

## Remote compositional analysis of spent-fuel residues using Laser-Induced Breakdown Spectroscopy

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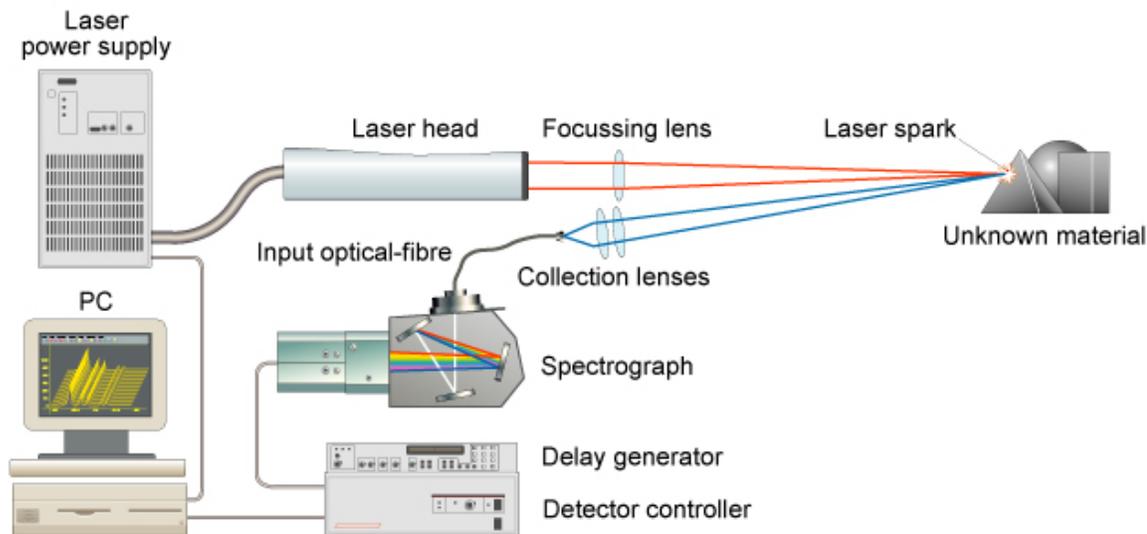
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### Abstract

We report on the application of a novel technique known as Laser-Induced Breakdown Spectroscopy (LIBS) for remotely detecting and characterizing the elemental composition of highly radioactive materials including spent-fuel residues and High-Level Waste (HLW). Within the UK nuclear industry, LIBS has been demonstrated to offer a convenient alternative to sampling and laboratory analysis of a wide range of materials irrespective of the activity of the material or the ambient radiation levels. Proven applications of this technology include in-situ compositional analysis of nuclear reactor components, remote detection and characterization of vitrified HLW and remote compositional analysis of highly-active gross contamination within a spent-fuel reprocessing plant.

### Introduction

LIBS is a form of atomic emission spectroscopy in which a pulsed laser is used as the excitation source. The basic principle is illustrated schematically in Fig. 1. 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> using only a compact laser device and simple focussing optics. 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 micro-plasma with instantaneous temperatures exceeding 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.



**Figure 1.** Schematic diagram illustrating the basic principle of LIBS. Only optical access to the material is necessary in order to perform an analysis.

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. As 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 a telescope LIBS instrument for distances of up to about 30 metres or alternatively with a fibre-optic probe instrument for distances of up to about 100 metres. These features make LIBS a particularly attractive option for analysis of hazardous or high-temperature materials, or for deployment in hostile environments. The telescope LIBS instrument opens up interesting possibilities by being able to characterize materials within a hot-cell simply by directing the laser beam into the cell through an existing lead-glass shield window.

During the past decade LIBS has found application in the UK nuclear industry in areas including power generation [1, 2], fuel manufacture [3] and spent-fuel reprocessing / waste management [4, 5]. A general review of the use of LIBS within the UK nuclear industry was presented at the LIBS 2002 conference held at Orlando, Florida during September 2002 [7].

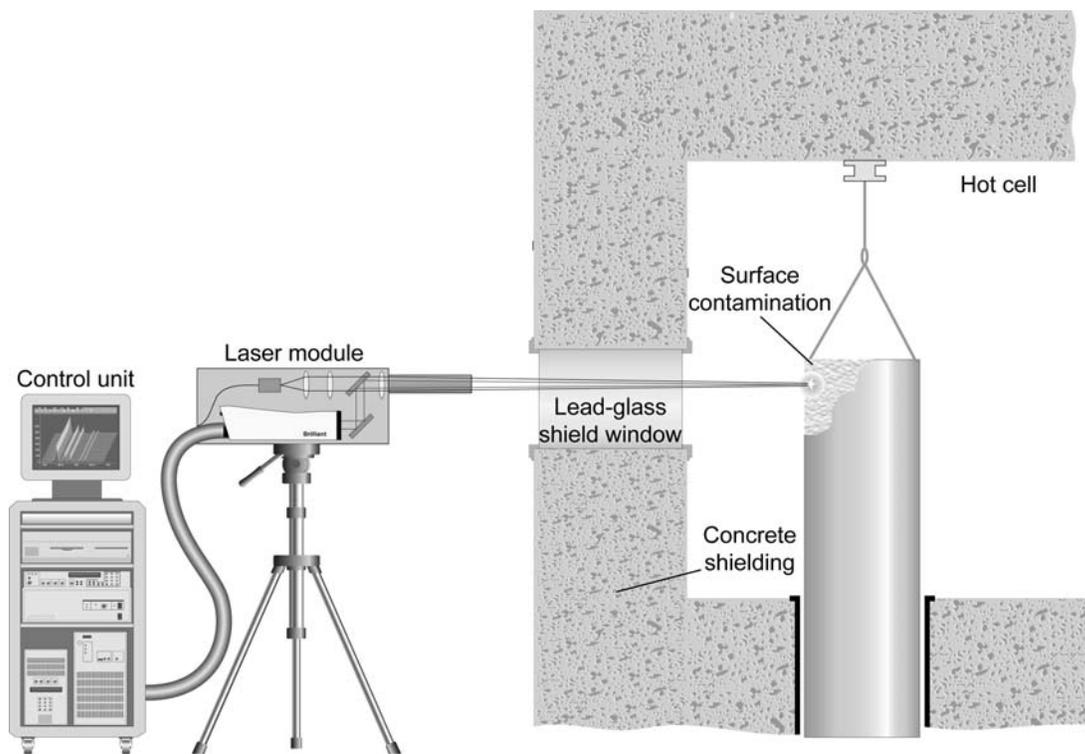
## Applications

### **In-situ compositional analysis of spent-fuel residues using a telescope LIBS instrument**

The first use of a telescope LIBS instrument to remotely analyse material within a hot-cell by directing the laser beam through a lead-glass radiation shield window was carried out in September 2001 at a nuclear reprocessing plant in the UK. A brief description of the background to this work is given.

Routine inspections of some steel components in a hot cell had identified an accumulation of a significant quantity of surface contamination. Characterisation of the contamination was required prior to decontamination and waste sentencing of the components. Radiometric measurements were taken to identify the radionuclide inventory of the contamination but as these provided no information on the non-active components, full characterisation was not possible. The material was highly radioactive making sample removal and laboratory analysis very difficult

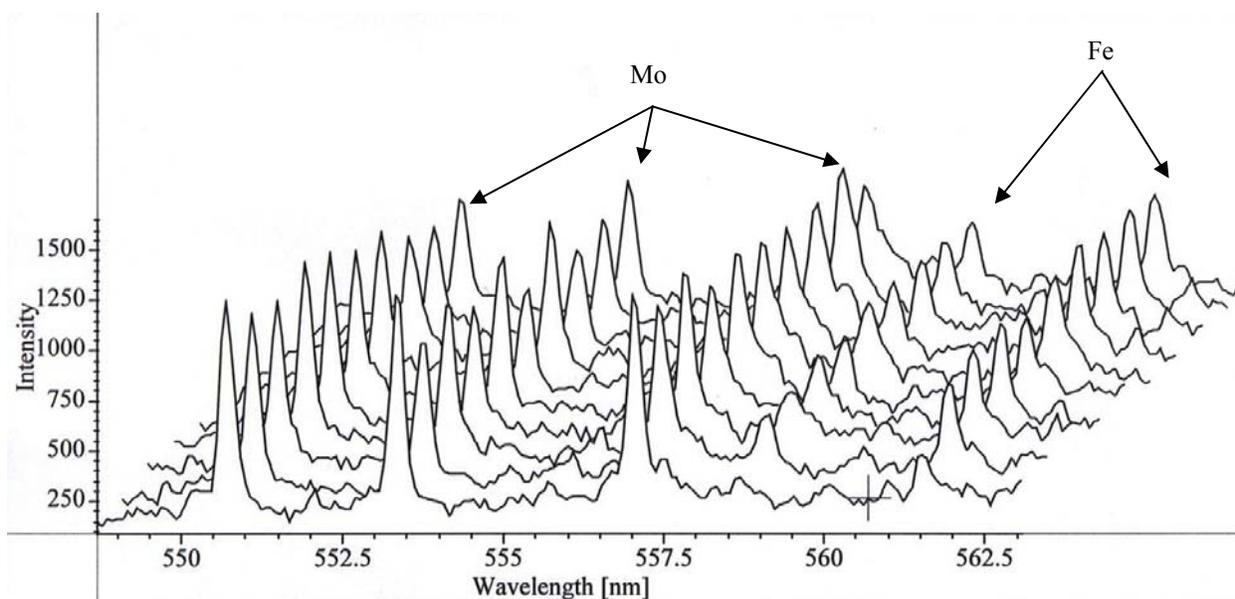
Optical access to the material was possible via a 1-metre thick lead-glass radiation shield window. The steel component could be positioned approximately 3 metres beyond the window and raised / lowered by means of a hoist within the hot-cell. The laser beam of the LIBS instrument could then be transmitted into the hot-cell via the lead-glass shield window and brought to focus on the contamination, as illustrated schematically in Fig. 2.



**Figure 2.** Schematic diagram illustrating the deployment of the telescope LIBS instrument

The optical properties of these shield windows are such that they are reasonably transparent to the laser radiation (>75% transmission @ 1064 nm) but effectively opaque to wavelengths shorter than about 500 nm. This limited the wavelength range over which the laser-induced plasma could be monitored to approximately 500 nm - 800 nm, the long wavelength limit being governed by the detector of the optical spectrograph. In order to prevent damage to the shield window, the intensity of the laser beam was maintained well below the damage threshold of the window components. In practice, this was achieved by ensuring that the diameter of the laser beam within the shield window is always sufficiently large to maintain laser energy densities at least a factor of ten below the damage threshold of the glass. An unavoidable consequence of this requirement is that the material being analysed must be located at some distance (typically >1.5

metres) from the inside face of the shield window. During use, the Nd:YAG laser was set to its maximum output energy, i.e. 350 mJ per pulse and test measurements were conducted to establish how many laser pulses were required to “drill” through the contaminant material. This was carried out by recording a kinetic series of ten spectra, where each spectrum consisted of the accumulation of 50 laser shots. By observing the intensity of the Fe emission lines at 558.7 nm and 561.6 nm, it was possible to estimate the number of laser pulses required to remove the contaminant material thus allowing the laser beam to interact with the steel of the component. As can be seen in Fig. 3, the steel was exposed after approximately 100 laser pulses. All further measurements, therefore, were limited to 50 laser pulses at any one position.

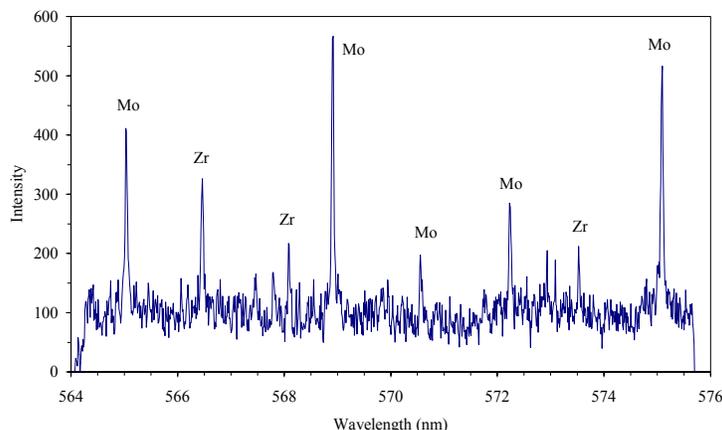


**Figure 3.** Kinetic series of 10 spectra, 50 accumulations (laser shots) per spectrum. The spectra are arranged with those taken first in the foreground. Fe emission lines start to appear after about 100 laser shots, indicating that the laser beam is interacting with the steel of the component.

The results of the measurements showed that the contaminant material was rich in zirconium and molybdenum; an example of a spectrum obtained during these measurements is given in Figure 4. Combining this information with existing knowledge of the chemistry of the plant process, it was reasonable to deduce that the contaminant material consisted mainly of zirconium molybdate - a material which is known to form during the reprocessing of spent-fuel and, due to its insolubility in nitric acid, readily precipitates out of solution [8].

To support the results of the plant experiments further laboratory experiments were undertaken. Using a mock-up hot-cell to simulate the measurement conditions of the reprocessing plant, the LIBS instrument was later used to record spectra from various inactive simulate materials containing i) various relative concentrations of  $ZrO_2$  and  $MoO_3$  and ii) zirconium molybdate. The results of these experiments confirmed that the LIBS measurements are sensitive to variations in the Zr:Mo ratio and that the LIBS spectra obtained from zirconium molybdate were found to closely match the spectra recorded for the contaminant material.

Although the LIBS measurements were not able to directly confirm the chemical form of the contaminant material, the results of the inactive experiments helped to provide support to the theory that the zirconium and molybdenum detected by the LIBS instrument were probably in the form of zirconium molybdate.



**Figure 4.** Example of a (single laser shot) spectrum obtained during “Through-Window” LIBS compositional analysis of the contaminant material. The detection of zirconium and molybdenum in relatively high abundance was consistent with the material being composed mainly of zirconium molybdate.

### **In-situ detection and characterisation of HLW residues using a fibre-optic probe LIBS instrument**

In some situations it is necessary to generate higher quality spectra than achievable using telescope LIBS. Use of a fiber optic cable to direct the laser light to the sample and take emitted light to the spectrograph allows a wider range of wavelengths to be detected since collection of the plasma light is not restricted by the optical properties of the shield window. Greater sensitivity is a further advantage. The deployment of this type of LIBS instrument requires the use of a remote probe attached to the control unit via a flexible umbilical containing an optical-fiber cable. The probe and umbilical are posted into the hot-cell via a suitable port and positioned within the cell using a Master-Slave Manipulator (MSM).

This instrument may be used to detect “fixed” contamination on the external surfaces of HLW drums, such contamination occasionally arising from splashing of the liquid glass during the drum filling process [6, 9]. This type of contamination is particularly difficult to detect using conventional methods such as robotic swabbing. Furthermore it cannot be detected in-situ by radiometric techniques since the background radiation levels in the vicinity of the HLW drum are often in excess of 1000 Sv / hr ( $10^5$  Rad / hr), thereby making it impossible to distinguish the gamma emissions of the contamination from those of the contained waste. A LIBS instrument, however, may be used to detect the presence of contamination by directly identifying the presence of either the active components (within the sensitivity limitations of the technique) or the inactive matrix (sodium, lithium etc).

In another application, the fiber-optic LIBS probe may be used to analyse various residues within a HLW vitrification plant as an alternative to conventional sampling and laboratory analysis. Work is currently underway to use the LIBS instrument to remotely determine the calcine (fission-product waste) content of various residues within the plant. A feasibility study using inactive simulate materials has demonstrated that the LIBS instrument is able to measure the

calcine content over the approximate range 1% to 80% with a measurement precision of approximately 15%. Deployment of the LIBS instrument at the HLW vitrification plant is planned for the first quarter of 2003.

## Conclusions and discussion

The LIBS technique has been shown to be a useful tool for remotely characterising highly radioactive materials and can often provide a convenient alternative to conventional sampling and laboratory analysis. Although still regarded as an emerging technology, LIBS has found application in the nuclear industry in areas such as power generation, fuel manufacture and spent-fuel reprocessing / waste management. The unique remote deployment capabilities of LIBS can offer significant benefits compared with sampling and off-line laboratory analysis of materials, including rapid measurement times, reduced risk of contamination spread, chemical analysis of difficult materials such as spent-fuel residues and vitrified HLW waste, and significant overall cost savings. LIBS offers an elegant and unique solution to the problem of detecting fixed contamination on vitrified HLW drums and also offers the potential for providing on-line compositional measurements of vitrified HLW feedstock and processed materials which may be used to enhance process control and product quality.

## References

1. A DUCKWORTH, "Remote metal analysis by laser-induced breakdown spectroscopy," *British Nuclear Engineering Society (BNES) Conference Proceedings, Remote Techniques for Hazardous Environments*, p259-263, (1995)
2. A.I. WHITEHOUSE, J. YOUNG, I.M. BOTHEROYD, S. LAWSON, C.P. EVANS, J. WRIGHT, "Remote material analysis of nuclear power station steam generator tubes by laser-induced breakdown spectroscopy", *Spectrochim. Acta Part B*, **56**, p821-830, (2001)
3. J. YOUNG, I.M. BOTHEROYD, A.I. WHITEHOUSE, "Trace element analysis of uranium metal fuel using laser-induced breakdown spectroscopy", *Conf. on Electro-Optics and Lasers (CLEO/Europe)*, Glasgow, UK, p201, (1998)
4. J YOUNG, I M BOTHEROYD, A I WHITEHOUSE, "Remote analysis of nuclear and non-nuclear materials using laser-induced breakdown spectroscopy", *Conf. on Electro-Optics and Lasers (CLEO/Europe)*, Hamburg, Germany, (1996), p152
5. I.M. BOTHEROYD, J. YOUNG, A.I. WHITEHOUSE, A. DUCKWORTH, "Remote analysis of steels and other solid materials using laser-induced breakdown spectroscopy (LIBS)", *Conf. on Lasers and Electro-Optics-Europe (CLEO/Europe)*, Glasgow, UK, p198 (1998)
6. Applied Photonics Ltd, "Laser spectroscopic remote detection of surface contamination", International Patent Application No. PCT/GB01/00866
7. A.I. WHITEHOUSE, J. YOUNG, C.P. EVANS, "Extreme LIBS", LIBS 2002 Technical Digest, Conference on Laser Induced Plasma Spectroscopy and Applications (organised by Optical Society of America), Orlando, Florida, September 25-28, (2002), pp. 2-4.
8. F.J. DOUCHET, F.J., GODDARD, D.T., TAYLOR, C.M, DENNISS, I.S., HUTSHISON, S.M. AND BRYAN, N.D. "The formation of hydrated zirconium molybdate in simulated spent nuclear fuel reprocessing solutions." *Physical Chemistry Chemical Physics* **4**, 14, pp3491-3499 (2002).
9. US Department of Energy. "Waste Acceptance Product Specifications for Vitrified High Level Waste Forms" <[www.em.doe.gov/waps/](http://www.em.doe.gov/waps/)> (last checked 02/07/03) section 3.7 (1996)