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A REVIEW ON LASER-INDUCED BREAKDOWN SPECTROSCOPY

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ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) is a type of atomic emission spectroscopy which uses a highly energeticlaser pulse as the excitation source. The laser is focused to form a plasma, which atomizes and excites samples. In principle, LIBS can analyse any matter regardless of its physical state, be it solid, liquid or gas. Because all elements emit light of characteristic frequencies when excited to sufficiently high temperatures, LIBS can (in principle) detect all elements, limited only by the power of the laser as well as the sensitivity and wavelength range of the spectrograph & detector. If the constituents of a material to be analyzed are known, LIBS may be used to evaluate the relative abundance of each constituent element, or to monitor the presence of impurities. In practice, detection limits are a function of a) the plasma excitation temperature, b) the light collection window, and c) the line strength of the viewed transition. LIBS makes use of optical emission spectrometry and is to this extent very similar to arc/spark emission spectroscopy.

Keywords: Laser-induced, plasma excitation temperature, optical emission spectrometry.

INTRODUCTION

Laser-Induced Breakdown Spectroscopy (LIBS) is a spectroscopic technique using laser-generated plasma to ablate and excite a sample, which can initially be in solid, liquid, or gaseous form. Emission generated from the plasma is used to identify material constituents and can be used to identify, sort, and classify materials [1].

LIBS can be used both in-process and in the laboratory for material identification. A very versatile method, it has the primary advantages of

	Rapid analysis
	No sample preparation for most samples
	Sensitive to a wide variety of elements
	Simultaneous reporting of elements

Since the development of LASER (Light amplification by stimulated emission of radiation) in 1960's, many new spectroscopic techniques utilizing the laser have been developed. The main characteristics of laser with compared of conventional light sources are directionality, coherence, high power, pulsed beam & monochromatically. Because of these characteristics of lasers, many new fields of applications in modern spectroscopy have been evolved, and they are considered as essential tool in modern spectroscopy. Each new spectroscopy technique has taken some of these laser characteristics.LIBS is one of the new spectroscopic techniques developed by adopting high power ,pulsed and narrow bandwidth characteristics of lasers.

" Laser induced breakdown spectroscopy (LIBS) is an analytical technique that allows for the determination of a sample's elemental composition based on laser ablation followed by atomic, ionic, and molecular emission processes coming from elements transferred into the plasma as a result of laser-induced breakdown."

In LIBS , a plasma is generated by introduction of a high power laser on to the target surface(solid sample), while the atomic emission signal from the plasma is detected for the elemental analysis of solid samples. Since the power density of the incoming laser beam needs to be higher than some threshold value to generate the laser induced plasma, laser used for LIBS studies are usually high power pulsed and narrow pulse width.

LIBS is an atomic emission spectroscopy

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technique which uses highly energetic laser pulses to provoke optical sample excitation.

The interaction between focused laser pulses and the sample creates plasma composed of ionized matter.

Plasma light emissions can provide "spectral signatures" of chemical composition of many different kinds of materials in solid, liquid, or gas state .

LIBS can provide an easy, fast, and in situ chemical analysis with a reasonable precision, detection limits, and cost.

Today, LIBS is considered as an attractive and effective technique when a fast and whole chemical analysis at the atomic level is required.

PRINCIPLE

When a high power laser pulse, generally in the 1-10 MW/cm2 range, is focused tightly, dielectric breakdown occurs leading to plasma composed of elemental and molecular fragments from the atmosphere and other objects in the immediate vicinity. As the plasma cools, the excited atoms emit light at characteristic wavelengths in the 200 –900 nm spectral region. The emission lines are spectrally resolved and recorded, typically about 1 micro-second after the laser pulse, to give information on the elemental composition of the sample.

A high energy laser pulse is focused down to target a gas, liquid, or solid substance creating a dielectric breakdown or "plasma spark". This high-temperature atomization provides sufficient energy to transition atoms into distinct atomic energy levels. The atoms then decay resulting in narrow "fingerprint" elemental emission line spectra [2].

SOURCE

A range of Nd:YAG lasers are used in analysis of elements in the periodic table. Though the application by itself is fairly new with respect to conventional methods such as XRF or ICP, it has proven to be less time consuming and a cheaper option to test element concentrations. Nd:YAG absorbs mostly in the bands between 730–760 nm and 790–820 nm. At low current densities krypton flash lamps have higher output in those bands than do the more common xenon lamps, which produce more light at around 900 nm.

Nd:YAG (neodymium-doped yttrium aluminum garnet; Nd:$Y_3Al_5O_{12}$)

Nd:YAG is a crystal that is used as a lasing medium for solid-state lasers. The dopant, triply ionized neodymium, Nd(III), typically replaces a small fraction of the yttrium ions in the host crystal structure of the yttrium aluminium garnet (YAG), since the two ions are of similar size. It is the neodymium ion which proves the lasing activity in the crystal, in the same fashion as red chromium ion in ruby lasers. Generally the crystalline YAG host is doped with around 1% neodymium by atomic percent.

Nd:YAG lasers and variants are pumped either by flashtubes, continuous gas discharge lamps, or near-infrared laser diodes (DPSS lasers). Prestabilized laser (PSL) types of Nd:YAG lasers have proved to be particularly useful in providing the main beams for gravitational wave interferometers such as LIGO, VIRGO, GEO600 and TAMA [3].

Other Lasers

- Fiber Laser (Ytterbium) 1070nm
- CO2 Laser (gas laser)
- Nd:YAG Flash Lamp Laser (solid state)
- Nd:YAG Diode Laser Pumped
- Vanadate (Nd:YVO4)

PRINCIPLE INVOLVED IN LASERS

In order for an atom (electron) to reach an excited level some type of energy must be applied via heat, light or electricity. Once an electron moves to a higher-state, it wants to return to its original state. When it does, it releases its energy as a photon a particle of light.

These photons of light are what we use in lasers. Although there are many types of lasers, they all have certain essential features. Either a rod or a gas tube is excited by light or electricity (flash lamp, diodes or RF frequency) to release photons of light [4].

FIBER OPTICAL CABLE

An optical fiber (or optical fibre) is a flexible, transparent fiber made of glass (silica) or plastic, slightly thicker than a human hair. It functions as a waveguide, or "light pipe", to transmit light between the two ends of the fiber. It consists of a bundle of glass threads.

Optical fibers typically include a transparent core surrounded by a transparent cladding material with a lower index of refraction. Light is kept in the core by total internal reflection. This causes the fiber to act as a waveguide. Fibers that support many propagation paths or transverse modes are called multi-mode fibers (MMF), while those that only support a single mode are called single-mode fibers (SMF). Multi-mode fibers generally have a wider core diameter, and are used for short-distance communication links and for applications where high power must be transmitted. Single-mode fibers are used for most communication links longer than 1,050 meters (3,440 ft) [5].

TERMINATION AND SPLICING

Optical fibers are connected to terminal equipment by optical fiber connectors. These connectors are usually of a standard type such as *FC*, *SC*, *ST*, *LC*, *MTRJ*, or *SMA*, which is designated for higher power transmission.

DETECTORS

We will consider simple CCD-based spectrometers, broadband array spectrometers, echelle spectrometers with intensified CCDs, Czerny-Turner spectrometers with intensified CCDs, and PMT-based spectrometers. These have the following attributes:

CCD-based spectrometers

Used in many applications, CCD-based spectrometers are inexpensive and have fairly broad wavelength coverage, depending on the CCD. Typically these cannot be gated faster than a few ms, and because of this, it is difficult to control the data acquisition time or make acquisition very short, which can influence the repeatability of the measurement [6].

Broadband diode array spectrometers

These spectrometers are arrangements of CCD-based detectors designed to cover a broad wavelength range. Typically uncooled, with multiple-CCD spectra stitched together to form larger broadband spectrum, these systems can provide relatively low cost with multi-element sensitivity.

Echelle spectrometers

Echelles provide broadband coverage which is usually combined with a cooled, intensified CCD that allows gating of spectral acquisition to 10s of nanoseconds. In an echelle, the incoming light is dispersed by a prism and a grating onto the detector, resulting in a 2-dimensional spectral field, the various orders (typically the relatively weaker higher orders) of which are sorted by software to assemble an entire spectrum [7].

Czerny-Turner spectrometers

These disperse light on a single dimension using a grating, generally using the first order of the grating. On a typical 256 x 1064 intensified CCD array, one thus collects the strongest dispersion of the light (the first order from the grating) and can chose to collect ("bin") from 1 to 256 rows high of data on the intensified CCD. The strong first order light combined with the choice of binning from 1-256 rows and variation of the gain on the camera intensifier of 1-256 results in an instrument with incredible dynamic range [8].

Photomultiplie Tube (PMT)-based spectrometers

Photomultipliers are point detectors with much greater potential gain than even an intensified CCD, due to the multiple gain stages – typically they can provide 10e7 signal amplification to the iCCD's 5 x 10e4 – more than two orders of magnitude improvement. However, as point detectors they need to be implemented either in broad arrays or in with multiple detectors in a Paschen-Runge spectrometer configuration. Hence.

ADVANTAGES

LIBS is considered one of the most convenient and efficient analytical techniques for trace elemental analysis in gases, solids, and liquids. Some of its major advantages include:

- Real-time measurements: online monitoring and quality control of industrial processes
- Noninvasive, nondestructive technique: valuable samples can be reused, sensitive materials can be analyzed, suitable for in-situ biological analysis
- Remote measurements can be done from up to 50 meters distance: can be used in hazardous environments and for space exploration missions on other planets
- Compact and inexpensive equipment: can be widely used in industrial environments, perfect for field measurements
- High-spatial resolution: can obtain 2D chemical and mechanical profiles of virtually any solid material with up to 1 µm precision
- Non or very little sample preparation is required: reduced measurement time, greater convenience, less opportunity for sample contamination
- Samples can be in virtually any form: gas, liquid, or solids
- Analysis can be performed with a very small amount of sample (nanograms): very useful in chemistry for characterization of new chemicals and in material science for characterization of new composite materials or nanostructures
- Virtually any chemical element can be analyzed, such as heavier elements unavailable for X-ray fluorescence
- Analysis can be done on extremely hard materials like ceramics and superconductors; these materials are difficult to dissolve or sample to perform other types of analysis
- In aerosols both particle size and chemical composition can be analyzed simultaneously [9].

APPLICATIONS

The fact that LIBS generally requires little-to-no sample preparation, simple instrumentation, and can easily be performed on-the-field in hazardous industrial environments in real-time, it is a very attractive analytical tool. The following are a few examples of real life applications, where LIBS is successfully used [10].

PHARMACEUTICAL APPLICATIONS

Blend Uniformity

- Uniform blending of API and exipients (lubricants, disintegrates, compaction agents) is directly related to product performance.
- Blend uniformity can be impacted by a variety of factors like Particle size and shape, surface characteristics, electrostatic interactions, moisture content, environmental humidity and blender configuration

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- LIBS can be used to monitor the homogeneity of a species (API, lubricant, etc.) within a tablet, within a batch, and between batches
- LIBS signal % RSD is the most useful indicator of blend homogeneity

Film Coating

- Film coatings are used to protect against air, moisture, light, to mask unpleasant taste, improve ease of swallowing
- Improved photo-stability often depends on thickness of film and amount of pigment
- LIBS can be used to monitor coating composition, thickness and uniformity with little-to-no sample preparation
- The depth profiling capabilities of LIBS also allows for layer analysis

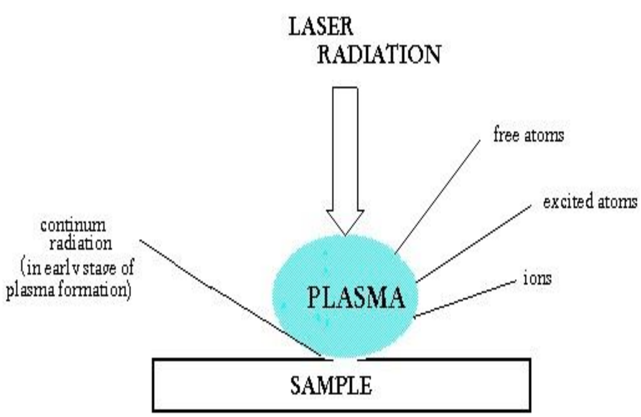
Quantification of various pharmaceutical components

- Phosphorous containing active API's in microcrystalline cellulose and hydrous lactose matrix were analyzed at w/w concentration ranges of 0-5% active agent (0 to 0.95%p).
- Mg has many atomic and ionic lines that can be chosen for measurement, in this case, calibration curves were constructed for Mg 518nm and Mg 285.21nm.

GENERAL APPLLICATIONS

- Express-analysis of soils and minerals (geology, mining, construction)
- Exploration of planets (such as projects using LIBS for analyzing specific conditions on Mars and Venus to understand their elemental composition)
- Environmental monitoring (Real-time analysis of air and water quality, control of industrial sewage and exhaust gas emissions)
- Biological samples (non-invasive analysis of human hair and teeth for metal poisoning, cancer tissue diagnosis, bacteria type detection, detection of bio-aerosols and bio-hazards, anthrax, airborne infectious disease, viruses, sources of allergy, fungal spores, pollen). Replacing antibody, cultural, and DNA types of analysis
- Archeology (analysis of artifacts restoration quality)
- Architecture (quality control of stone buildings and glasses restoration)
- Army and Defense (detection of biological weapons, explosives, backpack-based detection systems for homeland security)
- Forensic (gun shooter detection)
- Combustion processes (analysis of intermediate combustion agents, combustion products, furnace gases control, control of unburned ashes)
- Metal industry (in-situ metal melting control, control of steel sheets quality, 2D mapping of Al alloys)
- Nuclear industry (detection of cerium in U-matrix, radioactive waste disposal) [11].

Fig 1. Induction of sample



INSTRUMENTATION

Fig 2. Block diagram of Laser-Induced Breakdown Spectroscopy

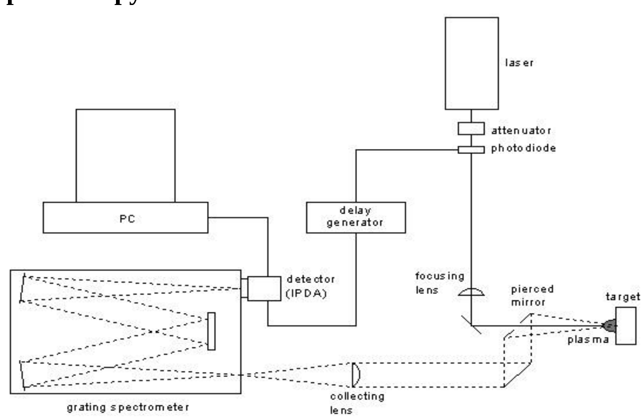


Fig 3. Nd:YAG solid-state laser

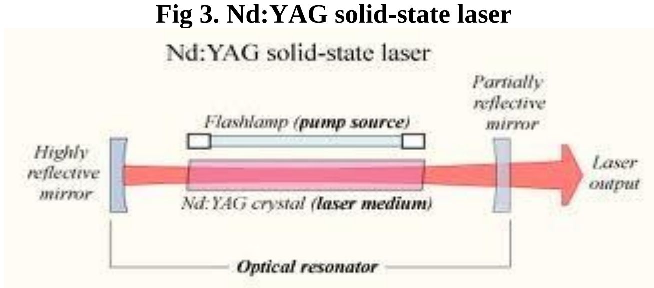


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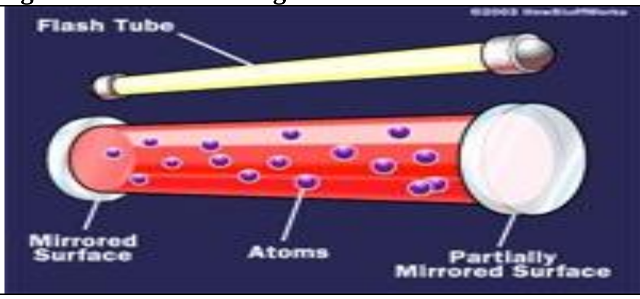
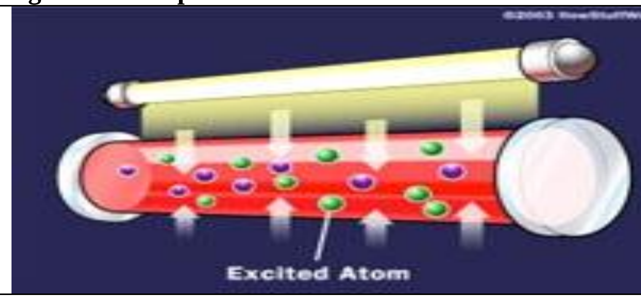
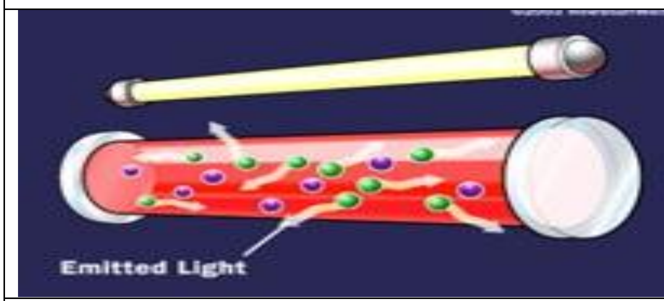
Fig 4. Laser in non-lasing state



Light from lamp excites atoms



Some atoms emit photons



Photons bounce back and forth on mirrors stimulating the emission of other photons; laser beam out one end

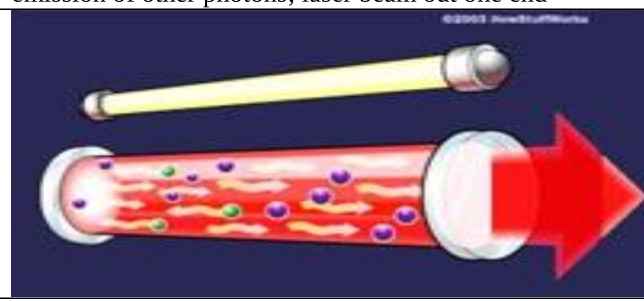
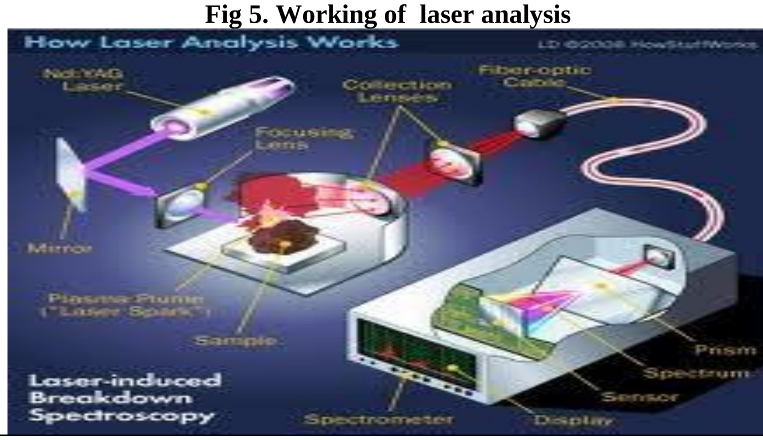


Fig 5. Working of laser analysis



CONCLUSION

TheLIBStechnologycananalyzeasampleinlessthan oneminutewithoutanysample preparationandisspecifictoelementscontainedinthechemical structureofpharmaceuticals. Qualitativeandquantitativedeterminationscanbeobtainedond rug formulationsindevelopmental stagesorinproductionfortroubleshootingandimprovedproces smonitoring.Examples havebeenprovidedontheuniquefeaturesofthetechnologythat candetectthesurface andinternaldistributionofpharmaceuticalmaterials,provides informationonblendandtablet uniformity,coatingthickness aswellas distributionof lubricants anddisintegrants. LIBS is one of the advanced method for elemental detection, the applications presented here illustrate the capability of LIBS to fulfill the requirements of various analytical tasks in environmental technologies. This technique was found to be useful in space research tool .For analysis of pharmaceuticals; LIBS proved to be a great instrument, it can be used for analysis of elements from different dosage form like tablet, oral solutions, suspensions etc. Online analysis of elements by LIBS provides an important tool for quality assurance of pharmaceutical manufacturing.

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