A new analysis workflow for discrimination of nuclear grade graphite using laser-induced breakdown spectroscopy

DOI:

[10.1016/j.jenvrad.2019.01.004](https://doi.org/10.1016/j.jenvrad.2019.01.004)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Horsfall, J. P. O., Trivedi, D., Smith, N. T., Martin, P. A., Coffey, P., Tournier, S., Banford, A., Li, L., Whitehead, D., Lang, A., & Law, G. T. W. (2019). A new analysis workflow for discrimination of nuclear grade graphite using laser-induced breakdown spectroscopy. *Journal of Environmental Radioactivity*, 199-200, 45-57.
<https://doi.org/10.1016/j.jenvrad.2019.01.004>

Published in:

Journal of Environmental Radioactivity

Citing this paper

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Manuscript Details

Manuscript number	JENVRAD_2018_374_R2
Title	A new analysis workflow for discrimination of nuclear grade graphite using laser-induced breakdown spectroscopy
Article type	Research Paper

Abstract

Stand-off, in-situ, laser induced breakdown spectroscopy (LIBS) offers a rapid, safe, and cost-effective method for discrimination of radioactive waste materials arising during the operation of nuclear plants and from decommissioning activities. Characterisation of waste materials is a critical activity in understanding the nature of the waste, ensuring hazardous material is managed safely and that waste can be segregated for reuse, recycle or sentenced for appropriate disposal. Characterisation of materials, often in hostile environments, requires the ability to remotely differentiate between materials in terms of their chemical composition and radioactivity. This proposition was tested using a case study on nuclear grade graphite. Graphite has been used extensively as a moderator material in many nuclear reactors. Internationally, over 250,000 tons of various nuclear-grade graphite, and graphite-bearing, materials exist and are a major issue for nuclear decommissioning and radioactive waste management, due to the long half-lives of the associated ^{14}C and ^{36}Cl isotopes. LIBS offers a method for discrimination of nuclear grade graphites and other carbon and non-carbon-bearing wastes. This paper describes the development of a workflow method, including LIBS measurement analysis, for the discrimination of pre-irradiated nuclear 'Pile Grade A' (PGA) graphite moderator rod and domestic lumpwood charcoal, which act as surrogates for nuclear grade graphite and other carbon-bearing wastes. A new analysis workflow comprising the examination of spectral characteristics, multivariate analysis and molecular isotopic spectroscopy is proposed to enable rapid segregation of graphite from a heterogeneous waste stream. Enhanced characterisation techniques have the potential to significantly reduce the cost of decommissioning large parts of legacy nuclear generation plants.

Keywords	LIBS fingerprinting; i-graphite; decommissioning; waste management
Taxonomy	Radioactive Waste Process, Radioactive Waste Disposal, Nuclear Decommissioning, Radioactive Waste Management
Corresponding Author	John Horsfall
Order of Authors	John Horsfall, Divyesh Trivedi, Nicholas Smith, Philip Martin, Paul Coffey, Stella Tournier, Anthony Banford, Lin Li, David Whitehead, Adam Lang, Gareth Law
Suggested reviewers	Leon Black, Fabienne Boue-Bigne, Shiv Sharma

Submission Files Included in this PDF

File Name [File Type]

Reviewers comments + Author decisions for Charcoal vs Graphite paper v6.docx [Response to Reviewers (without Author Details)]

Highlights.docx [Highlights]

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Reviewers feedback, and authors responses

Item	Reviewers' feedback	Authors' comments
1.	1/ Abstract: good length and content. lines 22-23: however, you cannot really say the paper is about "...the successful use of LIBS analysis for the discrimination...", as it is not about the application of LIBS for this segregation measurement itself at this point. No large numbers of samples were measured, nor blind measurement were performed, etc. The paper is rather about the "development of a workflow method including LIBS measurement" etc. So re-phrase this statement to reflect better what you have developed rather than implemented at this stage.	Revised.
2.	2/lines 37, 40 and 140: "tons" instead of "Te"?	Corrected.
3.	3/ line 40: "Over" instead of ">" (just word it)	Corrected.
4.	4/ lines 136 and 137: "into" instead of "in to"	Lines 137 & 138 corrected.
5.	5/ line 149: "...adjustment range of $\pm 7.5\text{mm}$..." Do you mean that is your depth of field and the beam is more or less focused within this 15 mm range? Otherwise, maybe specify whether the laser beam was focused on the samples' surface or behind it.	Yes, addressed in lines 151-152.
6.	6/ line 164. Is reference [23], Mansoori's paper on "quantitate analysis of cement powder by laser-induced breakdown spectroscopy" the one you mean to refer to regarding time delays for carbon measurement? As the paper appears to focus on Ca, Si, K, Mg, Al, Na, Ti, Mn and Sr.	Line 164 correct reference used.
7.	7/ In the 'Experimental methods' section, indicate whether the measurements were taken on a flat surface from cut sections of the samples, or not. It appears to be the case from the photographs in Fig.1 but please state it whether it is or not. The plane of measurement on the charcoal sample is possibly rougher.	Revised lines 175-6 and 179.
8.	8/ Overall, measurements seemed to be have been carried out on three samples types: 1/ the pre-irradiated graphite, 2/ the uncompressed lump of charcoal and 3/ the crushed, homogenised and pressed charcoal. It is unclear whether the two types of charcoal samples kept being used or not, as form Fig.5 it is referred to as "charcoal" only. Be more specific and if one of the sample type was not used anymore, please state it.	"Crushed compressed", and "uncompressed" now added to the relevant mentions of charcoal throughout the document.

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9.	9/ lines 174-175: it is stated that more compressed charcoal samples were used and that conditioning laser shots followed by ten pulses of measurement shots were used. What is the rationale for deviating from the original single-shot measurement? Explain please. It also means that the experiment is potentially less representative of a real-life situation where single-shot measurements were to be used.	Cleaning shots were used in case any contaminants had been introduced from the pressing process onto the pellet surfaces, as it was not possible to otherwise clean the pellet surface.
10.	10/ line 179: please remove "also" as the energy values tested are different: 90 mJ is not being tested anymore. Any reason for this? Many of the conclusions later on refer to what happens for energies below 100 mJ and at 90 mJ whereas this value was not used anymore in the latter experiments.	Line 180 revised.
11.	11/ lines 235-236: the following statement "... with varying relative intensity apparent as the composition changes across the sample." is possibly questionable. The graphs in Fig.3 display the twelve spectra obtained, without any normalisation of the intensity as far as I understand. Therefore, how can you be sure the variation in intensities between the various spectra illustrate the chemical variation across the samples? Given that the whole wavelength range of each spectra appears to increase and decrease from one spectra to the other, the effect observed could be due to different volumes ablated at each of the twelve laser shots. It could also be a combination of chemical variation across the sample and shot-to-shot ablation variation. There is nothing here to confirm one or the other. If you have other evidence, please state it. Have you checked the ablated volumes under a microscope for example?	<p>Microscope checks were not undertaken as there was no way of accurately targeting an area observed under a microscope, due to the setup of the LIBSCAN 100.</p> <p>The PCA analysis included Normalisation integral to the method; the Figures are meant to illustrate changes but the principle data evaluation was statistical. PCA took into account shot to shot variability. The measurements included rastered across samples and this variability is included in the analysis.</p> <p>If the chemistry was the same across the sample, the spectra would be identical once normalised and these are not (by eye). Thus the variation must be due to chemical composition variation.</p>
12.	12/ line 243: "compositional variations throughout each sample". Same observation as above in 11/.	See response to item 11.
13.	13/ Under "3.3 Multivariate analysis – PCA", state whether you used the whole spectra data or selected wavelength ranges early on. I got to understand it was the whole spectral range reaching line 290 of the manuscript.	Line 254 revised.
14.	14/ line 271: Figure 5(A). The "(A)" in the figure label as no significance in this manuscript. Please remove it, unless it is relevant for other documents not provided here. Same for Figure 6 (B).	Line 277 revised.

Item	Reviewers' feedback	Authors' comments
15.	15/ from the 2D PCA plot, the segregation obtained for 50 mJ is the only one to not display any overlap. Worth mentioning?	Line 278 revised.
16.	16/ line 284: Please correct the figure number in the text. Figure 6, instead of Figure 7.	Corrected.
17.	17/ Line 289: unless I am mistaken by not distinguishing properly the colours on the graph, points not included into the 95% confidence interval ellipses belong to all the conditions tested, not just the 100 mJ one.	<p>The colours are distinguished on the plot, and they do align with the 100 mJ results.</p> <p>The data points not included in the 95% confidence interval ellipses do indeed belong to all conditions tested, not just the 100 mJ conditions. We say that most of the points are.</p>
18.	18/ line 301: "Loadings in PC1 emphasise the different background levels in the six spectrometers used in the LIBS experimental setup." Do you also see a difference in the background between the two matrices, graphite and charcoal? Because of their structure difference, the charcoal might come with a higher background level that could be useful to distinguish both matrices possibly?	Background levels were different (background in terms of the areas to the side of sample peaks), which is why they showed up in PCA1. The reviewer is correct that this could have been used as a means of discrimination. We did not explore this as such differences might be a consequence of instrumentation rather than differences in the materials. However the chemical changes we picked up will be reproducible as a discrimination method.
19.	19/ In Table 3, Ca is detected in the graphite, with content level of 1 ppm, and Ca is not detected from ablation of the charcoal despite the fact it contains 600 times more Ca than the graphite? Different plasma temperature possibly?	<p>Lines 221-2 added.</p> <p>Ca added to line 461.</p>
20.	20/ in Table 3, remove the Word reference error.	Corrected.
21.	21/ Throughout the manuscript, the chemical elements are alternatively referred to in the text by their full name and by their symbol. Maybe choose one or the other for consistency.	Most changed to periodic table labels.

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22.	<p>22/ lines 342-343: "These results suggest that charcoal and graphite can be differentiated at 10-90 mJ ns laser pulse energies but not at 100 mJ". Indeed, from the dendrogram, the data obtained at 10 mJ appeared to be the least reliable. A few data obtained with 90 and 50 mJ are also in the overlap zone. In the end, only the data obtained at 10 mJ have no data in the overlap zone. Worth mentioning?</p>	<p>Lines 347-353 changed.</p> <p>The reviewer is thanked for this comment. We agree that it is indeed worth mentioning that there are a few data with 90 and 50mJ also in the overlap zone, but none for 10mJ. We were not quite sure whether the reviewer is referring to the reliability of the data per se, or the reliability of the result in enabling the assessment of differentiation between graphite and carbon. If the latter, we believe that the lack of data at 10mJ within the overlap zone suggests that these data are perhaps the most reliable (i.e. differentiation at 10mJ appears to be unequivocal), as opposed to being least reliable as the reviewer suggests (if we have interpreted the reviewer's comment correctly).</p> <p>However, the presence of a limited number of results at 50 and 90mJ within the overlap zone might suggest that the overall picture of differentiation at 50 and 90mJ is perhaps not unequivocal – i.e. less reliable than the 10mJ or 100mJ results (the indication of lack of differentiation at 100mJ appears to be unequivocal). This helpfully supports the view that more supporting evidence of differentiation (or not) at the various laser energies, which we describe later in the paper, is required. We have revised our text accordingly and thank the reviewer for highlighting this.</p>
23.	<p>23/ line 372: "These results show that CN formation in charcoal did not occur until 100 mJ pulse energies." From the experiment, it can be concluded that CN formation take place at least up to 50 mJ and does not happen at 100 mJ. There is no data available between 50 and 100 mJ. Please change a little your statement to reflect this. It is a shame that 90 mJ was not used anymore at this stage.</p>	<p>Lines 381-383 revised.</p>

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24.	24/ lines 373-375: statement that discrimination relying on the formation of CN is possible up to 90 mJ. Again, there is no data to support this. Results only showed it up to 50 mJ (Fig.9), unless I am mistaken.	True, at some energy between 50 and 100 mJ these peaks would have started to appear but we only used 3 energies. We have made a slight revision to lines 386-7.
25.	25/ lines 388-393 In the statement on CN violet series peaks being only present in the LIBS spectrum for charcoal at 100 mJ. Again, there is no data to show is they would have appeared at lower energies, between 50 and 100 mJ. Please adjust a little your statement.	True, at some energy between 50 and 100 mJ these peaks would have started to appear but we only used 3 energies. We have made a slight revision. Lines 401 and 406 revised.
26.	26/ line 442: again, not sure this illustrated (only) the compositional variation within each material.	See response to item 11 for the authors' response.
27.	27/ line 456: "In-situ analysis is certainly possible, and the analysis can be undertaken in ambient air". Isn't it an assumption to conclude that in-situ analysis will be possible at this stage of development? The current development was carried out in a laboratory environment, on clean samples it seems. Will not real situation samples be covered with liquids or other source of contamination? This could completely alter the outcome of this development. The work done is very promising but I cannot see how the statement above can be done at this stage.	Suggested changes made to lines 469-70 to remove 'in-situ'
28.	28/ line 463: "than" instead of "that".	Line 477 corrected.
29.	29/ line 492: again 90 mJ given as the value above which the segregation will not work but a large part of the experiment showed this up to 50 mJ only. Either the data exist to conclude this work up to 90 mJ, or this value needs to be taken down to 50 mJ.	Figure 12 revised. See response to item 22.
30.	30/ Figure 12. How can sodium be used in the decision tree as described in Figure 12? As sodium appeared to display a strong peak in either graphite or charcoal according to Fig.2 and Table 3. It appears contradictory that no sodium detection is associated with the graphite sample. On the other hand, the sodium content of graphite is 1 ppm, which would tie in with the logic in Fig 12, but not with the information given in Fig.2 and Table 3. Please explain.	Reassessment of the significant presence of Na in the graphite sample leads us to believe that this was due to contamination. The logical step involving Na has been removed from figure 12 to reflect this; and removed from the conclusions, line 504.
31.	Minor comment	

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32.	rephrase line 42-43: The inventory of these materials may also is also likely to grow in volume due to the 43 future use of high temperature reactors, such as pebble bed modular reactors 103-105 reduction in time compared to what technique?	Line 42 revised. Line 103-105: Other techniques are simply not available if has to be characterised in-situ. Hence a historical reliance on sample extraction to test elsewhere (e.g. mass spectrometry), or inference from available sampling points e.g. liquor purge, historical records, and possibly radioactive decay calculations. Sample routes are very often unavailable e.g. these have to have an agreed waste stream opened up that has regulatory approval. There is significant cost associated with setting up new approved waste routes.
33.	line 179 should be extended to include the total number of spectra collected for the purpose of this study	A total of 192 experiments were undertaken. This has been added to line 182.
34.	line 430-431 claim should have reference	Line 424 revised instead.
35.	463 line that -> than	Line 477 revised
36.	464 revise	Line 477-9 revised
37.	revise 484 and/or 486 (however used twice)	Line 499 revised
38.	499 delete is certainly possible or revise sentence	Line 514 revised
39.	499-501 delete final sentence if there is no reference and no further explanation how PLS-DA would be used	Line 516 reference added
40.	Major comments	
41.	An image of the laser system should be added to the paper to demonstrate its 'portability'	For commercial reasons we have chosen not to display the LIBSCAN 100. If any readers is interested in following up on this Google image search will provide quite a few images.
42.	Figure 9: would be more informative to see a comparison graph of both spectra on the same scale.	The details for Charcoal would be lost on the graphite data scale, hence these are deliberately kept separate.

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43.	Have the authors looked into distinguishing different types of graphite used in different reactor types as they hint towards in the introduction?	No, this was a differentiation between graphite and other “non – graphite” carbonaceous waste, this graphite is of known nuclear industry use so is significant to the industry’s challenge. It is not necessarily representative of all nuclear graphites, but we had limited access to clean nuclear grade graphite.
44.	It is clear that the spectra shown in the figures of this paper were averages of 10 spectra collected, but have the authors given a value of the uncertainty (at least e.g. for the major comparison wavelengths?)	No we haven’t as the LIBSCAN system does not present uncertainty on its data. PCA analysis is designed around uncertainty, identifying what is different to random variation. As the results are qualitative (no PLS-DA for instance), we do not include results - such as “mean +/- 1SD.
45.	Paper not really conclusive: lines 492-496 should quantify how good the multivariate analysis is in discerning between the different materials	“How good” is done through the use of calibrated materials. We are only at a “does this work at the conceptual experiment stage”, so a long way away yet from validation testing.
46.	The paper seems to lack some history on how the discrimination between graphite and charcoal (or different types of graphite) has been conducted in the past (i.e. only LIBS or perhaps XRF?). Using what techniques and why is LIBS more advantageous?	The aim of the study was not looking to discrimination between graphite types. The industry has no real need for that, whereas between graphite and charcoal impacts on the bottom line cost for UK plc. How have we discriminate at present – visual inspection, historical records, and location.
47.	There wasn't an author list anywhere.	This was supposed to be double blind so author details were deliberately omitted, as required by Elsevier

Item	Reviewers' feedback	Authors' comments
48.	<p>This article details the use of LIBS to identify nuclear grade graphite vs. other carbon species. The paper is well written, explained, and cited. I think the authors are claiming something they cannot deliver on. However, the work/science seem to be sound. If the authors want to tone back the "LIBS is the greatest for this problem" and present it more as a study on LIBS and graphite/charcoal preliminary study, it would be more appropriate for publishing.</p>	<p>The authors don't believe the paper says LIBS is the greatest.</p> <p>We have now amended the title as a new approach. Lines 28-29 refer to the characterisation benefits LIBS offers vs the challenges/constraints.</p> <p>Lines 100-106 explains the aim of the assessment of LIBS for the challenge.</p> <p>Line 333 'outcome' revised to 'aim'.</p>
49.	<p>I still, however, am left with some doubt if this will actually work in a non-laboratory setting. The authors used just one piece of graphite and one piece of charcoal, both of which have large geochemical variations. This is even more of an issue when it comes to identifying impurities in each species of carbon variant.</p>	<p>The paper is an investigation into the differentiation between both material types, with a view to a real world problem; as were identified prior to the development of other real world characterisation challenges. Transfer from a laboratory setting to a non-laboratory setting would have been seen as equally challenging for these now established non-laboratory settings, which provides evidence that similar paths out of the laboratory could be established for this discrimination.</p> <p>Using PCA the large geochemical variations did not present a problem in differentiation between samples.</p> <p>This work says that "there is a difference in LIBS data charcoal and graphite and we think this <i>might be</i> the basis for screening differentiation of carbonaceous waste materials"; it is not "this shows how we have <i>calibrated</i> LIBS to make this screening work" – lots of work to get from one to the other.</p>

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50.	Similarly, at a distance of 7.5mm, what is the practical application of this if people aren't allowed inside a reactor to perform these measurements at a distance of mm anyway?	<p>The ex-situ analysis of waste streams from in-situ. It is not beyond the realms of possibility of introducing fibre based LIBS into an unloaded reactor's core during decommissioning?</p> <p>Deploying LIBS over distance is commonly achieved, and widely reported in literature.</p> <p>Lines 27-8 specifically state a waste stream.</p>
51.	Also, given the step 3 in figure 12: "molecular emission analysis to confirm graphite or non-graphite waste" doesn't make LIBS the defining technique for this approach.	<p>The author's do not claim that this approach is the defining technique for molecular emission analysis. The investigation is to ascertain whether or not LIBS, that has the potential to be deployed in the industrial locations required, can be used to distinguish between graphite and other carbonaceous wastes.</p> <p>We did not say it was the only method: but the observed differences are a new finding that suggests that LIBS could be used; before this study, we would have said LIBS was not appropriate.</p> <p>The paper is about a LIBS-based workflow to discriminate – i.e. it's the workflow not LIBS itself that is the defining technique for the approach.</p>

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52.	<p>It seems that if the authors had infinite time and laser experiments, they could distinguish between the two: i.e., Figure 11. However, the paper is trying to sell this technique as the 'best and fastest' way to do this, and I am not convinced. The authors would need to characterize a suite of charcoal and graphite samples with their LIBS technique, at the same wavelength, delay time to make this case valid. Until then they are just claiming something that cannot be backed up.</p>	<p>We have tried to say that we are looking at the fundamental science of how, and why, LIBS could be used, at a screening level, to identify different materials, rather than just as a black box technique. It is true that this is not the only technique that you could use (e.g. portable XRF) and the only data interpretation method. Our explanation as to why we want to publish our findings is as follows: We have shown it is possible for certain molecular peaks from carbon clusters and CN bonds to arise only in particular circumstances and that they enable identification of the difference between two materials. The pre-work hypothesis would have been that the two materials should have produced more or less the same spectra when heated by a plasma (i.e. mostly atomised/ionised carbon). The findings here are of intrinsic scientific interest. The carbon spectral emission lines of interest will not have been affected by the presence of trace elements, so we don't think that our findings would be altered by having many different samples of charcoal and graphite. We suspect that the differences are due to the density of carbon packing in the different materials rather than the material provenance, and that our new hypothesis is being investigated at the present time in a follow up study. In other words, we are focussing on providing answers as to why and how carbon spectra are different between the two materials at particular LIBS settings.</p>

Item	Reviewers' feedback	Authors' comments
53.	Figures 10, 11, and 12 should remove the grey backgrounds. It would give the figures a more consistent look throughout the paper.	Replaced.
54.	Minor comments	
55.	Line 80: Where are these 'databases'? Are they commercial? Home-built? Some citations or clarification on these would be useful for other people interested in LIBS	Reference added.

Key Highlights

- A new approach to graphite waste segregation using LIBS in nuclear decommissioning
- Multivariate analysis of LIBS spectra enables identification of graphite
- LIBS molecular emission fingerprinting key to graphite identification
- Laser pulse (ns) energies > 90 mJ unsuitable for analysis
- A LIBS analysis workflow for nuclear grade graphite identification is proposed

Abstract

Stand-off, in-situ, laser induced breakdown spectroscopy (LIBS) offers a rapid, safe, and cost-effective method for discrimination of radioactive waste materials arising during the operation of nuclear plants and from decommissioning activities. Characterisation of waste materials is a critical activity in understanding the nature of the waste, ensuring hazardous material is managed safely and that waste can be segregated for reuse, recycle or sentenced for appropriate disposal. Characterisation of materials, often in hostile environments, requires the ability to remotely differentiate between materials in terms of their chemical composition and radioactivity.

This proposition was tested using a case study on nuclear grade graphite. Graphite has been used extensively as a moderator material in many nuclear reactors. Internationally, over 250,000 tons of various nuclear-grade graphite, and graphite-bearing, materials exist and are a major issue for nuclear decommissioning and radioactive waste management, due to the long half-lives of the associated ^{14}C and ^{36}Cl isotopes. LIBS offers a method for discrimination of nuclear grade graphites and other carbon and non-carbon-bearing wastes. This paper describes the development of a workflow method, including LIBS measurement analysis, for the discrimination of pre-irradiated nuclear 'Pile Grade A' (PGA) graphite moderator rod and domestic lumpwood charcoal, which act as surrogates for nuclear grade graphite and other carbon-bearing wastes. A new analysis workflow comprising the examination of spectral characteristics, multivariate analysis and molecular isotopic spectroscopy is proposed to enable rapid segregation of graphite from a heterogeneous waste stream. Enhanced characterisation techniques have the potential to significantly reduce the cost of decommissioning large parts of legacy nuclear generation plants.

John. P. O. Horsfall^{a,b}, Divyesh Trivedi^{a,b}, Nick. T. Smith^{a,b,c,e*}, Philip A. Martin^d, Paul Coffey^d, Stella Tournier^{e,f}, Anthony Banford^{a,d,e}, Lin Li^b, David Whitehead^b, Adam Lang^g and Gareth. T. W. Law^g

^aNational Nuclear Laboratory, Chadwick House, Warrington Road, Birchwood Park, Warrington, WA3 6AE, United Kingdom.

^bSchool of Mechanical, Aerospace and Civil Engineering, The University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom.

^cSchool of Earth, Atmospheric and Environmental Sciences, The University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom.

^dSchool of Chemical Engineering and Analytical Sciences, The University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom.

^eCentre for Innovative Nuclear Decommissioning (CINDe), National Nuclear Laboratory, Workington, Cumbria, CA14 3YQ, United Kingdom.

^fSchool of Electronics and Electrical Engineering, The University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom.

^gCentre for Radiochemistry Research, School of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom.

* corresponding author E-mail address: nick.t.smith@nnl.co.uk (N.T.Smith).

* Telephone: +44 (0) 161 306 0514; email: nicholas.smith@manchester.ac.uk

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LIBS fingerprinting; i-graphite; decommissioning; waste management.

1. INTRODUCTION

Graphite, a crystalline allotrope of carbon, is used across the world as a neutron moderator and reflector in nuclear reactors. This results in an accumulation of radioactivity by neutron activation of both the constituent elements of graphite, of impurities, as well as potential contamination of its surface, producing i-graphite [1]. The current global inventory of i-graphite, is in excess of 250,000 tons. The management of large quantities of i-graphite is a significant decommissioning and waste disposal challenge, due to the long half-lives of the associated ^{14}C and ^{36}Cl isotopes, and is the subject of international research [2][3][4][5][6][7]. The current legacy includes over 250,000 tons of i-graphite, as well as a range of related carbon bearing materials resulting from typical i-graphite decontamination processes [1]. The inventory of these materials is also likely to grow in volume due to the future use of high temperature reactors, such as pebble bed modular reactors [7][8].

Safe and rapid characterisation of multiple forms of i-graphite, graphite-bearing materials, and mixed waste streams of these materials, alongside materials that contain no graphite or carbon, is of importance to cost effective nuclear decommissioning. Waste components, such as steels and concrete, can be easily distinguished from graphite. However, the separation of graphite (including the segregation of different nuclear grade graphite's from each other) from other carbon containing materials (e.g. AGR reactor core carbon deposits, incinerator ash, wood, polymers - such as VITON and bitumen) is challenging.

Materials characterisation is required during decommissioning to ensure that waste is handled appropriately, thus helping to minimise dose uptake to the workforce and ensuring that the waste is treated, sentenced, and / or disposed of safely, thus reducing waste volumes to reduce life cycle impacts of decommissioning [9]. Sample retrieval and analysis can be particularly challenging, when one considers mixed wastes (solid and liquid wastes of different material compositions and provenance)

from historic facilities and waste stores, where materials may have changed physically or chemically during storage.

Much of this waste is found in physically inaccessible locations that provide potentially hazardous environments, and where access to humans is limited, or precluded for safety reasons, increasing the decommissioning challenge [10]. As a consequence, it is not always possible to obtain samples, or do so in adequate numbers to ensure representative characterisation. One way to address this is to undertake *in-situ* characterisation of graphite (and other potentially hazardous materials) without the need for human intervention, sample collection, preparation, or offsite analysis.

With an ability to rapidly identify the different elemental compositions of materials, at relatively high sensitivity and reliability [11], laser-induced breakdown spectroscopy (LIBS) is a form of atomic emission spectroscopy that uses a high-energy density laser pulse as an excitation source [12][13]. The increasing use of LIBS for elemental analysis in industry and academia [12][13][14][15] includes quality control in the pharmaceutical industries, planetary exploration, and forensic analysis [16][17][18][19][20][21]. It is particularly useful where rapid, multi-element analysis of solids, liquids, and gases [22][23][24][25], with little or no sample preparation, is required. Most LIBS instruments use a Nd:YAG, or a diode pumped, solid state laser, with a beam wavelength of 1064 nm [26] focused onto the surface of a sample to provide the excitation source. The fast expansion and cooling of the resulting high-density plasma, produced by the heating of material ablated from the surface at the focus of the laser beam, induces the release of radiation characteristic of the chemical composition of the sample. This is monitored by a detection instrumentation (including a spectrometer) that measures the wavelength and intensity of the emission [27]. Since all elements will emit a characteristic emission spectrum on cooling of the plasma, and indeed some molecular species will provide characteristic emissions, theoretically LIBS has the ability to identify many substances, no matter whether they are in solid, liquid, gas, or aerosol states. Emission lines collected by the spectrometer can be identified using appropriate software and emission spectra databases e.g. NIST [28].

There are some examples of the practical application of LIBS to characterize materials specifically from the nuclear arena in published literature. To date, the successful identification of fission products, actinides, radionuclides, and activated corrosion products has been reported within a range of supporting materials that include mixed oxide fuels [29], vitrified high level waste [30], and molten salt

electrolytes [31]. These include the use of LIBS to analyse specific radioactive materials such as uranium or plutonium, and radionuclides such as ^{90}Sr and ^{137}Cs [30][32][33][34][35][36].

A number of studies have focussed on the issues surrounding the development and deployment of LIBS instrumentation for remote, in-situ detection of radioactive material inside nuclear plants [37][38]. However, little has been published about the LIBS spectroscopic characteristics of nuclear waste materials common to nuclear decommissioning, including graphite. Myakalwar et al (2015) [39] noted that the utilisation of LIBS for materials identification has been hindered by the lack of robustness of developed classification models, often due to the presence of spurious correlations, but suggested that this may be addressed by algorithm-developed wavelength selection for determining maximally discriminatory features in spectral data (i.e. using subsets of the full LIBS broadband). The most prominent peaks in LIBS spectral data are often not those that provide the most diagnostic utility. The use of algorithms developed from knowledge of a material's composition, and applied to the whole dataset to remove uninformative or spurious data (in some cases up to 99% of the full dataset [39]), could provide a much increased classification capability based on judicious feature selection.

In this new study, we undertake a range of LIBS analyses to explore the use of multivariate statistical analysis techniques for discriminating between graphite and charcoal, which is used to represent other carbon-bearing materials and represents a challenging test case. Our primary aim is to investigate whether LIBS can be used to distinguish the two different types of carbon based materials. We use our data to define and propose a new analysis workflow that enables rapid, in-situ, analysis of results, which could result in a significant reduction in time (and therefore cost) for decommissioning and waste management.

2. MATERIALS AND METHODS

2.1. Material choice and sample preparation

A number of nuclear grade graphites have been produced for UK reactors [40], corresponding to different reactor designs. All the UK's Magnox reactors are closed and currently being decommissioned. All of the UK's Advanced Gas Cooled (AGR) reactors are still in operation, and therefore most graphite waste in the UK is currently within Magnox power stations. These used 'Pile Grade A' (PGA) graphite, derived from petroleum [41] and created by extrusion of 'needle' coke [40]. AGR reactors used

Gilsocarbon graphite, which was developed from the extrusion of Gilsonite coke, produced from the refining of asphalt [41]. In this study we used compressed un-irradiated PGA graphite.

Aside from impurities accumulated during a reactor's operational phase, nuclear-grade moderator graphite also has a number of inherent impurities present within its matrix. Whilst this is the case for all nuclear grade graphites, it should be noted that composition does vary across different graphite grades. For instance, Ancius et al (2005) [42] noted that the largest components of RBMK-1500 graphite (used in many Russian reactors) include S (5-52 ppm), Fe (18 ppm) and Ca (52 ppm) [42], whereas the composition of PGA graphite (for example) is slightly different, with the three largest components being S (50 ppm), Si, and Ca (both 35 ppm) (Table 1).

Table 1 Impurity levels in PGA graphite used in Magnox reactors [43] (no reported measurement uncertainties)

Waste streams, derived from the various nuclear grade graphites, are likely to comprise both pure graphites, and mixed waste, where graphite is likely to be one of perhaps several components. With carbon being the dominant element, this study focused initially on the differences in impurity composition as the primary basis for discrimination; using molecular carbon peaks as a secondary differentiator. Several authors suggest that aside from carbon, domestic charcoal contains many different types of hydrocarbons, organic and inorganic chemicals, water, oxygen and other trace elements [8][44][45][46][47], whilst Syred et al [26] note that lumpwood charcoal for Brazilian blast furnaces may contain between 3 and 10% ash, and, up to 26% volatile matter, against 75-80% char (solid carbon). Accordingly, we use a combination of uncompressed and crushed, sieved, and pressed lumpwood charcoal with the composition listed in Table 2 in this study as a material that is representative of other carbon bearing mixed wastes. For the crushed and sieved graphite, a small portion of a stock lumpwood charcoal was crushed and ground into a powder using a ceramic mortar and pestle. The powder was then sieved into two size groups: <710 μm and <212 μm , using test sieves conforming to BS ISO 3310-1:2016 [48]. 1 g of powder of each grain size group was placed into a 13 mm diameter die and compressed under force for 5 mins, using a Specac hydraulic press. Pellets of each grain size were generated at 10 tons and at 14 tons pressing force. The choice of grain size and pressure was driven by tablet strength: lumpwood charcoal tablets formed from larger grain sizes, or under lower pressures tended to form more weakly bound tablets, which crumbled easily.

2.2 Experimental methods

This study utilised an Applied Photonics Ltd. LIBSCAN 100 comprising a Q-switched Nd:YAG pulsed laser (Quintel Big Sky CFR Ultra GRM) with a fundamental wavelength of 1064 nm, with an ICE 450 liquid cooling group / power supply. The temporal laser beam width was 7 ± 2 ns, focused to a point approximately 3.5 mm from the end of a laser head plastic nozzle, using an in-built lens-based beam expander. The factory settings produced a beam focused approximately 3.5 mm below a sample's surface, for a sample flush with the nozzle [49]. Samples were placed, flush to the nozzle in a small interlocked sample chamber with a moveable X-stage with manual control, allowing the sample to be moved in one direction relative to the laser focus. For multivariate analysis, four laser pulse energies (10 mJ, 50 mJ, 90 mJ and 100 mJ) were used in a surrounding atmosphere of air and then nitrogen, to enable assessment of an optimal pulse energy range. For each analysis, a laser pulse with no conditioning was utilised in order to replicate as close as possible, the assumed conditions for in situ analysis of (for example) conveyor-controlled waste streams from decommissioning. The emission from the cooling plasma was collected by plano convex quartz lenses, with focal length of 75 mm, into the entrance slits of six fibre optic spectrometers [49]. The dispersed plasma light was gathered by an inbuilt detector system and converted to spectra covering a LIBS broad-band of 182.88 - 904.80 nm; this permitted identification of the necessary elements through their unique spectral features.

For most of the study, the pulse to emission capture start delay time was fixed at the equipment minimum of 1.28 μ s with a gate width of 1.1 ms, based on previous results that have demonstrated that short (≤ 10 μ s) delay times yield the most intense signal for carbon and for other elements reported in this work [50]. Samples were placed on a horizontal X-Y sample stage. For multivariate analyses, single shot spectra with no conditioning shots were gathered at the four energy levels noted, in a gas purge of air and then of nitrogen. For each energy level, and in each of the two gases, each sample was moved to a new location using the X-Y stage, so that an emission was gathered from twelve locations along the sample (Figure 1).

Figure 1 (A) Sample of pre-irradiated graphite showing locations of LIBS shots; (B) sample of uncompressed lumpwood charcoal showing locations of LIBS shots.

The same graphite sample was analysed using the experimental set up described above, resulting in no discernible damage to its flat surface. However, the uncompressed charcoal suffered damage to its

rough surface (due to the friability of charcoal), so further additional samples of crushed compressed charcoal (prepared as described above) were then used. Here, rather than a single shot with no conditioning, three conditioning laser pulses were followed by analysis averaged over ten pulses to its flat surface (the number of analysis pulses were limited to ten to avoid full penetration of the sample by the laser). Additionally (to explore optimal experimental set ups) the delay time was increased in ten steps from 1.28 μ s to 6 μ s (still with a gate width of 1.1 ms). Laser pulse energy was increased in three steps of 25, 50 and 100 mJ. A total of 192 experiments were undertaken.

3. RESULTS

3.1. Charcoal analysis

The composition of the charcoal used is presented in Table 2.

Table 2 Elemental composition of domestic lumpwood charcoal impurities determined using XRF. The instrumental error associated with the reported results above was calculated as 0.33% (1 SD), based on 10 repeated analyses of the river bed standard GBW07311.

3.2. Spectral analysis

Figure 2 shows the initial LIBS spectra for graphite moderator rod and uncompressed lumpwood charcoal, collected at 100 mJ and using a delay time of 1.28 μ s. Spectral peak matching, where signature peaks with different wavelengths represent particular elements, was used to show the similar bulk compositions of carbon-bearing waste materials, and to attempt initial elemental identification. The key atomic and molecular emission lines identified in spectra obtained are summarised in Table 3. Analysis was undertaken in air so, as expected, spectral lines from atomic and molecular nitrogen and oxygen were observed between 750-850 nm in all spectra for both materials.

Figure 2 LIBS spectra for uncompressed charcoal and graphite at 100 mJ pulse energy and 1.28 μ s delay time.

Clear atomic C(I) lines are present at 193.09 nm and 247.86 nm within the graphite spectrum (Figure 2, labels (i) and (ii)), but these are lost in noise in the charcoal spectrum and thus were not useful for this study. Lines representing molecular carbon were also identified, allowing further analysis using molecular isotopic spectroscopy [51], as described later. This includes several sets of molecular emissions from C₂ [52]; the most distinctive set includes the 516 nm line at the head of the

Swan system (0,0) group of transitions (Figure 2 label (iii)), and the 619 nm line, representing the head of the Swan system (0,2) group of transitions (Figure 2 label (iv)). Of the distinctive molecular emissions from CN species, the CN line in at 358.58 nm [53] (Figure 2 label (v)) is much greater for graphite moderator material than for charcoal.

The lines representing the Violet CN series with its band head at 388 nm (Figure 2 label (vi)) can be readily identified. These occur when carbon bearing materials containing nitrogen are ablated, and from atomic carbon recombining with nitrogen in air [51]. Other studies [50][54] have investigated the formation of CN groups by atomised carbon and nitrogen in air utilising high resolution spectrometers and femtosecond delay times, and such studies may provide better understanding of atomic and molecular carbon reaction pathways.

Three peaks present in graphite at 279.65 nm, 280.26 nm and 285.23 nm (Figure 2 labels (vii)-(ix) respectively) are likely to be of Mg(II) (representing the $2p^63s$ to $2p^63p$ transition) [53]. Taking into account the 1.28 μs delay time it is unlikely that the distinct, high intensity lines at 393.4 nm and 396.9 nm (Figure 2 label (x)) in both spectra represent C(III) and C(IV) transitions (which may be possible for a shorter delay time, or higher laser energy). Instead, these are more likely to represent Ca(II), which is the largest of the impurities present in both materials and corresponds to the $3p^64s$ to $3p^64p$ transition of Chamberlain (2012) [55]. Despite a lower Ca content in graphite the associated higher intensity peak for Ca is theorised as being due to a hotter plasma for graphite. Spectral lines representing Na(I) are also readily identified in both spectra, including the classic doublet at 588.98 nm and 589.54 nm (Figure 2 label (xi)). A summary of lines, their relevant transitions and wavelengths for graphite moderator and lumpwood charcoal is provided in Table 3.

Table 3 Elemental and molecular lines examined in this study.

Rastering across each sample provides a more comprehensive dataset, and also allows visual examination of the composition of moderator graphite compared to charcoal, and of the variations in composition within each sample. Spectra for the twelve laser shot locations for each sample are shown in Figure 3 A and B.

Figure 3 Visualisation of the variations in spectra obtained from twelve locations on each sample of (A) graphite moderator and (B) uncompressed lumpwood charcoal.

'Chamberlain's peaks', representing the $3p^64s - 3p^64p$ transition of Ca(II) within graphite [55], are visible at 393.37 nm and 396.85 nm (Figure 3 A(i)). Here the relative intensity is low, compared to (for example) the nitrogen and oxygen atomic lines (from air) at the other end of the spectrum. There is little variation of relative intensity, (illustrating the amount of Ca present as an impurity within graphite) across the sample. However, at the same location for charcoal (Figure 3 B (i)) they appear not to be present at all so no variation can be seen. The Ca(I) line at 422.67 nm ((ii) in Figure 3 (A) and (B)), however is visible in the spectra for both samples, with varying relative intensity apparent as the composition changes across the sample. The Fe(I) lines visible at 610.22 nm, and 612.03 nm (see Table 3) are also identifiable in the graphite spectra, and it is possible to trace the variation in the relative intensity of both lines across the graphite sample (Figure 3 A (iii)). However, the large number of lines visible at that wavelength in the spectra for lumpwood charcoal, mean it is difficult to identify both of the lines and any variation across the sample (Figure 3 B (iii)).

Therefore, initial analysis of spectral peaks on a 2D graph proved of some use in identifying some the key components and 3D spectra of a raster of locations from each sample enabled visual observation of compositional variations throughout each sample. However, neither technique appears to be able to provide suitable information about the actual composition of the sample, and cannot be used for discrimination between materials. No intensity normalisation was undertaken for the instrument response function.

3.3 Multivariate analysis – Principal Component Analysis (PCA)

For multivariate, principal component analysis (PCA), spectra were analysed, for full spectra, using the CHEMOSPEC package [56] utilised with the R statistical environment [57]. Firstly 'scree plots' were created to identify the most important new variables (principal components, or 'PCs'). These showed the percentage of total variability that could be assigned to each of the new principal components. To provide a robust classification, the Ward's bootstrap method [58] was applied to experimental results to enable both the proportion of the data explained by each principal component to be calculated, and to calculate the uncertainty associated with that assignment. This is shown for the whole dataset in Figure 4. The figure suggests that the first three principal components (PC1-PC3) can clearly explain > 50%, > 10%, and another 10% of the variability in the data respectively. The min-max ranges of the first 3 PCs also do not overlap which indicates that they are

distinctive, providing a unique contribution to sample variability, whereas the remaining PC terms are less distinguishable from each other and make only small contributions to data variability.

Figure 4 Scree plot of the principal components using a bootstrap method (e.g. Ward's [58]) - lines above and below each box represent min-max ranges, indicating $\pm 5\%$ uncertainty about each mean PC value.

2D 'PCA biplots' were created to compare the behaviour of spectral line components that differentiate between two principal components. These plot the new scores, as recalculated values, for each analysis of two PCs, in different colours. In this study biplots were created for the six combinations of the first three PCs. These represented combinations of specific material type/laser pulse energy in different colours, with coloured ellipses surrounding data points representing a 95% confidence interval. If all ellipses overlap then it is likely that there is no unique PC1 vs PC2 combination to distinguish between different materials, whereas separation of the ellipses would suggest discrimination between materials. Figure 5 shows an example of the six biplots for PCs 1 and 2 for the two materials at a range of laser pulse energies. With the exception of both materials at 50 mJ, all of the confidence ellipses overlap at least one other material/pulse energy combination, suggesting that there is no unique PC1 vs PC2 combination that can distinguish the different materials.

Figure 5 Biplot of PC1 and PC2 for uncompressed lumpwood charcoal and graphite, based on 10, 50, 90 and 100 mJ laser ns pulse energies.

Figure 6 3D plot of PCs 1, 2, and 3 showing clear separation between groupings of ellipses representing 95% confidence limits for graphite and uncompressed lumpwood charcoal.

Further interrogation of the data was undertaken by plotting three PCs in 3D. Rotation of the axes allowed full 3D visualisation of the confidence ellipses (defined using the same 95% confidence interval), allowing any segregation in the data to be highlighted. This is shown in Figure 6 where it can be seen that the confidence ellipses clearly located in two distinctive groups, based upon whether the sample is charcoal or graphite, thus indicating that these two materials can be distinguished by LIBS.

293 Also visible, however, are those data points that lie outside the 95% confidence interval. These still
 294 show clear separation between uncompressed charcoal and graphite.

295 The loadings [59] for each PC relate to the contributions that each spectrometer channel makes to the
 296 overall principal component for an analysis. Loadings allowed the relative importance of peaks
 297 present in the spectra in terms of their ability to discriminate between materials to be studied, thus
 298 highlighting some of the key elements that the discrimination between materials was actually based
 299 on.

300 An examination of the loadings for the first three PC's provides an indication of the elements they
 301 represent. Figure 7, which also shows an example reference spectrum, shows the relative importance
 302 of the peaks outlined in Table 3 in terms of their ability to separate graphite and uncompressed
 303 charcoal. PCs 1 to 3 all have high loading values between 750-850 nm that reflects emissions from
 304 atomic and molecular nitrogen and oxygen in air. As they occur in all three principal components,
 305 these do not support differentiation between graphite and charcoal.

306 Loadings in PC1 emphasise the different background levels in the six spectrometers used in the LIBS
 307 experimental setup. This instrumentation-related factor also does not appear to support distinguishing
 308 between the samples. However these features could be removed, using post-processing algorithms,
 309 to improve the sensitivity of the technique. The loadings for the first PC also contain the classic Na
 310 doublet at 588.98 nm and 589.54 nm, several atomic calcium emission lines e.g. at 480 nm and
 311 559 nm. As expected, these lines are found with much greater intensity in charcoal and reflect the
 312 composition of charcoal as described earlier, suggesting a possible reason for the confidence ellipse
 313 separation in PCA.

314 However, as Figure 7 shows, loadings for the second and third PC's include: (i) spectral lines
 315 between 240-450 nm, (ii) two sets of readily identifiable lines corresponding to molecular emissions
 316 from carbon (C_2) clusters [52] – one with the head of the Swan system (0-0) group of transitions at
 317 516 nm; and the other with the head of the Swan system (0-2) group of transitions at 619 nm.
 318 Additionally, carbon atomic emission lines are observed at 407 nm and 588-89 nm. Finally, visible
 319 within PC3 are the distinctive molecular emissions from CN species within the violet (0,0) series are
 320 visible, with the head at 388.3 nm.

During PCA analysis and examination of the loadings, differences were noted in the intensities of the molecular emission lines from C₂ and CN under the same conditions. It was postulated that these may provide a key factor in differentiating graphite and uncompressed charcoal below 100 mJ, and it was decided to perform further examination of these features.

It is known that the formation of these free radicals and the intensity of their emissions can vary as a function of both pulse energy and delay time [60][61], so understanding why the spectral emissions from atomic carbon and C₂ and CN molecular species change as a function of delay time and pulse energy will support identification of LIBS settings that enable optimal separation of these carbon-rich materials.

Figure 7 Plot of PCA loadings for PCA3 (top), PCA2 (2nd), PCA 1 (3rd) and a uncompressed charcoal sample reference spectrum (100 mJ pulse energy with 1.28 μ s delay time).

The ultimate aim of this research area is to enable the deployment of LIBS for routine sorting and screening of radioactive wastes. To reach that point all analysis equipment artefacts as shown in PC1 and PC2 in Figure 7 would have to be eliminated so the only significant variations measured by routine LIBS analysis will be due to the material type, as shown in PC3.

3.4 Multivariate analysis – Hierarchical Cluster Analysis (HCA)

In order to gain further understanding, the scores (the eigenvalues from PCA analysis) were examined using Hierarchical Cluster Analysis (HCA). As with PCA, this is an unsupervised method that in this case classifies data into clusters depending upon its similarity. A dendrogram (tree diagram) was created using Ward's method [62]. This classifies all of the measurements used in the study, where, mathematically, the separation between data values is calculated by their Euclidean distances. The clusters selected are therefore those that were generated with minimum variance in their Euclidean distances from groups selected by random sampling.

Figure 8 shows the HCA dendrogram analysis. The highest level data from this study are clearly located into two clusters representing graphite (g) and charcoal (C) at laser pulse energies of 10, 50, and 90 mJ, whilst data for graphite and charcoal at 100 mJ occur across both groups. Overall the dendrogram indicates that differentiation of charcoal and graphite appears to be possible at ≥ 10 mJ to ≤ 90 mJ, but not at 100 mJ ns laser pulse energy. However, whilst the overlap zone contains

predominantly results at 100 mJ ns laser pulse energies, a small number of other data (at 50 and 90 mJ but none at 10 mJ) were also identified, suggesting that although the overall picture is one of differentiation, it does not appear to be unequivocal at 50 and 90 mJ, and some other supporting evidence to further enhance the differentiation would be useful.. The causes of this change in behaviour are likely to be caused by fragmentation processes occurring in the LIBS plasma and are discussed below.

Figure 8 Hierarchical cluster analysis (HCA), utilising the principal component analysis scores (laser energy colour code is same as Figure 5). Note the segregation of graphite (g) and uncompressed carbon (c), and the overlap due to no segregation at 100mJ

3.5 Analysis of molecular emissions

The above analysis suggests that discrimination could be based on two features: (i) the presence of CN molecular lines in charcoal samples, and (ii) the presence of molecular C₂ Swan system lines in graphite samples. Analysis of the molecular emissions was undertaken on crushed compressed charcoal to confirm this, to ascertain optimal laser pulse energies (and in particular to address the lack of discrimination at 100 mJ), and to note any effect of varying delay times. This also enabled examination of the mechanism of formation of CN emissions [57][58][62].

C₂ molecular emission lines can form by direct ablation of clusters of carbon fragments, or through recombination of C atoms post-ablation [50][63][64][65]. Nitrogen in the CN groups could be formed directly from N and C in the sample as has been shown for N bearing organic molecules [50]. This is unlikely to be the case here as nitrogen is not a chemically bound constituent of either material. If an impurity then this was below the limit of detection for the XRF analysis. However, CN can also be generated by the reaction of C atoms with nitrogen in air; either by ionised C atoms (i.e. 2C + N₂ →

2CN) or C₂ groups reacting with nitrogen (i.e. C₂ + N₂ + E_{kin} $\xrightleftharpoons[k2]{k1}$ 2CN + E'_{kin}) [64][66], where E_{kin} and

E'_{kin} are respectively the kinetic energies of molecules before and after the reaction). The latter reaction is highly endothermic (with an activation energy of 1.8 eV [68]), and has been shown to require high temperatures of the type that occur in the shockwave generated during initial plasma formation [63].

Figure 9 A shows the variation with 25, 50, and 100 mJ pulse energies of the CN violet series at 388.3 nm for graphite (i) and compressed charcoal (ii). Graphite shows a distinctive set of peaks at all pulse energies, but these peaks only formed at 100 mJ in charcoal. XRF analysis of the charcoal confirmed that significant nitrogen was not present in charcoal (Table 2); therefore CN could only be produced by the interaction of either C₂ or atomic carbon with atmospheric nitrogen. From the latter experiments, it can be concluded that CN formation takes place at least up to 50 mJ and does not happen at 100 mJ. Only the data obtained at 10 mJ have no data in the overlap zone.

Therefore, since the formation of CN spectral lines was a significant statistical contributor to the differentiation between crushed compressed charcoal and graphite, discrimination of the two materials using these features was deemed only possible up to 50 mJ pulse energy from the data presented.

With a fixed delay time of 1.28 μ s, the C₂ Swan series, with a head peak at 516 nm, was observed at all pulse energies for graphite, with a major increase in intensity at 100 mJ (Figure 9 B(i)), but was difficult to distinguish above background for crushed compressed charcoal, with only the head peak being clearly discernible at 516 nm (Figure 10 B(ii)). It is possible that adjacent stronger intensity peaks, belonging mainly to calcium in the charcoal (e.g. Ca(III) at 513 nm and Ca(I) at 518.8 nm), may hide the weaker C₂ peaks. However it is also possible that Swan series emissions are low intensity because very small amounts of C₂ clusters are present below a laser pulse energy of 100 mJ.

Figure 9 (A) CN violet system spectral lines (head line at 388.3 nm) for crushed compressed charcoal and graphite; (B) C₂ Swan series (head at 516 nm) for charcoal and graphite. All at 1.28 μ s delay time and 25, 50 and 100 mJ pulse energies

In summary, at 1.28 μ s, (i) CN violet series peaks (with the head peak at 388.3 nm) can be identified in LIBS spectra for graphite at all 3 laser pulse energies used, but are only present in the LIBS spectrum for crushed compressed charcoal at 100 mJ; and (ii), C₂ Swan Series peaks (with the head peak at 516 nm) can be identified in LIBS spectra for graphite at all laser pulse energies but not in LIBS spectra for charcoal (although the head peak is visible at 516 nm at 100 mJ laser pulse energy). Thus, LIBS discrimination was achieved, utilising the molecular CN violet and C₂ Swan series of peaks within LIBS spectra for graphite and charcoal, at ns laser pulse energies up to 50 mJ.

Table 4 Summary of molecular emission analysis results for graphite and crushed compressed charcoal at various laser pulse energies (delay time 1.28 μ s)

The same C₂ Swan series spectral lines were investigated as a function of delay time (but with a fixed pulse energy of 50 mJ) to assess any impact on the discrimination noted above. Figure 10 (A) shows that Swan series lines are prominent in graphite, even at short delay times. The high intensities, observed at short delay times, are indicative of the ablation of C₂ clusters from graphite surfaces [53][62]. For charcoal, a different relationship was observed: peak intensities were significantly higher after 3 μ s, with almost no signal at shorter delays. This is suggestive of an alternative mechanism whereby carbon atoms recombine to form C₂ or larger carbon clusters formed during laser ablation then dissociate to C₂ later in the plasma. In that process, higher C₂ emission intensities are generated at longer delay times due to the formation of C₂ clusters as the plasma cools.

Figure 10 C₂ Swan series (with head at 516 nm) spectra for various delay times for (A) graphite and (B) crushed compressed charcoal (all at 50 mJ laser pulse energy)

In summary, between 1 and 3 μ s the C₂ Swan series peaks are prominent in graphite spectra, but not in spectra for charcoal, whereas between 3 and 15 μ s, the opposite is true. This highlights that whilst discrimination, based on the C₂ Swan series peaks, was successfully achieved at a delay time of 1.28 μ s, the ability to discriminate at other delay times may vary.

3.6 Discrimination using atomic carbon lines

It was also expected that, in addition to C₂ and CN molecular species, it would be possible to identify lines for atomic carbon. Lines for the molecular species could be resolved on graphite LIBS spectra, alongside lines for atomic C - represented for example, by the 247 nm line, which could be identified at all laser pulse energies and delay times (Figure 11 A and B). The same C line could not be resolved in any situation for charcoal (same figure). The presence of an atomic C line in LIBS graphite spectra and corresponding lack of the same line in LIBS charcoal spectra potentially allows an extra discriminatory feature between the two materials. This is perhaps not surprising considering the relatively high thermal conductivity of graphite compared to that of charcoal, which has a thermal conductivity that is an order of magnitude lower, and its relatively low vaporisation point.

Interestingly, this finding also indicates a lack of atomic carbon in the plasma for charcoal, where it is present in the graphite plasma, suggesting charcoal ablation releases C_2 molecular fragments, whereas graphite ablation releases both molecular C_2 and atomic C.

The lack of atomic C, the presence of molecular C_2 in the crushed compressed charcoal plasma, and assuming CN is only formed at 100 mJ in charcoal (as per this study), also suggests that the CN is formed by reaction of atmospheric nitrogen with C_2 molecular fragments [69]. It was not possible, using these results, to suggest the reason for the presence of CN peaks in graphite spectra (for example, it may be due to the differing thermal properties for each material). However, further investigation is outside the scope of this paper.

Figure 11 Elemental C spectral line at 247.8 nm for crushed compressed charcoal and graphite with (A) 1.28 μ s delay time and various laser pulse energies; (B) various delay times at 50 mJ pulse energy

4 DISCUSSION: A new workflow for rapid characterisation of graphite, graphite bearing, and miscellaneous carbon-bearing materials using LIBS and stand-off LIBS.

Here we propose a new workflow to enable the speedy characterisation of graphite, graphite bearing and miscellaneous C-bearing materials using LIBS and stand-off LIBS. 2D and 3D analysis of spectra obtained from single-shot rastering across each sample illustrated the compositional variation within each material, and whilst some peak identification was possible, particularly of the various carbon species, it did not lead to a decisive fingerprint for each material.

PCA provided a good discrimination between the two materials, based on differences in principal components. HCA supported this, and both together provided an indication that discrimination at up to 50 mJ ns laser pulse energy was possible. Examination of PC loadings further endorsed this, and suggested that the PCs comprised a combination of impurities (e.g. Na & Ca) and atomic and molecular carbon species, created during the LIBS process; but with differing features depending on the material. Molecular isotopic analysis further investigated these features, and identified molecular carbon species formed during LIBS of graphite that were not formed during LIBS of crushed compressed charcoal (apart from at 100 mJ), including CN and C_2 species. Additionally, it was noted that the 247 nm peak representing atomic C was present in graphite LIBS spectra but not in those for

crushed compressed charcoal, suggesting another discriminatory feature. Experimentally, the above findings suggest that optimal conditions for LIBS discrimination of graphite and charcoal include a ns laser pulse energy lower than 90 mJ and a laser delay time of 1.28 μ s. Distinction between graphite and other carbonaceous materials analysis is certainly possible, using C peaks; and the analysis can be undertaken in ambient air.

Findings in published literature support the postulate that C within mixed graphite-bearing wastes can indeed be used as a discriminator[51][67][70][71][72][73][74], whilst several authors report the use of PCA for discrimination of complex materials (e.g. [75]). It is noted that many other multivariate methods could also have been used that also allow systematic investigation of a very large number of variables such as SIMCA (soft independent modelling of class analogues and neural networks). There is no assumption that PCA is more or less appropriate than these methods; it is simply noted that it in this case the method provided the required information to allow for material discrimination [59].

From this study a new workflow has been developed to enable rapid discrimination analysis of graphite and C-bearing wastes (Figure 12 A and B) comprising: (A) Optimal LIBS set up and (B) the analysis workflow itself. The latter comprises: (1) Visual analysis of spectra and peak identification; (2) Multivariate analysis of the whole spectral broadband utilising all the results, including (2a) bootstrapping, (2b) PCA, (2c) HCA, (2d) loadings analysis; and (3) molecular isotopic analysis of C species.

Figure 12 Fingerprint-based workflow for the characterisation of graphite and graphite-bearing materials during nuclear decommissioning

5 CONCLUSIONS

This study has shown that LIBS, coupled with an analysis workflow, comprising multivariate statistical analysis and molecular emission spectroscopy of C species resulting from the LIBS process, can be used to discriminate easily between graphite and other materials with high elemental C content in ambient air. The new workflow is suitable for discrimination of nuclear grade graphite and other C-bearing wastes during nuclear decommissioning and waste management of graphite wastes. Having demonstrated this utility for the test case of different C based materials, future work will extend the evaluation to other typical decommissioning materials.

For graphite and both compressed and uncompressed charcoal the primary C peaks (including those of new species created during the LIBS process), and some impurity peaks can be easily identified through visual inspection of 2D and 3D spectra. Yet, the latter also serves to highlight the immense difficulties associated with discriminating between the two materials.

However, multivariate analysis comprising bootstrapping, PCA, HCA and examination of loadings was used to successfully discriminate between PGA graphite and other C-bearing materials (in this case compressed and uncompressed lumpwood charcoal). This was based on PCs present in the LIBS plasma, including atomic and molecular C species formed during the LIBS process. Analysis of the spectral lines, produced by the latter, identified the presence of lines for the CN (violet) and C₂ Swan series within the spectra for graphite, but not for charcoal.

Multivariate analysis also showed that a ns laser pulse energy higher than 90 mJ was not suitable for gathering appropriate data, but all the above findings suggest that an inexpensive commercially available in-situ LIBS set up, using standard Czerny-Turner spectrometers, a laser pulse energy no higher than 90 mJ, and a fixed laser pulse delay of 1.28 μ s, could be used to discriminate between nuclear grade graphites and other C-bearing materials.

Further optimisation of data processing is possible that could support progressing from the current research based equipment into an automated monitoring tool that can be utilised to screen high C content wastes. For instance a statistically supervised method, such as partial least squares-discriminant analysis (PLS-DA), can be used to calibrate an automated LIBS based screening process [76].

6 ACKNOWLEDGEMENTS

This study acknowledges funding from National Nuclear Laboratory Waste Management and Decommissioning Characterisation Innovation, Research & Development Programme, and the Centre for Innovative Nuclear Decommissioning and Engineering (CINDe) Programmes, the University of Manchester, the EPSRC, and the Royal Society Industry Fellowship.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 10

Figure 11

Figure 12

LIBS Experimental set up:

- 1.28 μ s delay time
- ns laser pulse duration
- Up to at least 50 mJ laser pulse energy
- Raster across surface of mixed wastes
- In-situ possible
- In air

A

Table1

Element	ppm	Element	ppm
S	50	Zn	0.13
Si	35	W	0.12
Ca	35	B	0.1
V	12	Mg	0.1
N	10	Mo	0.1
Ti	3	Bi	0.08
Cl	2	Li	0.05
Ba	1.5	In	0.05
Na	1	Sm	0.04
Al	1	Cd	0.04
Ni	1	Be	0.02
Sr	0.4	Co	0.02
Cr	0.35	Eu	0.005
Pb	0.15	Ag	0.001

Table 2

Element	ppm	Element	ppm
C	951430	P	39
Ca	21623	Fe	28
K	9490	Te	27
Mg	3197	Rb	8.3
Si	312	Mn	7.9
Sr	135	Hg	7.4
Na	134	Sn	5.3
S	76	Cs	4.3
Al	64	U	3.5

Table 3

Atom *	Transition Upper to lower	Wavelength (nm)	Comment	Visible in graphite (Y=yes; N=no)	Visible in charcoal (Y=yes; N=no)
C(I)	$2s^2 2p^3 s - 2s^2 2p^2$	193.09 nm &		Y	N

		247.86 nm			
C ₂	d ³ Π _g - a ³ Π _m	516 nm	Head peak for Swan series (0,0)	Y	Y
Ca(II)	3p ⁶ 4s - 3p ⁶ 4p	393.37 nm,	Chamberlain (2012) [54]	Y	N
Ca(II)	3p ⁶ 4s - 3p ⁶ 4p	396.85 nm,			
Ca(I)	3p ⁶ 4s4p - 3p ⁶ 4s2	422.67 nm			
CN	B 2Σ ⁺ - X2Σ ⁺	358.58 nm Head band 388.25 nm	Line much more dominant in graphite. CN series clear in both materials	Y	Y
Fe(I)	3d ⁷ (4F)4d - 3d ⁷ (4F)4p 3d ⁶ (5D)4s4p(3P°) - 3d ⁷ (4F)4s	610.22 nm & 610.32 nm, 612.03 nm	Unresolved double peak	Y	N - due to noise
Mg(II)	2p ⁶ 3s - 2p ⁶ 3p	279.65 nm, 280.26 nm, 285.23 nm		Y	N - due to noise
Na(I)	2p ⁶ 3p - 2p ⁶ 3s	588.99 nm, 589.59 nm		Y	Y

*Spectroscopic notation is that the neutral atom is labelled (I): subsequent oxidation by (II), etc.

Table 4

Series	Laser pulse energy (mJ)	Graphite peaks	Crushed Compressed Charcoal	Reason	Discrimination possible?
CN (Violet) 388.3 nm	25	Y	N		Y
	50	Y	N		Y
	100	Y	Y	CN produced by interaction of either C ₂ clusters, or atomic carbon with atmospheric N	No - Not at this laser pulse energy
Swan series 516 nm	25	Y	Y – but only head at 516 nm		N
	50	Y	N		Y

	100	Y	N		Y
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The Editor
Journal of Environmental Radioactivity
Elsevier B.V.
Radarweg 29
1043 NX Amsterdam
The Netherlands

13/Jun/2018

Your Ref: Article title: "A new analysis workflow for discrimination of nuclear grade graphite using laser-induced breakdown spectroscopy"

National Nuclear Laboratory
5th Floor
Chadwick House
Warrington Road
Birchwood Park
Warrington
WA3 6AE

T. +44 (0)1925 289800
E. customers@nnl.co.uk
W. www.nnl.co.uk

Article submission to the Journal of Environmental Radioactivity

Dear Editor ,

We would be grateful if you would consider our manuscript entitled "A new analysis workflow for discrimination of nuclear grade graphite using laser-induced breakdown spectroscopy" for publication within the Journal of Environmental Radioactivity.

Over 250,000 tons of various nuclear-grade graphite, and graphite-bearing, materials exist throughout the world, and are a major issue for nuclear decommissioning and radioactive waste management, due to the long half-lives of the associated ^{14}C and ^{36}Cl isotopes.

Characterisation of such waste materials is a critical activity in understanding the nature of the waste, ensuring hazardous material is managed safely and that waste can be segregated for reuse, recycle, or sentenced for appropriate disposal. However, characterisation of materials, often in hostile environments, is ideally undertaken in-situ to differentiate between materials in terms of their chemical composition and radioactivity.

This paper describes the successful use of LIBS analysis for the discrimination of pre-irradiated nuclear 'Pile Grade A' (PGA) graphite moderator rod and domestic lumpwood charcoal, which act as surrogates for nuclear grade graphite and other carbon-bearing wastes respectively. Within the paper we propose a new analysis workflow utilising LIBS. Subsequent examination of spectral characteristics, multivariate analysis, and molecular isotopic spectroscopy is proposed to enable rapid segregation of graphite from a heterogeneous waste stream. Enhanced characterisation techniques, such as those described in this paper, have the potential to significantly reduce the cost of decommissioning large parts of legacy nuclear generation plants.

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This paper marks the first time LIBS has been used as a fingerprinting and discriminatory tool for the characterisation of graphite and heterogeneous carbonaceous wastes. Particular highlights we present include:

- A new approach to graphite waste segregation, using LIBS, in nuclear decommissioning,
- How multivariate analysis of LIBS spectra enables identification of graphite,
- How LIBS molecular emission fingerprinting is key to graphite identification,
- Laser pulse (ns) energies of greater than 90 mJ are experimentally determined as being unsuitable for analysis,
- A LIBS analysis workflow for nuclear grade graphite identification is proposed.

The word count for this paper is 6663.

Thank you for your consideration.

Yours sincerely

Prof Nick Smith (corresponding author)

E. nick.t.smith@nnl.co.uk

T. 01925 289899

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Article submission to the Journal of Environmental Radioactivity: "A new analysis workflow approach for discrimination of nuclear grade graphite using laser-induced breakdown spectroscopy"

Dear Gabi,

Thank you for your help so far with our research paper submission. We have responded to all reviewers' comments and have compiled them into a supporting document to help them review our responses.

We would like to say thank you to the reviewers for their time and effort, this is very much appreciated and helped make for a better article.

We would be grateful if you would consider our revised manuscript for publication.

Best wishes

Owen Horsfall