Deployment of an ST-LIBS instrument at the High-Level Waste Vitrification Plant, Sellafield (2003)

Overview of application

A ST-LIBS instrument was deployed at BNFL's Waste Vitrification Plant (WVP) by directing the laser beam into the cell through a lead-glass shield window to analyse various materials.

Sellafield site, Cumbria, UK

Location:	High-Level Waste (HLW) Vitrification Plant, Sellafield, UK
Inspection task:	In-situ characterisation of HLW residues
Environment:	Hot cell with dose rates up to 3,000 Sv / hr
Location of material:	Directly in front of a lead-glass shield window
Access:	Line-of sight optical access to sample via shield window

ST-LIBS instrument design

This ST-LIBS instrument was of the basic design described earlier in this report. The ST-LIBS instrument incorporated a Q-switched, pulsed, Nd:YAG laser operating at a wavelength of 1064 nm and capable of producing a maximum pulse energy of 260 mJ in a 5 ns pulse length. The laser could be operated in either a manual, single pulse, mode or at a pulse repetition frequency of 20 Hz. A low-power (Class 1, eye-safe), visible He-Ne laser beam, transmitted collinearly with the Nd:YAG laser beam, was used to aid alignment of the LIBS instrument with the material to be analysed prior to making a measurement. Since the LIBS instrument is by design an "open beam" Class 4 laser device, all personnel within the work area were required to wear appropriate laser goggles during activation of the Nd:YAG laser. A 500 mm focal length spectrograph fitted with a 600 lines/mm diffraction grating and an intensified, time-gated, photodiode array detector was used to record the plasma light detected by the LIBS instrument. The measurement data obtained from the ST-LIBS instrument were in the form of emission spectra within the wavelength range 450 to 900 nm.

Applied Photonics Limited Unit 8 Carleton Business Park, Skipton, North Yorkshire BD23 2DE United Kingdom
Telephone: +44 (0)1756 708900 **Email:** mail@appliedphotonics.co.uk **Website:** www.appliedphotonics.co.uk

The spectral emission lines were identified according to the National Institute for Standards and Technology (NIST) atomic spectra database (http://physics.nist.gov/PhysRefData/ASD/lines_form.html).

The sample was positioned within the cell so that the distance from the inner surface of the radiation shield window to the sample was approximately 2 metres, therefore ensuring that the energy / power density of the laser beam within the shield window was sufficiently low so as not to cause damage to the window material. The sample was also positioned so that a direct line of sight from the instrument to the sample was achieved. The Nd:YAG laser beam was focused onto the sample so as to generate a plasma on the sample surface. A number of test shots were taken so that adjustment of the focal length of the ST-LIBS instrument could be made to achieve maximum plasma brightness as determined by monitoring the intensity of the spectra recorded by the instrument.

In order for the instrument calibration to be valid for the in-cell measurements conducted at WVP, it was necessary to reproduce the measurement conditions used during the inactive calibration conducted at APL's facilities. The principal measurement conditions that needed to be satisfied were:

1. The composition of the unknown material must be within the range of the calibration reference samples used to produce the calibration data.
2. The laser energy incident on the surface of the unknown material must be similar to that used during the calibration measurements (ie. ~180 mJ at the sample corresponding to ~230 mJ exiting the LIBS instrument).
3. The laser beam should be correctly focussed on the surface of the unknown material (spot size ~1 mm).

The optical absorption properties of the WVP shield window should be similar to those of the shield window of APL's mock-up hot cell.

Data analysis

Two samples were made available for analysis within the WVP cell; Sample A, a deposit contained within an aluminium receptacle (the inside compartment of an in-cell vacuum cleaner) and sample B, a deposit on the inside surface of a cylindrical filter component.

After having aligned the LIBS instrument with sample A, test shots showed that it was difficult to produce a suitably bright plasma on the surface of the material. This was thought to be due to a combination of i) the inside face of the shield window being coated in a residue which was attenuating the laser beam and ii) the WVP shield window is 1.0 m thick whereas the shield window used during the inactive calibration measurements was 0.75 m thick. To overcome this, the laser pulse energy exiting the ST-LIBS instrument was increased from ~230 mJ to ~260 mJ, i.e. the maximum pulse energy attainable. The increased pulse energy made it possible to produce a plasma on the surface of the sample but, on observing the intensity of the detected plasma light, it was judged that the pulse energy at the sample was significantly less than the ~180 mJ used during the inactive calibration measurements. The reduced intensity at the sample could invalidate the calibration of the ST-LIBS instrument although it should be possible to overcome this by recalibrating the instrument using a reduced laser pulse energy – the new calibration could be performed at a later date and so data recorded during the WVP in-cell measurement campaign would still be useful.

The nomenclature used in the following paragraphs for describing the various spectral emission lines is, using sodium (Na) as an example, as follows:

Na(I):	emission line from atomic sodium (atomic emission line)
Na (II):	emission line from singly ionised sodium ion (first ionic emission line)
2 x Na(I):	two unresolved sodium atomic emission lines

Measurements were made on Sample A by acquiring 100 laser pulses per sample position and repeating for seven different positions. The recorded spectra are illustrated in the figure below. An additional measurement of Sample A was made over an extended wavelength range (using the "step and glue" function of the spectrograph software) covering the wavelength range 450 nm – 700 nm; the resulting spectrum is illustrated in the figure below.

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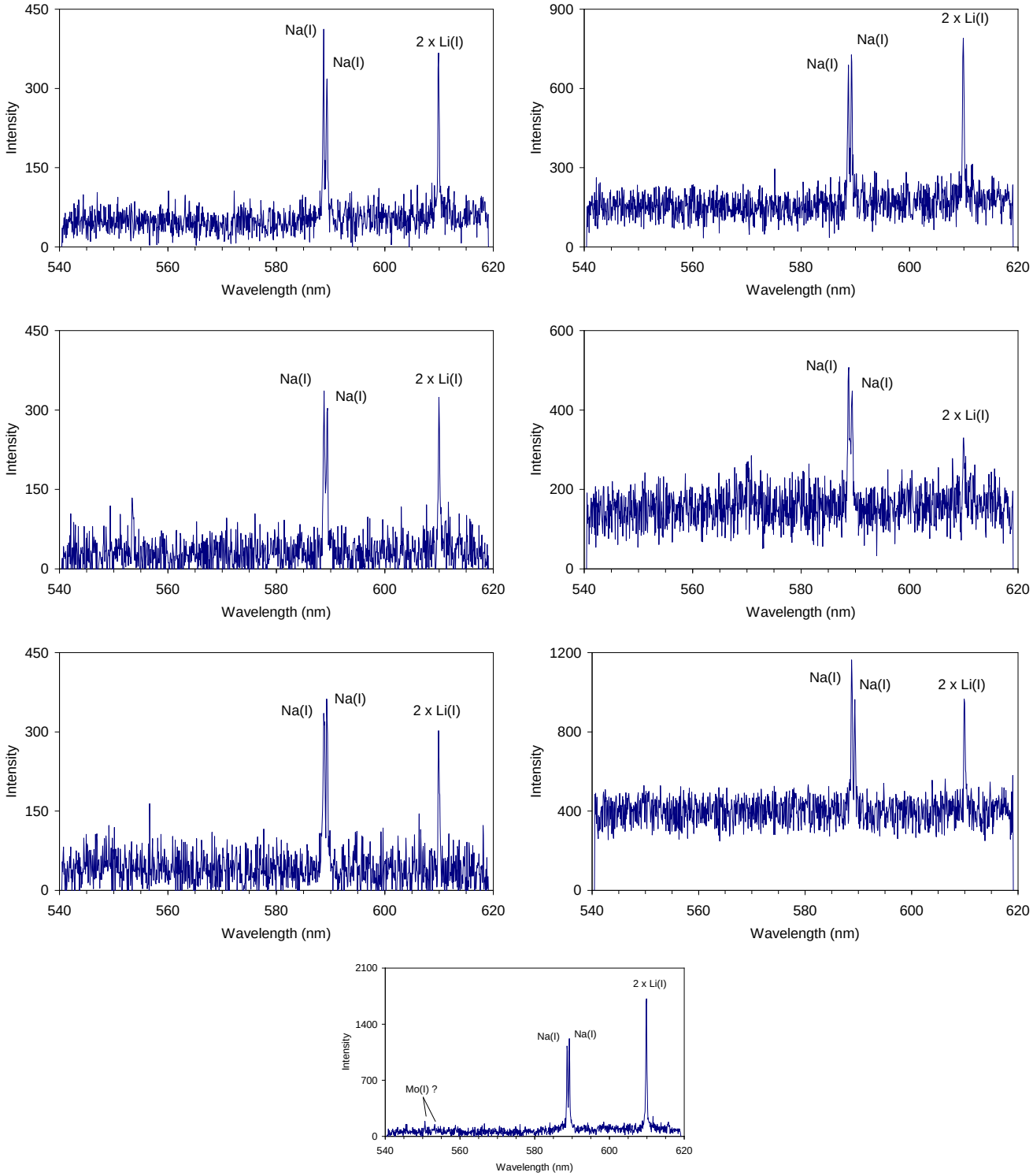
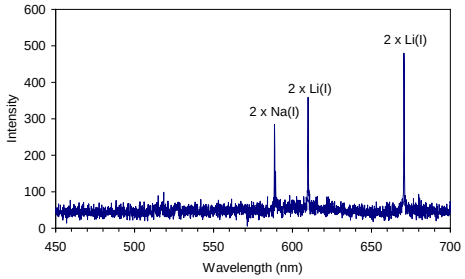
Telephone: +44 (0)1756 708900 **Email:** mail@appliedphotonics.co.uk **Website:** www.appliedphotonics.co.uk



Spectra acquired from seven positions on sample A, showing spectral emission lines characteristic of Na (589.0 nm and 589.6 nm) and Li (610.35 nm and 610.37 nm) with evidence of weak Mo emissions at 550.6 nm and 553.3 nm



Extended emission spectrum obtained from sample A over the wavelength range 450 to 700 nm.

Applied Photonics Limited Unit 8 Carleton Business Park, Skipton, North Yorkshire BD23 2DE United Kingdom
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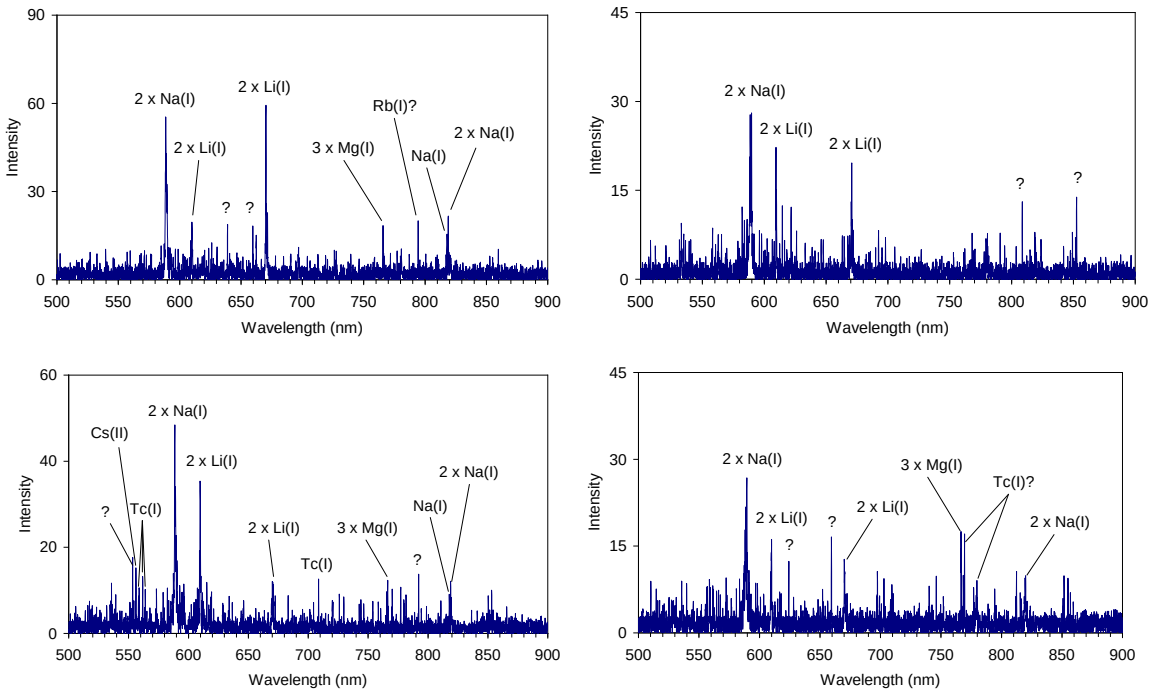
Measurements were then made on sample B, but the powder-like nature of the material was such that multiple pulses of the laser radiation quickly removed the material from the filter component. It was necessary, therefore, to record a single-pulse spectrum and then realign the laser beam to a new area of sample to record the next single-pulse spectrum and so on. Since each spectrum was formed by a number pulses covering different wavelength ranges, which were merged using the "step and glue" function, this was a time-consuming process and only four spectra were recorded; these are illustrated below.



Extended emission spectra acquired from sample B, all of which exhibit spectral lines characteristic of Na and Li, while some spectra appear to also exhibit lines characteristic of Mg, Rb, Cs and Tc.

The spectral emission lines identified through NIST for spectra recorded for samples A and B are summarised in the following tables.

Element	Ionisation State	Wavelength (nm)
Na	Atomic	588.995 589.592
Li	Atomic	610.353 610.366 670.776 670.491
Mo	Atomic	550.649 553.305

Summary of identified emission lines from sample A.

Element	Ionisation State	Wavelength (nm)
Na	Atomic	588.995 589.592 818.326 819.479 819.482
Li	Atomic	610.353 610.366 670.776 670.791
Mg	Atomic	765.760 765.915 765.990
Rb	Atomic	794.760
Cs	First ionic	556.302
Tc	Atomic	558.902 562.045 564.213 708.618

Summary of identified emission lines from sample B.

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The residue on the inside face of the shield window is believed to have resulted in a significant attenuation of both the laser beam being transmitted into the cell and the plasma light exiting the cell. The thicker shield window of the WVP cell compared to that of the mock-up hot cell (i.e. 1.0 m as opposed to 0.75 m) would also have contributed to the increased attenuation. The consequent reduction in the intensity of the laser beam incident on the sample, as evidenced by the difficulties experienced in achieving a sufficiently bright plasma, compromised the validity of the calibration of the ST-LIBS instrument. Furthermore, the data obtained during the measurements at WVP showed that samples A and B were not of the same composition as the inactive reference materials previously used to calibrate the ST-LIBS instrument since significant quantities of sodium (Na) were present in both samples. Hence the calibration of the ST-LIBS instrument was not valid for the materials analysed within the WVP cell. The detection of sodium in both samples suggested that glass was present. Some of the spectra recorded for sample A showed evidence of molybdenum but the characteristic emission lines were only just discernible above background noise. Sample B appeared to contain detectable concentrations of elements characteristic of calcine (i.e. caesium and technetium) but the signal-to-noise ratio was poor since the powder-like nature of the material restricted the measurements to single laser pulse spectra. The poor signal-to-noise ratio and limited optical resolution of the spectrograph were such that we could not be certain that the observed emission lines are due to caesium and technetium.

References

A I Whitehouse, J Young, C P Evans, A Brown (Applied Photonics Ltd.), J Franco, A Simpson (BNFL Instruments Inc.), *Remote Characterization of HLW using Laser-Induced Breakdown Spectroscopy*, Presented at: 10th International High-Level Radioactive Waste Management Conference (IHLRWM), March 30 - April 2, (2003), Las Vegas, Nevada, USA.

A I Whitehouse, J Young, C P Evans, A Brown (Applied Photonics Ltd.), J Franco, A Simpson (BNFL Instruments Inc.), *Remote compositional analysis of spent-fuel residues using Laser-Induced Breakdown Spectroscopy*, Presented at: Waste Management 2003 Symposium (WM '03) February 23 - 27 (2003), Tucson, Arizona, USA.

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