Remote characterisation of high-level radioactive waste at the THORP nuclear reprocessing plant (2001)

Overview of application

This application was the first known use of ST-LIBS to analyse materials through a radiation shield window. As a consequence, extensive work was required to investigate the properties of the shield window and to assess and minimise the possibility of any potential damage caused to it by the laser radiation.

In the THORP (Thermal Oxide Reprocessing Plant) facility at Sellafield, West Cumbria, spent fuel from nuclear reactors around the world is sheared into short pieces between 2.5cm and 10cm in length as a precursor to fuel dissolution. The sheared fuel pieces, comprising metal cladding and fuel, fall down a chute into a perforated basket which is suspended in hot (90ºC) 7M nitric acid. For operational reasons, the plant uses a total of seven baskets. As a consequence of increased levels of corrosion of the baskets it became necessary to replace them to allow continued operation of the dissolution cycle.

Thermal Oxide Reprocessing Plant (THORP), Sellafield, UK

Routine camera inspections had identified an accumulation of a solid material in the upper, vapour area of the basket. Characterisation of this surface residue material (SRM) was required to aid waste sentencing of the redundant baskets. Radiometric measurements were taken to identify the radionuclide inventory of the deposit but as these provided no information on the non-radioactive components, full characterisation was not possible. Due to the difficulties in taking an active sample from behind the biological shield and the subsequent difficulties with laboratory analysis, a remote method for analysis was investigated.

Location:	Basket Handling Cave (spent-fuel dissolution), THORP plant, Sellafield, Cumbria, United Kingdom
Inspection task:	Characterisation of gross contamination
Environment:	Hot Cell (HLW - on the order of 100 Sv/hr)
Location of material:	Upper section of dissolver baskets
Access:	Optical access via lead-glass shield window

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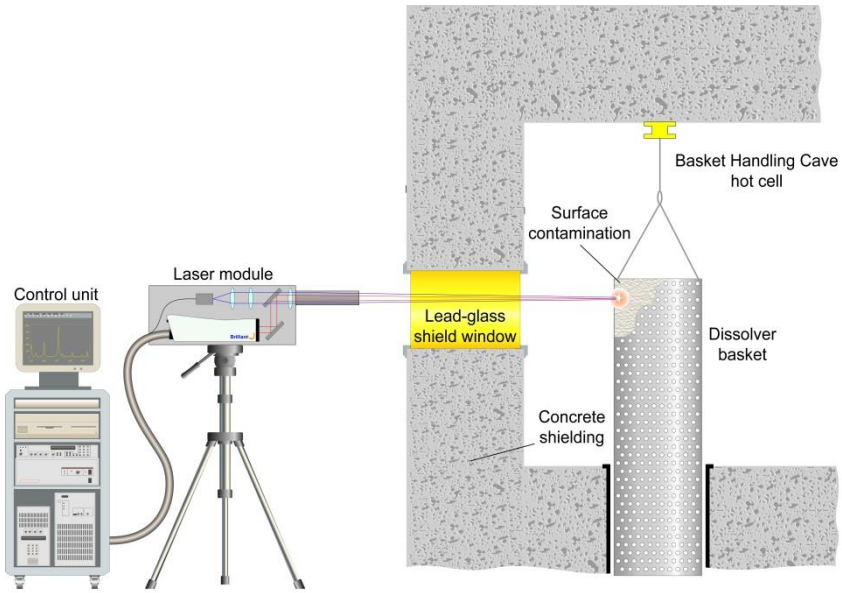
ST-LIBS instrument design

This ST-LIBS instrument was of the basic design described earlier in this report.

Optical access to the material was possible via a 1-metre thick lead-glass radiation shield window. The component could be positioned approximately 3 metres beyond the window and raised / lowered by means of a hoist within the hot cell.



Schematic illustrating the deployment of the ST-LIBS instrument at the Basket Handling Cave, THORP

Shield window data

The customer provided information on the properties of the radiation shield window and these data were used to inform the design of the LIBS instrument used to perform the analyses. This information and the associated design considerations are summarised in the following paragraphs.

Two types of RS 253 G glass are available for use as shielding glass, RS 253 G 18 and RS 253 G 25 and are designated by the concentration of cerium oxide within the glass. RS 253 G 25 is a highly stabilised shielding glass and is suitable for high radiation dose rates. From the internal transmittance versus wavelength figures supplied for both glasses, the lower cut-off wavelength for RS 253 G 25 offers the worst case scenario, where the transmittance is given as ~ 10% at 400 nm wavelength (for 100 mm thick glass). The approximate internal transmittance for RS 253 G 25 at various key wavelengths is given in the following table.

Wavelength (nm)	Approximate Internal Transmittance (%)
400	10
450	58
500	78
550	85
700	95

Approximate internal transmittance for 100mm thick glass RS 253 G 25 at various wavelengths

Also, from internal transmittance data on other types of glass such as BK7, synthetic fused silica, crown glass and borosilicate glass, the transmittance remains essentially constant at >90% for wavelengths from 700nm to >1200nm.

The radiation shield window used at the Basket Handling Cave (Thorp) is a Harwell type 51 window. The supplied drawing indicated that the window glass is comprised of 5 sections of thickness, 103, 258, 203, 203 and 203 mm. The total thickness of glass (970 mm) was assumed to be 1000 mm for the purposes of internal transmittance characteristics of the whole window. This is summarised in the following table.

Wavelength (nm)	Approximate Internal Transmittance (%)
400	~0
450	<1
500	8
550	20
700	60

Approximate internal transmittance for radiation shield window Harwell type 51 using glass RS 253 G 25

From the values given in this table, only wavelengths of approximately 500 nm and higher can be considered as being effectively transmitted by the radiation shield window.

The optical faces of the glass have had 'anti-reflection treatment'. The anti-reflection (AR) treatment is probably a broadband AR coating applied to the glass and designed to be most effective at the sodium D-line emissions at ~590 nm. The reflection per glass surface is quoted as approximately 0.5%, for normal incidence light at D-line wavelengths. The AR coating will, however, give a different reflectance for different incident wavelengths (e.g. the laser wavelength of 1064 nm).

Generally, for LIBS measurements, the spectral range that can be viewed by the spectrograph is approximately 180 to 1000 nm. The transmittance characteristics of the shield window, however, dictate that the effective spectral range that can be viewed is limited to approx. 500 to 1000 nm. The three strongest atomic (I) and the strongest ionic (II) emission wavelengths for the elements of specific interest (i.e. U, Sb, Zr, Mo, Cs, Co) over this spectral range are given in the table below.

Element	Emission Type (I/II)	Wavelength* (nm)	Emission Intensity
U	I	502.7	170
	I	591.5	230
	I	644.9	110
	II	549.3	160
Sb	I	563.2	100
	I	784.4	80
	I	792.5	200
	II	600.5	100
Zr	I	612.7	680
	I	709.8	540
	I	716.9	590
	II	519.2	100
Mo	I	550.6	7800
	I	553.3	5200
	I	557.1	2500
	II	-	-
Cs	I	672.3	3300
	I	697.3	4800
	I	794.4	3300
	II	522.7	75000
Co	I	521.3	50
	I	523.0	50
	I	524.8	50
	II	-	-

Spectral emissions from elements of interest and their relative intensities (according to NIST)
(* Wavelength through air)

The wavelengths and intensities given in this table are quoted from the National Institute for Standards and Technology (NIST), "Standard Reference Database 38, On Spectroscopic Properties Of Atoms And Atomic Ions", 1992. All wavelengths given in this table are for propagation of light through air.

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In addition to the elements in this table, other elements that may be of interest are given in the following table. Most of these elements were selected as they represent some of the highest yield products derived from thermal fission. Iron was chosen as this is the major constituent element of the stainless steel plant.

From the information in the above and following tables, the spectral emission from some elements is significantly stronger than others. The detection of an elemental species is, however, dependent on both the line emission intensity and the concentration (% by mass) of the element.

Element	Emission Type (I/II)	Wavelength* (nm)	Emission Intensity
Sr	I	548.1	7000
	I	640.9	9000
	I	650.4	5500
	II	-	-
Tc	I	509.6	5000
	I	516.2	2000
	I	558.9	3000
	II	-	-
Ba	I	706.0	6000
	I	712.0	2400
	I	728.0	3000
	II	614.2	20000
Ce	I	516.0	280
	I	569.7	300
	I	569.9	370
	II	508.0	470
Fe	I	516.8	2500
	I	522.7	1000
	I	527.0	1200
	II	645.6	200

Spectral emissions from other elements of potential interest and their relative intensities (according to NIST).
(* Wavelength through air)

Risk assessment and method statement

Prior to deployment of the instrument on the customer's site a full risk assessment was conducted and a method statement developed. An important part of this process was to assess the potential risk of laser damage to the shield window.

The ST-LIBS instrument was designed to maintain the laser beam diameter within the window / alpha plate at a sufficiently large diameter to ensure that the intensity of the laser radiation was typically an order of magnitude below the damage threshold of glass. The ST-LIBS instrument was tested using the shield-window in APL's inactive hot-cell mock-up facility. Previous work conducted by APL used very high intensities through the lead-glass window of this facility to establish the onset of damage and to assess the degree of damage. The damage identified during this work consisted essentially of what appeared to be localised (i.e. very close to the focal point of the laser beam) micro-cracking / discoloration of the glass. It is important to note that in order for such damage to occur, the laser beam needed to be tightly focussed within the lead-glass. The deployment of the ST-LIBS instrument was such that the focal-plane of the laser beam was set to be not less than about 1.5 metres from the alpha plate (i.e. the minimum focal-length of LIBS instrument was approximately 3.5 metres). This required that the material being analysed be positioned at approximately 2 metres beyond the window inside the hot cell.

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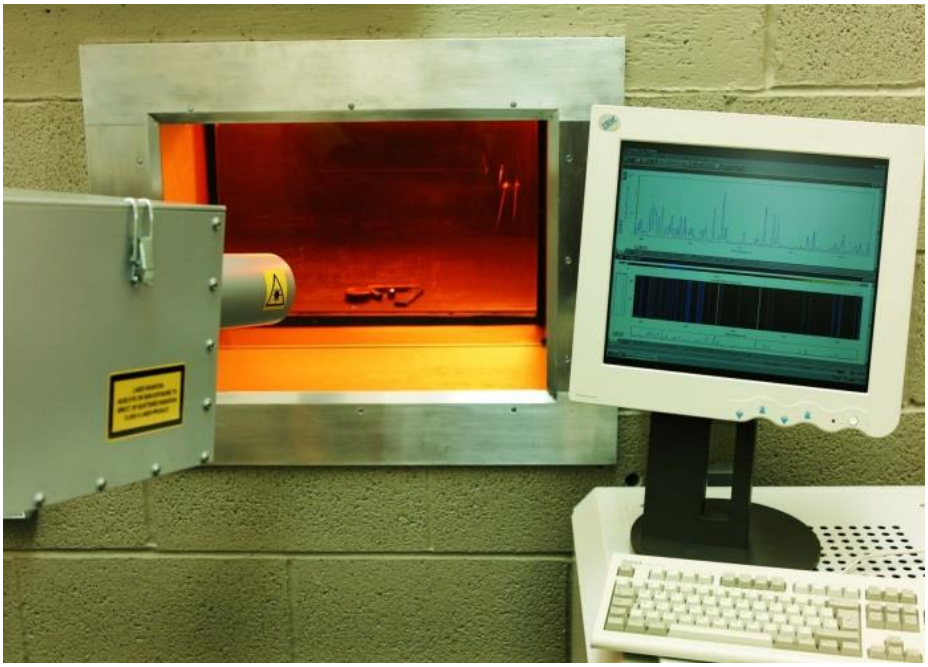

Testing the ST-LIBS instrument in an inactive mock-up hot cell with 0.75-metre thick lead-glass shield window

Data analysis / Plant trials

In September 2001 APL carried out the first reported use of remote analysis of a material within a hot cell by directing the laser beam of an ST-LIBS instrument through a lead-glass radiation shield window.

The Nd:YAG laser was set to its maximum output energy, i.e. 350 mJ per pulse. The laser radiation was brought to focus on various positions of the SRM and spectra recorded across the wavelength range 500 nm to 800 nm. In order to check that the analysis was of the surface deposit rather than the underlying steel, a number of kinetic series spectra were recorded and used to observe changes in elemental composition as the laser "drilled" through the material. The kinetic series spectra, illustrated in figure 1, indicated that at least 50 laser pulses could be used without the laser beam interacting with the underlying steel. After approximately 100 laser shots, Fe emission lines (558.676 nm and 561.564 nm, NIST relative intensities of 120 and 200 respectively) started to appear in the spectra indicating that the laser beam was probably interacting with the underlying steel. Accordingly, all subsequent spectra were obtained by taking an accumulation of 50 laser shots.

The optical spectrograph settings were:

- Delay: 850 ns
- Gate: 25000 ns
- Slit width: 50 microns
- Detector intensifier: Full gain

The recorded spectra showed that only Mo, Zr, Cr and Cs were present in the SRM at significant concentrations (ie. within the sensitivity limitations of the LIBS instrument). Due to the nature of the application, it is difficult to predict a generalised limit-of-detection (LOD) for the ST-LIBS instrument, although 1000 ppm would not be unrealistic for most elements. No emission lines for U, Sb or Co were observed in the spectra. The weak emission lines of these elements, however, would mean that they would have to be present at relatively high concentrations; for example, it was estimated that Co would have to be present at percentage levels in order to be detected by the LIBS instrument.

The general spectral intensity for each acquired spectrum varied from measurement to measurement since it was not possible to accurately focus the laser beam when targeting a new area of the SRM. Other wavelength regions did not exhibit any useful emission lines and hence are not included in this report.

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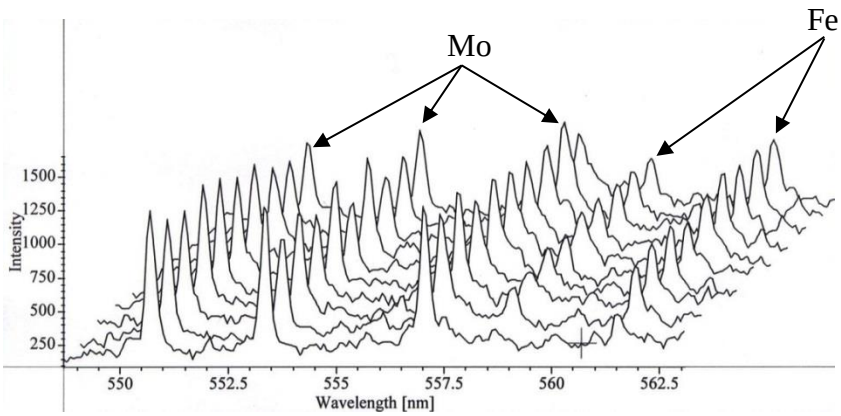
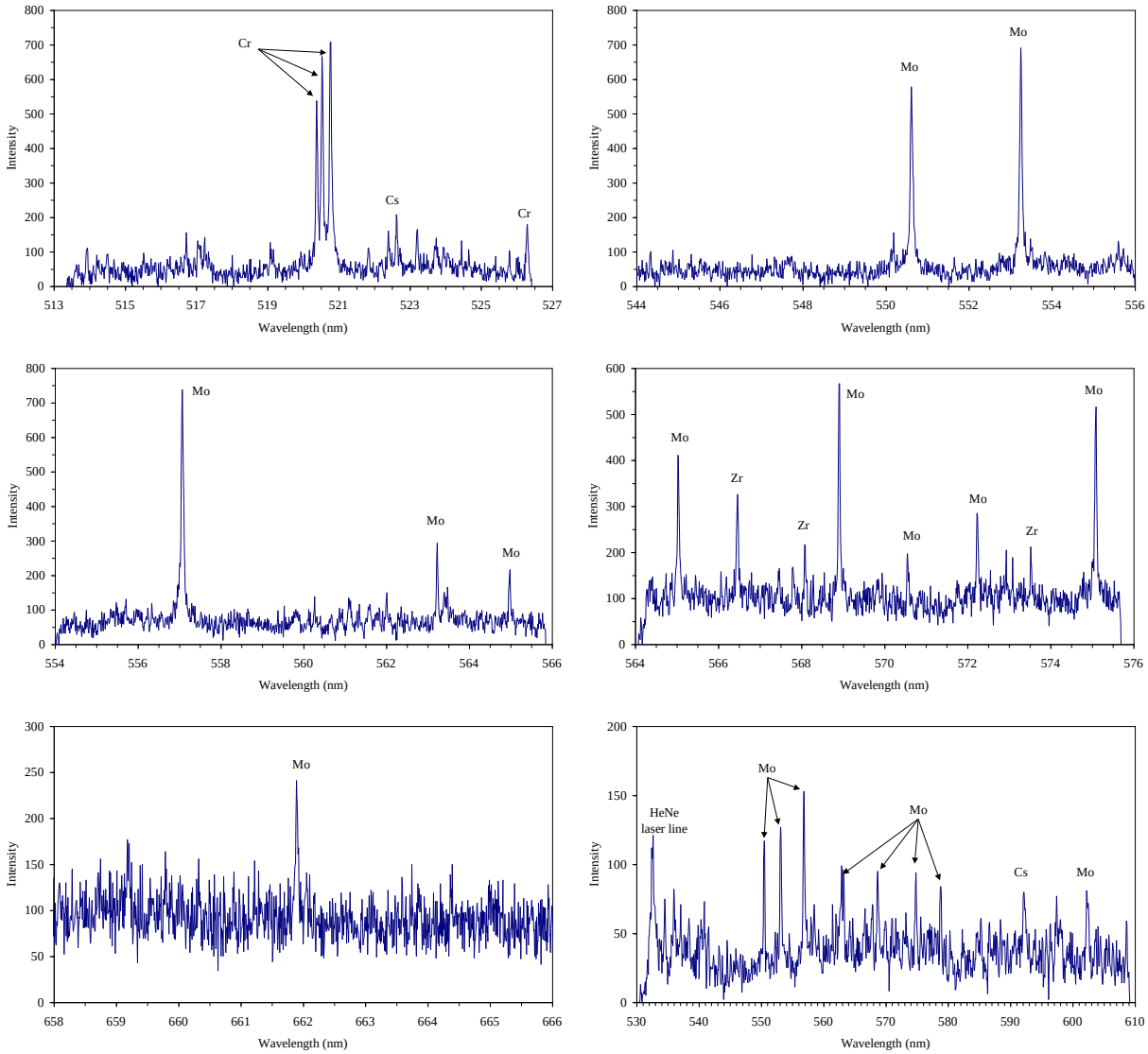


Kinetic series of 10 spectra, 50 accumulations (laser shots) per spectrum. Fe emission lines start to appear after about 100 laser shots, indicating that the laser beam is probably interacting with the steel of the dissolver basket.



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Element (I=atomic, II=1st ionic)	Emission wavelength (nm)	NIST relative intensity
Mo(I)	550.649	7800
	553.305	5200
	557.045	2500
	563.247	330
	565.013	230
	568.914	460
	570.572	80
	572.274	210
	575.140	620
	579.185	520
	603.066	1300
	661.913	230
Zr(I)	566.451	160
	568.090	120
	573.570	120
	579.774	160
	612.744	680
	614.320	440
Cr(I)	520.452	5300
	520.604	8400
	520.844	11000
	526.415	530
Cs(II)	522.704	75000
	592.563	56000

Wavelengths and NIST emission intensities for the elements identified in the SRM

Due to the lack of appropriate calibration of the ST-LIBS instrument for this application, it was not possible to give measured concentration values for each of the elements detected. On reviewing the results and using our experience of LIBS, it was attempted to provide a rough estimate of the composition of the SRM by comparing predicted (NIST) intensities and measured intensities of the various emission lines. In order for this approach to have any validity, the assumption had to be necessarily made that the material was homogenous - the existence of Zr fines, for example, within the material would significantly affect the results and make the rough estimate unreliable. Additional LIBS measurements of inactive simulate materials were highly desirable as a means of providing further information that could be used to support or dismiss the following conclusions:

Mo and Zr were present within the SRM at relatively high concentrations, estimated to be in the 10's of percent range. Cr was present at lower concentrations, perhaps between 1% and 10%. Cs was present at much lower concentrations, probably less than 0.1%.

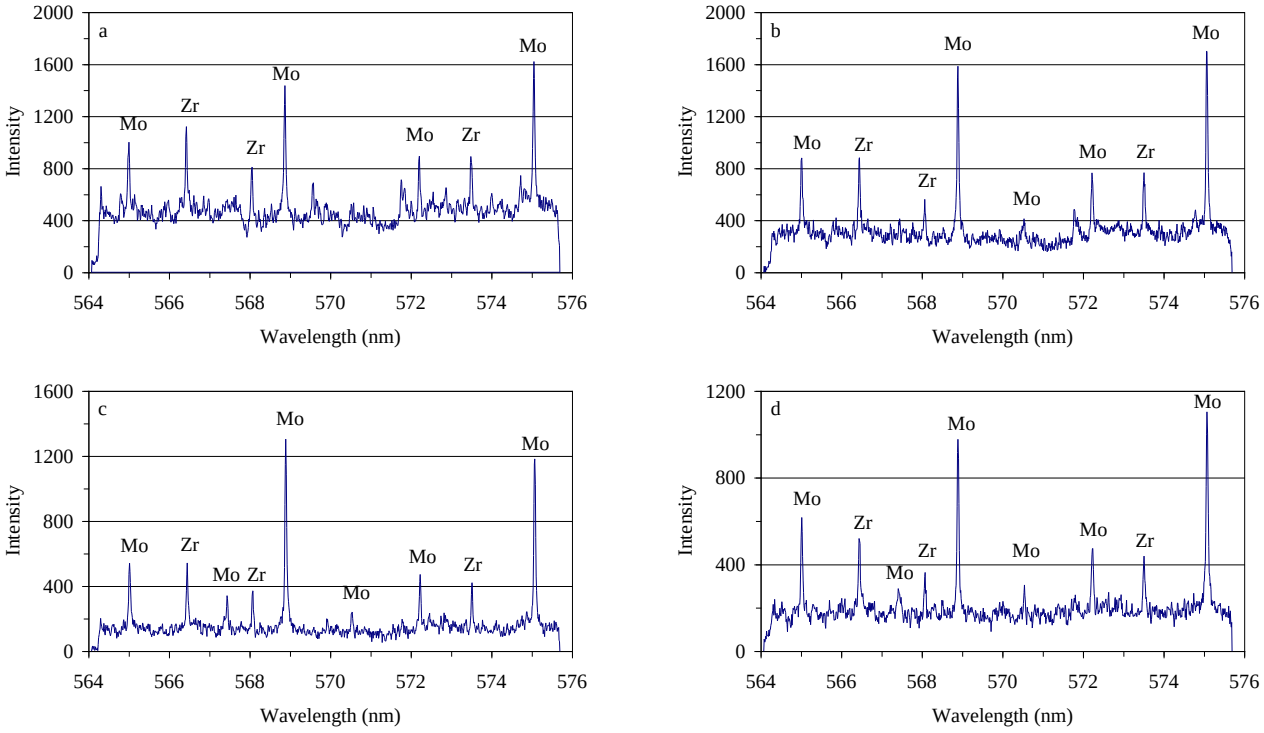
It was recommended that further ST-LIBS measurements were performed on simulate samples (eg. zirconium molybdate, a molybdenum compound containing Zr fines) under similar conditions to those of the Basket Handling Cave measurements. This work could be carried out at APL's premises using the mock-up hot-cell facility. The results of these experiments could be used to confirm (or dismiss) the rough estimate offered for the composition of the SRM.

Inactive comparative trials

The aim of this work was to perform remote LIBS analysis of inactive samples of zirconium molybdate under similar conditions to those of the Basket Handling Cave measurements and compare the results with those obtained for the SRM. Four inactive samples of zirconium molybdate were supplied by BNFL and labelled as "plated conversion solids", "ZM3", "ZM8" and "RJ4", the last three samples being in the form of a fine powder.

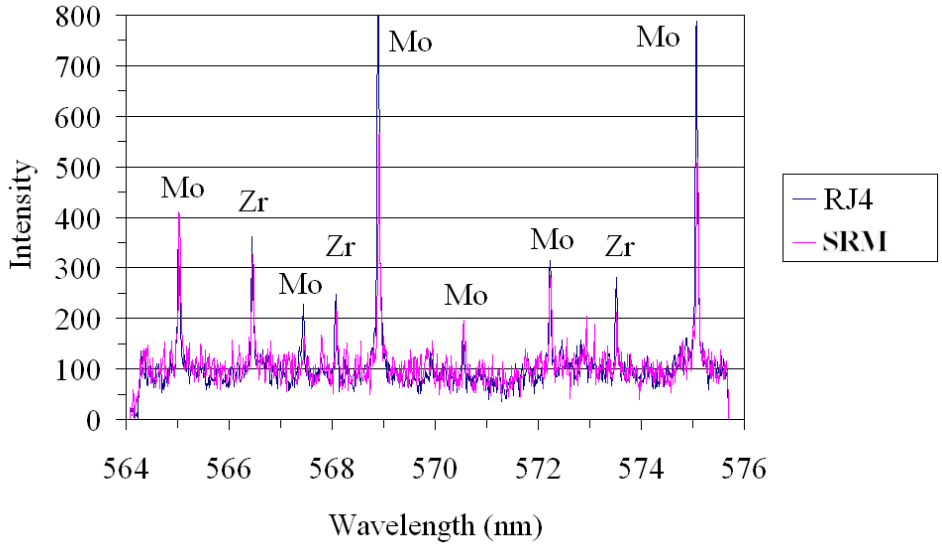
The ST-LIBS instrument was set up to direct the laser beam through the shield window of our mock-up hot-cell with the samples placed approximately 1.5 metres beyond the window. As far as possible, the measurement conditions were kept the same as those used at the Basket Handling Cave. The optical properties of the shield window used in these experiments are similar to those of the Basket Handling Cave window.

During some initial tests, it was found that the laser plasma ejected relatively large quantities of the powder samples making it difficult to take multiple measurements of the same sample. The solid sample gave less of a problem in this respect. It was decided, therefore, to mix each of the powder samples with an epoxy resin and allow the mix to set hard overnight. The experiments were repeated and emission spectra recorded with a centre wavelength of 570 nm as this region is rich in Mo and Zr lines



LIBS spectra obtained from samples “plated conversion solids”, ZM3, RJ4 and ZM8.

The spectra obtained from sample RJ4 and the SRM were compared (see below).



Comparison of spectra obtained from the SRM and sample RJ4.

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In order to establish the sensitivity of the ST-LIBS measurement to variations in relative concentrations of Zr and Mo, further samples were prepared as follows:

Three samples containing different concentrations of zirconium oxide (ZrO_2) and molybdenum oxide (MoO_3) were mixed with epoxy resin. The Zr:Mo ratios, calculated by molar fraction, for each sample were approximately 1:1, 1:2 and 1:3 respectively. LIBS spectra were recorded for each of these samples under similar condition as the earlier experiments. The results clearly showed that the relative intensities of the Zr emission lines decrease as the relative concentration of Zr decreases. This demonstrates that the ST-LIBS measurements are sensitive to variations in the Zr:Mo ratio.

Comparison of the SRM results with the results obtained from LIBS analysis of the inactive zirconium molybdate samples suggested that the SRM may contain zirconium molybdate in high abundance. The sensitivity of the LIBS measurements to variations in the Zr:Mo ratio provides further support to this claim. It could not be ruled out, however, that the SRM contained a compound or mixture of zirconium and molybdenum which by chance gives similar LIBS spectra to zirconium molybdate.

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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