques usually require time-consuming and labor-intensive and expensive procedures. LIBS can directly analyze aerosols in an on-line and *in-situ* fashion. Furthermore, LIBS can also perform quasi-continuous analysis of automatically sampled filters or on a filter band. Process control is expected to be a significant LIBS application in the future. Due to the poor accuracy and precision of LIBS, there is certainly room for future improvement in the aerosol LIBS. LIBS have many applications in industry. In the metals and alloys processing industry, there are increasing requirements for quality and productivity control of on-line chemical compositional analysis. Since LIBS can directly sample the specimen in the product line by the laser itself, LIBS is predestined for this task. For example, automatic inspection equipment called LIFT (laser identification of fittings and tubes) based on LIBS has been developed to prevent any mix of material grades, which can inspect more than different material grades [12]. In steel industry, LIBS is applied to quantitative slag analysis [13] and liquid steel analysis. It is believed that there will be more and more industrial applications of LIBS in the future. The analysis of biological and medical samples is another interesting LIBS application. The knowledge of the presence or absence of certain elements in the human body is of vital importance. For example, the accumulation of cadmium (Cd) or mercury (Hg) in excess concentration may have toxic effects. LIBS provide a simple and fast qualitative and quantitative elemental analysis of solids. Researchers have done extensive work in the analysis of calcified tissue materials, teeth, bones, human hair, plants, and some other biological samples. Because of the poor statistics, reproducibility, and sensitivity of LIBS, these kinds of applications are still in their infancy. LIBS can be used for surface and three-dimensional mapping of target elements [17]. For example, LIBS is expected to be a quick method to measure the surface and internal distribution of many pharmaceutical materials in the pharmaceutical industry. Figure 3 shows a LIBS system for the pharmaceutical industry which is commercialized by Pharma Laser. Microanalysis of tool steel and microelectronics with LIBS has been studied recently.



Figure 3. LIBS instrument for pharmaceutical industry.

4. Materials and methods

Lipstick is not solid that is between a solid and fluid, Four lipstick samples of different brands and price range (from cheap to expensive) sold at the local market. The four lipstick samples were procured from cosmetic shops in the Sudan. Sample #1 and sample #2 were low cost unbranded lipsticks manufactured in China and India while sample #3 and sample #4 were branded as LIP Care and Rouge Allure Luminous Satin. As we know that the lipstick is not in the form of solid rather is in a fluid state which is not trivial to analyze by LIBS technique. Special treatment of the samples was necessary to study the LIBS spectrum.

Ultraviolet-visible spectroscopy

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometer (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared [NIR]) ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

Principle of ultraviolet-visible absorption

Molecules containing π -electrons or non-bonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbital's. The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb.



Figure (4) uv\vis device

Instrumentation and working of UV spectroscopy

Instrumentation and working of the UV spectrometers can be studied simultaneously. Most of the modern UV spectrometers consist of the following parts-
Light Source

Tungsten filament lamps and Hydrogen-Deuterium lamps are most widely used and suitable light source as they

cover the whole UV region. Tungsten filament lamps are rich in red radiations; more specifically they emit the radiations of 375 nm, while the intensity of Hydrogen-Deuterium lamps falls below 375 nm.

Monochromatic

Monochromators generally composed of prisms and slits. The most of the spectrophotometers are double beam spectrophotometers. The radiation emitted from the primary source is dispersed with the help of rotating prisms. The various wavelengths of the light source which are separated by the prism are then selected by the slits such the rotation of the prism results in a series of continuously increasing wavelength to pass through the slits for recording purpose. The beam selected by the slit is monochromatic and further divided into two beams with the help of another prism

Sample and reference cells

One of the two divided beams is passed through the sample solution and second beam is passed through the reference solution. Both sample and reference solution are contained in the cells. These cells are made of either silica or quartz. Glass can't be used for the cells as it also absorbs light in the UV region.

Detector

Generally two photocells serve the purpose of detector in UV spectroscopy. One of the photocell receives the beam from sample cell and second detector receives the beam from the reference. The intensity of the radiation from the reference cell is stronger than the beam of sample cell. This results in the generation of pulsating or alternating currents in the photo cells.

Amplifier

The alternating current generated in the photocells is transferred to the amplifier. The amplifier is coupled to a small servo meter. Generally current generated in the photocells is of very low intensity, the main purpose of amplifier is to amplify the signals many Times so we can get clear and recordable data

Recording devices

Most of the time amplifier is coupled to a pen recorder which is connected to the computer. Computer stores all the data generated and produces the spectrum of the desired compound.

UV/VI Spectrophotometer application

UV/Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analyses, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied.

- Solutions of transition metal ions can be colored (i.e., absorb visible light) because d electrons within the metal atoms can be excited from one electronic state to another. The color of metal ion solutions is strongly affected by the presence of other species, such as certain anions or ligands. For instance, the color of a dilute solution of copper sulfate is a very light blue; adding ammonia intensifies the color and changes the wavelength of maximum absorption (λ_{\max}).

- Organic compounds, especially those with a high degree of conjugation, also absorb light in the UV or visible regions of the electromagnetic spectrum. The solvents for these determinations are often water for water-soluble compounds, or ethanol for organic-soluble compounds. (Organic solvents may have significant UV absorption; not all solvents are suitable for use in UV spectroscopy.)

Ethanol absorbs very weakly at most wavelengths.) Solvent polarity and pH can affect the absorption spectrum of an organic compound. Tyrosine, for example, increases in absorption maxima and molar extinction coefficient when pH increases from 6 to 13 or when solvent polarity decreases.

- While charge transfer complexes also give rise to colors, the colors are often too intense to be used for quantitative measurement. The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length, UV/Vis spectroscopy can be used to determine the concentration of the absorber in a solution. It is necessary to know how quickly the absorbance changes with concentration. This can be taken from references (tables of molar extinction coefficients), or more accurately, determined from a calibration curve.

A UV/Vis spectrophotometer may be used as a detector for HPLC. The presence of analyze gives a response assumed to be proportional to the concentration. For accurate results, the instrument's response to the analyze in the unknown should be compared with the response to a standard; this is very similar to the use of calibration curves. The response (e.g., peak height) for a particular concentration is known as the response factor. The wavelengths of absorption peaks can be correlated with the types of bonds in a given molecule and are valuable in determining the functional groups within a molecule. The Woodward-Fieser rules, for instance, are a set of empirical observations used to predict λ_{max} , the wavelength of the most intense UV/Vis absorption, for conjugated organic compounds such as dienes and ketones. The spectrum alone is not, however, a specific test for any given sample. The nature of the solvent, the pH of the solution, temperature, high electrolyte concentrations, and the presence of interfering substances can influence the absorption spectrum. Experimental variations such as the slit width (effective bandwidth) of the spectrophotometer will also alter the spectrum. To apply UV/Vis spectroscopy to analysis, these variables must be controlled or accounted for in order to identify the substances present.

Conclusion

Three different samples of lipstick were analyzed the comparison was done between them as there is deference between both cheap and expensive , Get a total of components each sample and found that the sample made in India are the best samples in terms of the elements also found some of the elements that can cause the gravity on the human body, and contain the some elements toxic and carcinogenic Pollutants (lead, chromium, cadmium and zinc) are present in The red lipstick samples collected from local markets in Sudan

Measured using LIBS system These data indicate that the ongoing The use of these cosmetics can lead to an increase in

the trace Metal levels in the eye and the human body outside the system Acceptable limits. This application of cosmetics must be it is the source of lead, cadmium and chromium in the evaluation Patients who suffer from the symptoms of lead poisoning in Sudan.

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