

# LIBS Technique

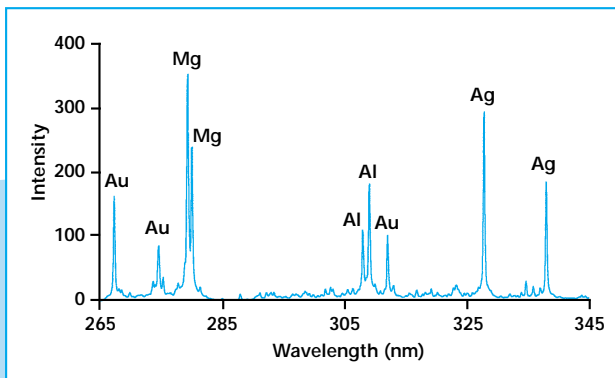
Laser-Induced Breakdown Spectroscopy

An Introduction to

## Laser-Induced Breakdown Spectroscopy

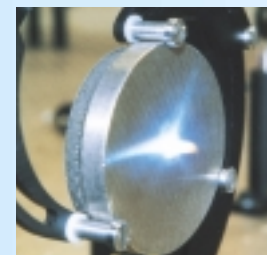
### how it works

Laser Spark Spectroscopy (LASS), Laser-Induced Plasma Spectroscopy (LIPS) or, as it is more often known, Laser-Induced Breakdown Spectroscopy (LIBS) is a form of atomic emission spectroscopy in which a pulsed laser is used as the excitation source. The basic principle is illustrated in the schematic diagram. The output of a pulsed laser, such as a Q-switched Nd:YAG, is focussed onto the surface of the material to be analysed. For the duration of the laser pulse, which is typically 10 nanoseconds, the power density at the surface of the material can exceed 1 Gigawatt per cm<sup>2</sup>



LIBS spectrum obtained from gold ore

using only a compact laser device and simple focussing lenses. At these very high power densities, a fraction of a microgramme of material is ejected from the surface by a process known as laser ablation and a short-lived but highly luminous plasma with instantaneous temperatures reaching 10,000°C is formed at the surface of the material. Within this hot plasma, the ejected material is dissociated into excited ionic and atomic species. At the end of the laser pulse, the plasma quickly cools as it expands outwards at supersonic speeds. During this time the excited ions and atoms emit characteristic optical radiation as they revert to lower energy states. Detection and spectral analysis of this optical radiation using a sensitive spectrograph can be used to yield information on the elemental composition of the material.



Laser spark on a solid surface

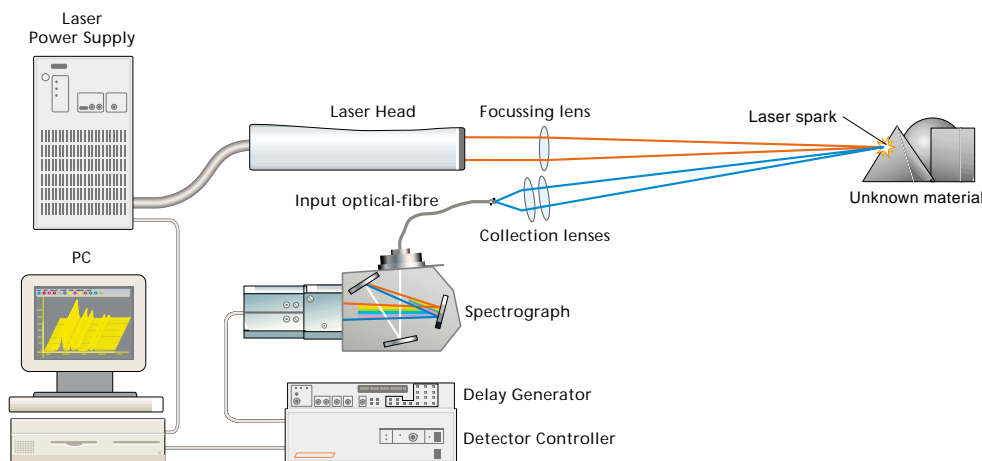


Laser spark on a liquid surface



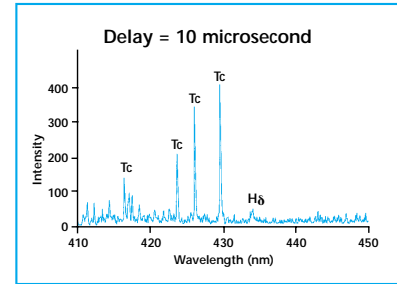
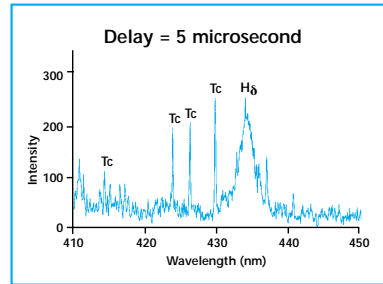
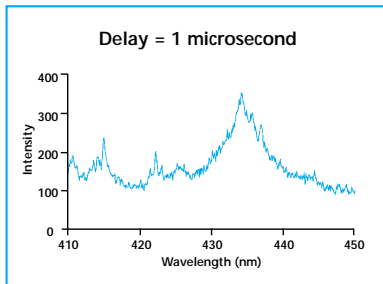
Laser spark in a gas

### Basic principle of LIBS



Time-gated detectors are employed which allow the optical emission from the laser plasma to be recorded at some time delay after the laser pulse. This is important

since the characteristic atomic and ionic emission lines only start to appear after the plasma has expanded and cooled. This can be seen in the following spectra where the characteristic technetium emission lines reach maximum intensity with a detector delay of 10 microseconds.



## virtually non-destructive analysis of any material

As only a minute amount of material is consumed in the process, LIBS is regarded as virtually non-destructive. Heating of the sample is negligible as the average power incident on the material is typically less than 1 Watt. In principle, LIBS is able to perform elemental analysis of any material, irrespective of its physical state. Solids, liquids, gases and various admixtures such as sludges, slurries, ores, waste material and effluents have been successfully analysed.

## remote analysis capabilities

Because LIBS is essentially an all-optical technique, only optical access to the material is required to carry out an analysis. This may be achieved by a direct line-of-sight method using one of our LSA T-Series telescope instruments for distances of up to about 10 metres or alternatively with one of our LSA F-Series optical-fibre probe instruments for distances of up to about 100 metres. These features make LIBS a particularly attractive solution for analysis of hazardous or high-temperature materials, or for deployment in hostile environments.

## Periodic table of the elements

1 H Hydrogen 1.00794																	5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	
3 Li Lithium 6.941	4 Be Beryllium 9.012182																	13 Al Aluminium 26.981538	14 Si Silicon 28.0855	15 P Phosphorus 30.973761	16 S Sulphur 32.066
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050	19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938049	26 Fe Iron 55.845	27 Co Cobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.92160	34 Se Selenium 78.96				
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60						
55 Cs Cesium 132.90545	56 Ba Barium 137.327	57 La Lanthanum 138.9055	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.078	79 Au Gold 196.96655	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98038	84 Po Polonium (209)						
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 (269)	111 (272)	112 (277)	113 (284)	114 (289)								
58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421										
90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)										

## no sample preparation necessary

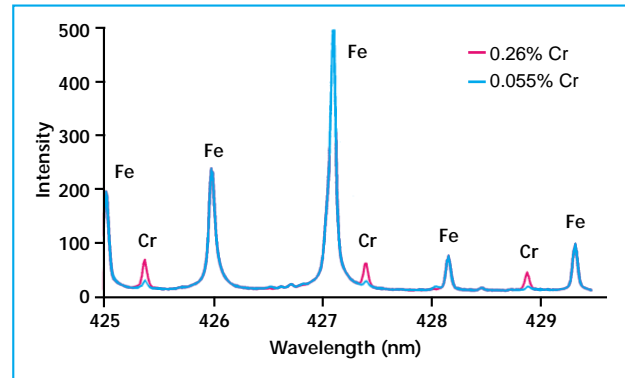
LIBS is able to analyse a material directly without the need to prepare the sample beforehand. Should the sample material be coated with another material (eg. oxidised or painted steel), the laser radiation may be used to first clean the surface of the sample in order to expose the underlying material to allow chemical analysis to be carried out. The efficiency of the laser cleaning process depends upon the type of material being removed and the power of the laser. As a general guide oxide, oil or paint layers of several hundred microns can be quickly removed using a compact and relatively low-power laser. The acoustic shock-wave of the laser plasma is particularly effective at removing the semi-liquid or viscous materials such as sludges. For example, LIBS has been used to analyse metals coated in several centimetres of magnesium hydroxide sludge.

## quantitative measurements of minor elements

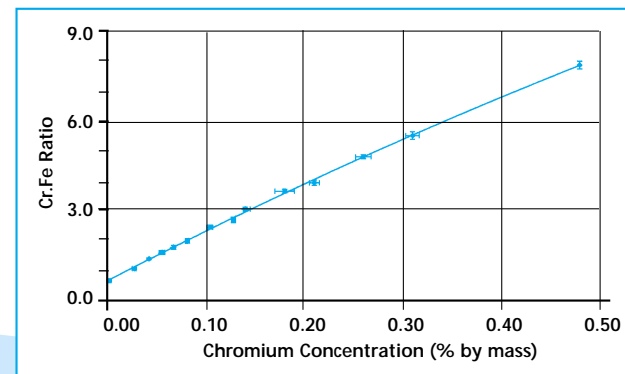
The LIBS instrument may be calibrated to perform quantitative measurements of minor elements within a matrix material; examples being chromium in steel, magnesium in aluminium alloy, iron in glass, copper in copper sulphate solutions. Calibration is achieved using matrix-matched certified reference materials containing various amounts of the analyte to be measured. A process known as "internal standardisation" is usually employed in which the intensity of the analyte line is ratioed with that of a matrix emission line; this helps to minimise the effects due to changes in plasma conditions caused by shot-to-shot fluctuations in laser energy. Good analytical performance can be achieved with careful design of the LIBS hardware and the use of appropriate measurement methodology. The measurement sensitivity of LIBS depends on many factors including the analyte / matrix combination and the distance over which the LIBS instrument is to operate should remote analysis be required. Measurement accuracy and precision of better than 10% and 5% respectively is possible; typical detection limits for the elements are given in the periodic table.

2 He Helium 4.003	10 Ne Neon 20.1797
F Fluorine 984032	18 Ar Argon 39.948
36 Kr Krypton 83.80	54 Xe Xenon 131.29
86 Rn Radon (222)	71 Lu Lutetium 174.967
Yb Ytterbium 3.04	103 Lr Lawrencium (262)

### Typical detection limits for LIBS



LIBS spectra obtained from steel showing Fe and Cr emission lines



Chromium calibration curve using Internal Standardisation

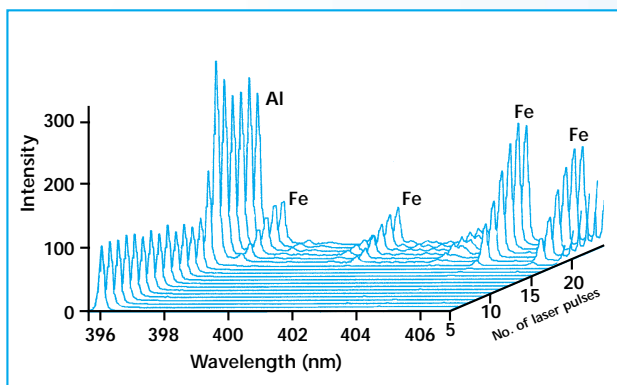
## high-speed, non-contact capabilities

In many cases, only one laser pulse is needed to analyse a material, allowing a large number of samples to be rapidly identified. This, together with the non-contact nature of LIBS, is important in applications such as the recycling of scrap metals, alloys or plastics where it can be used to identify a large number of particles moving at high speed on a conveyor belt. No other material analysis technique can match the performance of LIBS in this area.

## depth-profiling of layered structures and surface coatings

Since the laser may be used to remove surface coatings in a controlled manner, depth-profiling of layered structures is possible with LIBS. Spectroscopic measurements may be performed as the laser "drills" into the material, providing information on the elemental composition of the material as a function of distance into the layered structure.

Generally, this technique is effective only for materials that are relatively easy to ablate using laser powers typical of a LIBS instrument. Examples include compositional analysis of zinc coatings on steel for process control during manufacture, detection of heavy metals (lead, uranium, plutonium) in paint and detection of elemental contamination in concrete.



Depth-profile of galvanised steel showing increasing aluminium and iron signal as zinc coating is ablated

## applications

- Remote, non-invasive analysis, characterisation and identification of materials
- Remote detection and elemental analysis of hazardous materials (high-temperature, radioactive, chemically toxic materials)
- In-situ detection of radioactive contamination on storage containers (vitrified high-level waste, intermediate level waste)
- In-situ compositional analysis of steel components in difficult-access environments (nuclear reactor pressure vessels etc)
- Rapid identification of metals and alloys during recycling of scrap materials
- Positive Metal Identification (PMI) of critical components during manufacturing and assembly
- On-line compositional analysis of liquid metals and alloys for process control (carbon, silicon, phosphorus etc in steel)
- On-line compositional analysis of liquid glass for process control (iron, lead etc)
- In-situ identification of materials submerged in water (metals, alloys, ceramics, minerals, radioactive materials)
- Depth-profiling and compositional analysis of surface coatings (galvanised steel, plastic coatings, heavy-metals in paint)
- On-line monitoring of particulates in air (stack emission monitoring)
- Compositional analysis of complex shape objects

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