

Laser Induced Breakdown Spectroscopy for Identification and Quantification of Elemental Composition of Subsea Structures: A Study of Early Stage Rust Behaviour in Steel

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Abstract: A review on the research work progress achieved and a realistic research plan for the remainder of the programme is outlined in this report. A brief literature of underwater LIBS and LIBS in general illustrates a recap on the first year transfer report along with added background knowledge of the subject. The progress summary emphasises on the results from experiments conducted, courses attended, presentations, journal/conference papers in preparation related to the research work. The research plan for the remainder of the programme will primarily focus on underwater experiments to meet the latter part of the research objectives. Preliminary results obtained will contribute to writing a technical research paper for publication.

Keywords: LIBS, Underwater Libs.

1. INTRODUCTION

Laser Induced Breakdown Spectroscopy (LIBS) is a useful technique for material characterisation in terms of elemental composition and quantification. Because of its relatively fast measurement, LIBS can be used for real time, *in-situ* analysis without the hassle of exporting the target sample back to the laboratory. Furthermore, LIBS is suitable for non-destructive and non-invasive testing of materials since a small amount of mass and surface area is usually interrogated by the laser. LIBS for field applications require no elaborate equipment set-up and sample preparation [1-3].

LIBS analysis mainly involves the identification of atomic constituents of a sample (qualitative analysis) and determining its relative concentration (quantitative analysis). The wavelength position of the emission line fingerprints the element and when properly calibrated, the intensity of the line permits quantification. However, since LIBS method involves atomisation of the sample, it is not suitable to determine the nature of compounds [3].

The target sample probed by the laser can be in any form of matter i.e., solids, liquids, gases, aerosols, hydrosols. For this reason, LIBS is regarded as a widely used technique as it can be applied to a variety of sample composition.

Over the years, LIBS has been used for stand-off and remote measurements to detect elements present in non-reachable and hazardous areas. This has made LIBS useful in a number of applications ranging from process monitoring in industries, medical operations and soil sample testing to underwater study of geological and archaeological structures [4-13].

1.1 Underwater Libs:

Underwater LIBS usually involves interrogation of either the bulk liquid (water in most cases) or submerged solid. Common LIBS applications used underwater in general range from environmental monitoring of cooling and waste waters from industries and thermal power plants, geological and archaeological studies of deep sea mineral deposits, hydrothermal vents, Remotely Operated Vehicles (ROVs), Autonomous Underwater vehicle (AUVs) to mobile drilling systems [10] [11] [14-15].

Some of the experiments conducted in the past have shown that conventional single pulse of relatively shorter durations applied to submerged solids exhibits strong plasma confinement and quenching effects making the weak recorded signals unsuitable for quantitative analysis [16]. This has resulted in spectra typically dominated by intense background light with

little spectroscopic information and broadened emission lines due to the high optical density of the plasma. Only major elements from bulk water or ablated samples could be detected.

Poor signal output was attributed to the thermal conductivity, density and incompressible nature of water. Also, majority of the pulse energy after absorption losses was used to create vapour cavity on the solid surface with little or no energy used for excitation purposes. These poor signals can be enhanced by the use of double pulse or a long single pulse LIBS set-up to produce well resolved, narrow spectral lines. The theory behind signal improvement suggests that the first pulse or earlier pulse from a double or long pulse respectively is needed to form a vapour cavity or bubble in water. The second pulse or the later part of the long single pulse then excites the momentary gaseous state inside the bubble during which mechanisms similar to LIBS in air can occur [2] [9-11] [16-19].

Other experiments have shown ways to better improve the signal quality from double pulse LIBS by hitting the cavity bubble with an appropriately timed second laser pulse to produce relatively strong plasma. It was understood that optimal inter-pulse duration increases the optical coupling to the largest bubble present in the focal point. The use of buffer gas flows for single pulse LIBS set-up has also been able to create quasi-gaseous environment underwater for the plasma. The gas displacement of the water makes analysis independent on the optical transparency of water to laser and plasma radiation [4] [16-17] [20-21]. A summary of a novel and distinct contribution of the research work to underwater LIBS is outlined in the next section.

1.2 Research Objectives:

This research work will involve the experimental set-up of a LIBS system for qualitative and quantitative analysis of submerged steel samples for possible deepwater applications. The project will focus on the following key areas

- LIBS analysis on steel samples in air
- LIBS analysis on submerged steel samples
- LIBS analysis on corroded steel samples in air
- LIBS analysis on corroded steel samples underwater
- Effects of pressure on signal characteristics from submerged steel samples

Intended research work is initially to verify findings from previous laboratory based experiments before extending research to novel real-time material characterisation applications such as corrosion monitoring and decommissioning of selected subsea structures. Successful results will furthermore prove LIBS as an *in situ* material analysis technique suitable for deployment in the subsea environment.

2. PROGRESS SUMMARY

In this chapter, an outline of the research work progress achieved with summarised results to show as evidence. This will provide a platform for what can be realistically achieved for the remainder of the programme. An update on the experiments conducted to meet project objectives includes:

- Qualitative analysis to detect major and minor elements of certified steel samples in air. Over 40 samples were interrogated to confidently or tentatively assign a particular line to an element (figure 2.5). The National Institute of Standards and Technology (NIST) atomic spectra database lines and the MIT (Massachusetts Institute of Technology) wavelength tables were used for element identification. Samples with detectable concentrations of elements of interest such as Chromium, Titanium, Lead and Tin (Figures 2.1-2.4) were probed and its sensitive lines compared with certified samples whose elements have been tentatively identified. Elements that were not detected could have been a result of:
 - a) The presence of strong and numerous Fe and Cr lines that may cause interference with the element of interest present in the same wavelength or an adjacent wavelength. This was observed on occasions in the spectrum graph as lines overlapped.
 - b) Sensitive lines in the Ultraviolet (UV) spectral region (180nm to about 290 nm) that were attenuated by the 1064 nm notch filter.
 - c) Sensitive lines belonging to an element specie of higher ionisation energy (above 10ev) [5] and thus were not observed in sufficient amounts in air e.g. Carbon [C (II)] once ionised species.

- d) Relatively low concentrations present in the samples that could not allow for detection.
- Laser pulses were accumulated and averaged over measurement times to reduce the effect of plasma variation from each spark. Precision in terms of deviation of a set of 6 repeated measurements were obtained from laser pulses ranging from 30 to 1500. Replicate measurements of the observed 520.8 nm Chromium line intensity were used to determine the best fit precision based on the number of averaged pulses. The precision followed a trend of increment from 30 to 600 pulses. However, repeated measurement involving 900 pulses and above did not show further increased precision (Figure 2.6). This may have been due to the sample inhomogeneity [4] [8] [22] and the formation of crater depths great enough to reduce the power density and permit shielding effects of the plasma formed within the crater [3]. Consequently, the replicate measurements did not obey normal distribution as the intensity values experienced a continuous decline thus affecting the precision value. Terminating the precision experiment at 600 pulses to reduce the extended measurement time and avoid possible formation of deep craters yielded better results (Figure 2.7).
 - Quantitative analysis of certified steel samples in air. Internal standardisation method was used to obtain linear calibration curves. The analyte lines [Cr (520.8 nm) and Mn (403 nm)] were normalised to several matrix lines (Fe) and plotted against analyte concentration to obtain each curve (Figures 2.8-2.10). The best fit matrix line was selected based on linear correlation coefficient, precision and Limit of Detection (LOD) assessments. Blind samples were also interrogated with its concentration predicted based on its normalised analyte emission signal from the calibration curve (Table 2.1). 3 concentration ranges were used for the analytes. The concentrations for each range were evenly spaced for adequate correlation values. The resulting linear calibration curves showed relatively good correlation coefficient with values as high as 0.9729 obtained for the Chromium analyte while correlation value of 0.7322 was obtained for the Manganese analyte. The use of standard reference materials from the same “low alloy steel” type may be the reason for the improvement in correlation as a majority of the calibration samples have similar chemical properties. This was evident in the low concentration deviation for the set of calibration samples which indicate an internal standard with constant concentrations. However, it is assumed that the intensity of the internal standard is not dependent on the target composition in the range of concentrations used for the standards and the samples, so that any variation of line intensity can be related to the physical properties of the target [20]. From the quantitative analysis experiments, high precision values do not necessarily imply accurate measurements. This explains why random blind samples were selected to predict concentration and further evaluate accuracy. Varying values of pulse energy used for construction of calibration curves and blind sample measurements may have contributed to the accuracy error in predicting the concentrations. This sort of random error due to fundamental limitations on the experimental procedure was difficult to avoid because the pulse energy can never be set to the exact value used for calibration. Making replicate measurements ensured these errors were minimised.

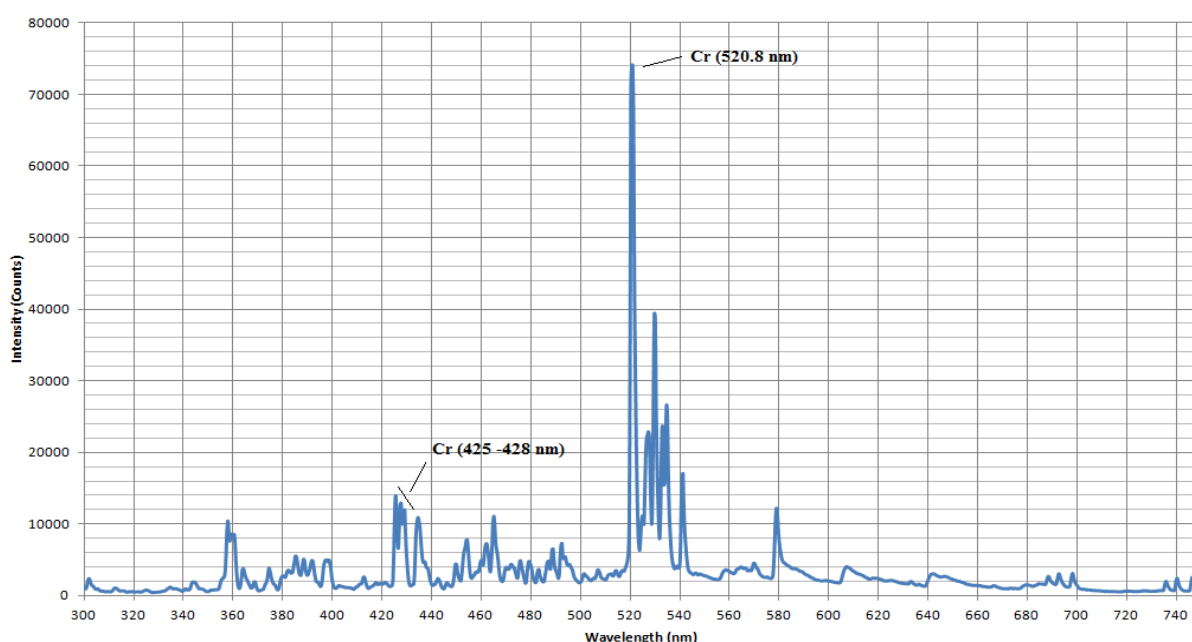


Fig 2.1 Spectrum of Chromium sample showing sensitive lines

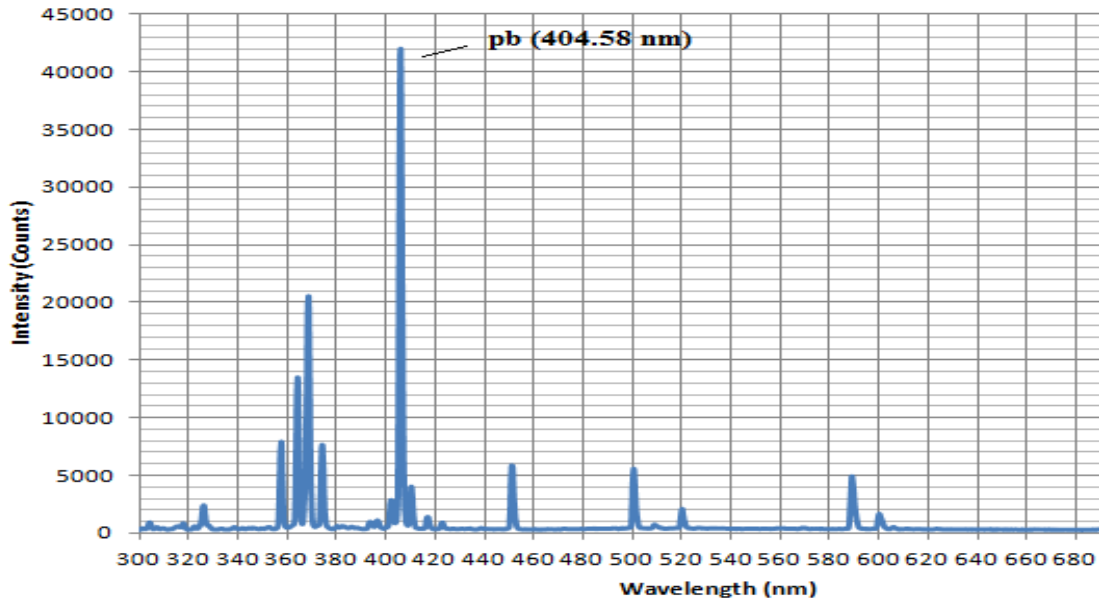


Fig 2.2 Spectrum of Lead sample showing sensitive lines

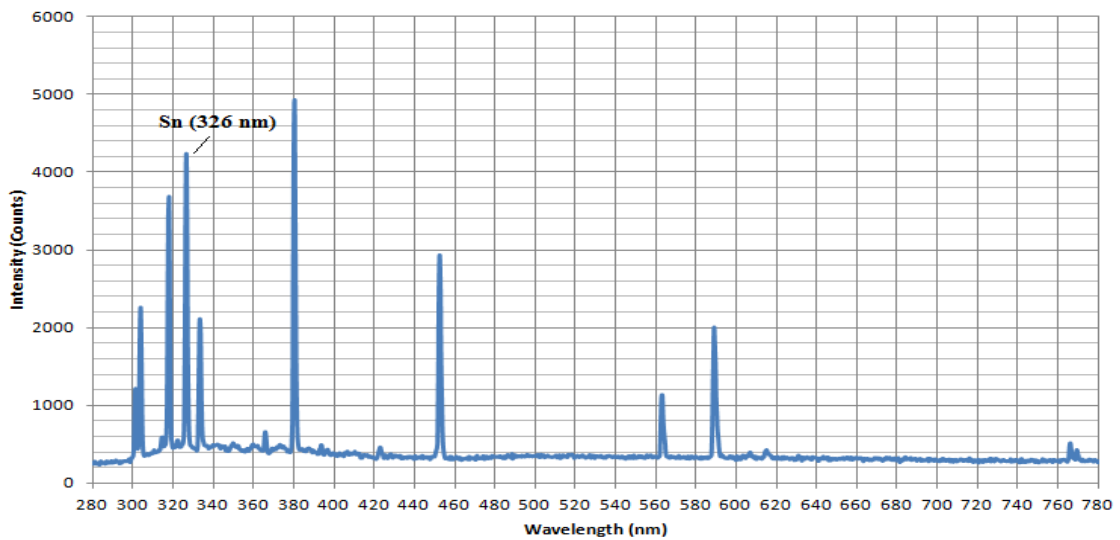


Fig 2.3 Spectrum of Tin sample showing sensitive lines

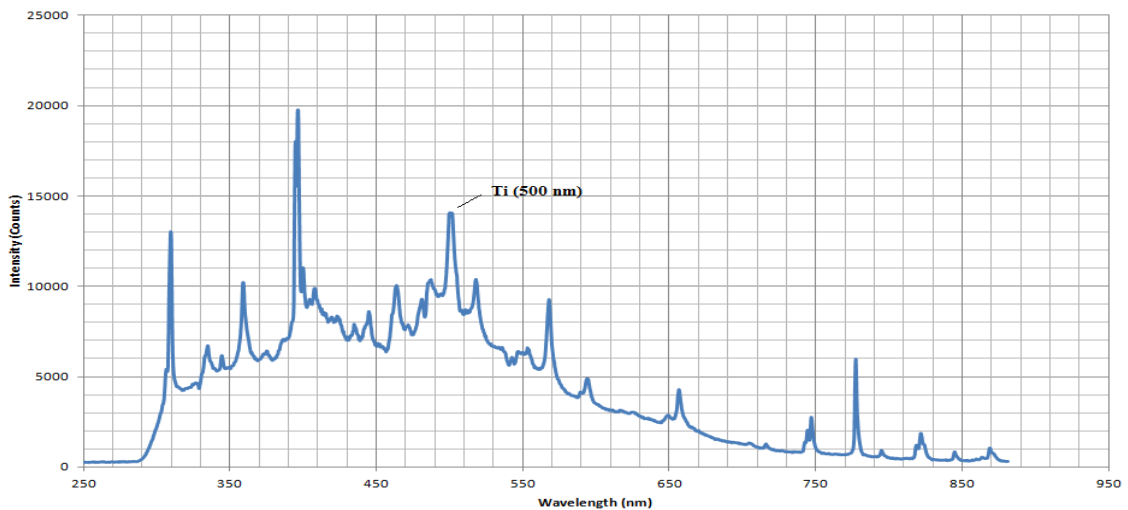


Fig 2.4 Spectrum of Titanium sample showing sensitive lines

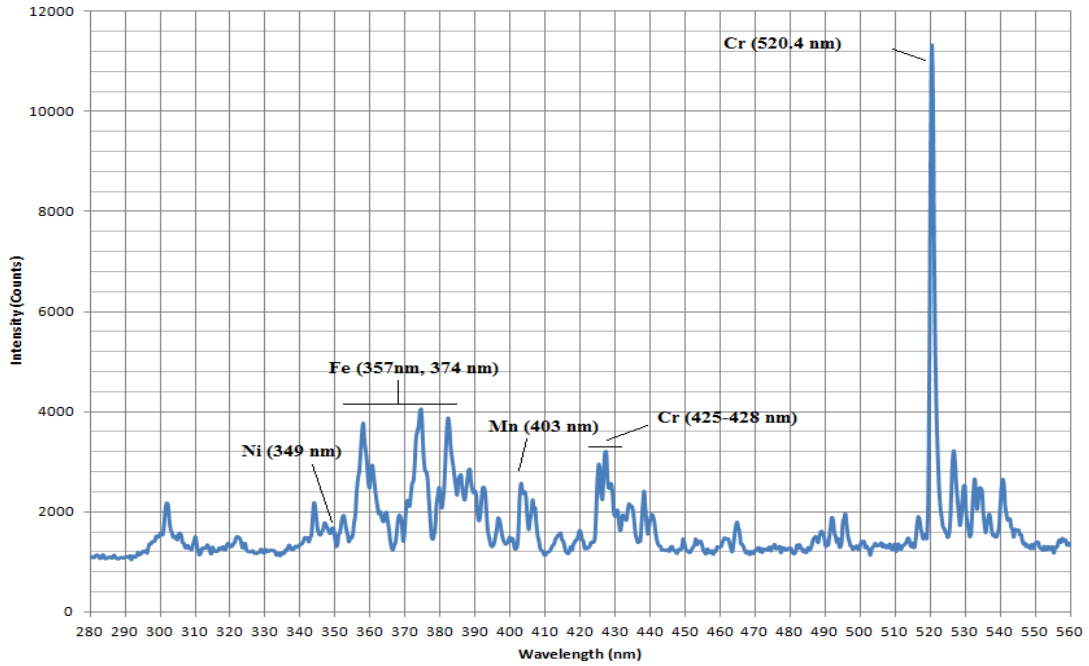


Fig 2.5 Spectrum of ferritic stainless steel sample

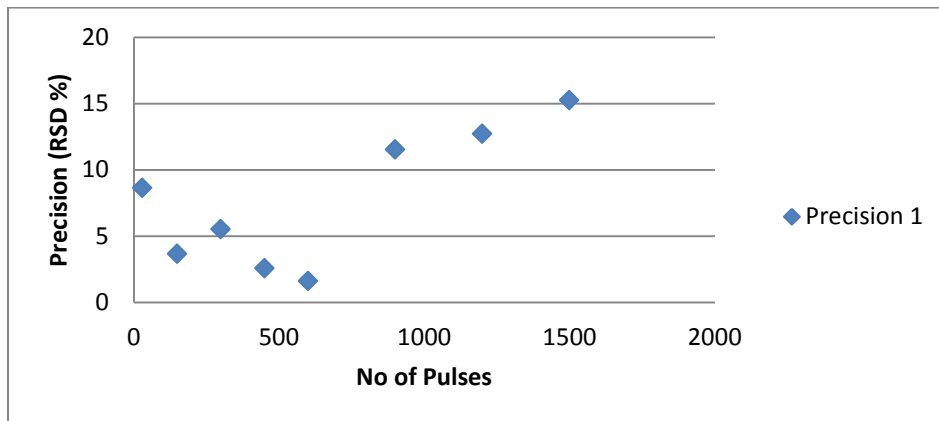


Fig 2.6 Graph of measurement precision plotted against the number of averaged pulses showing a reduction in precision after 600 pulses

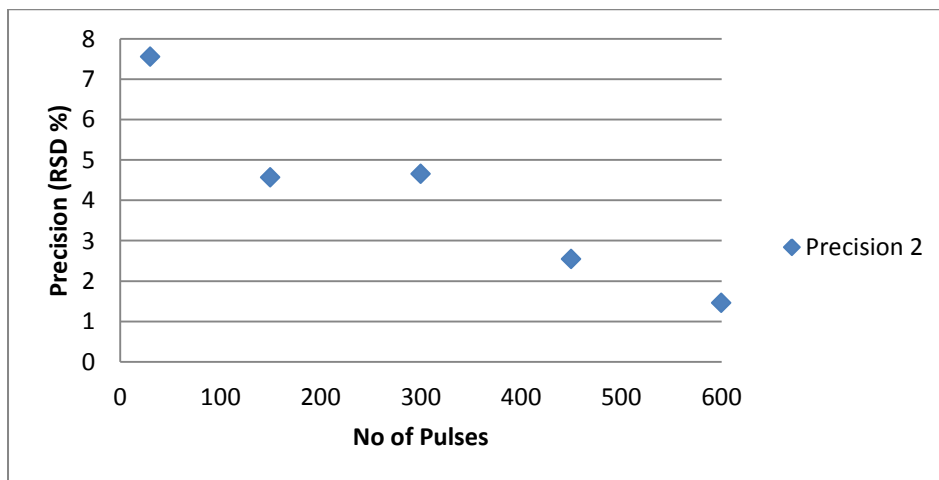


Fig 2.7 Graph of measurement precision plotted against the number of averaged pulses showing an improved trend with increased precision

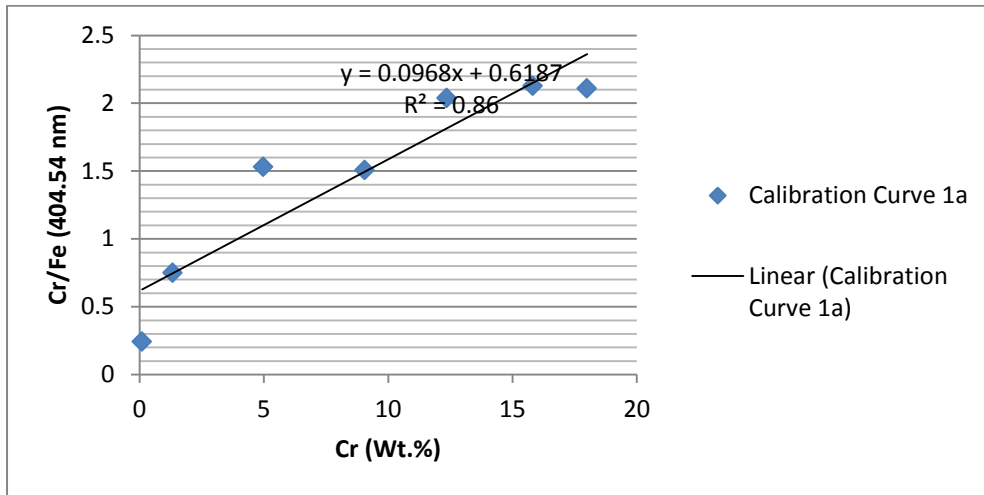


Fig 2.8 Calibration curve for chromium from a set of standard reference steel samples

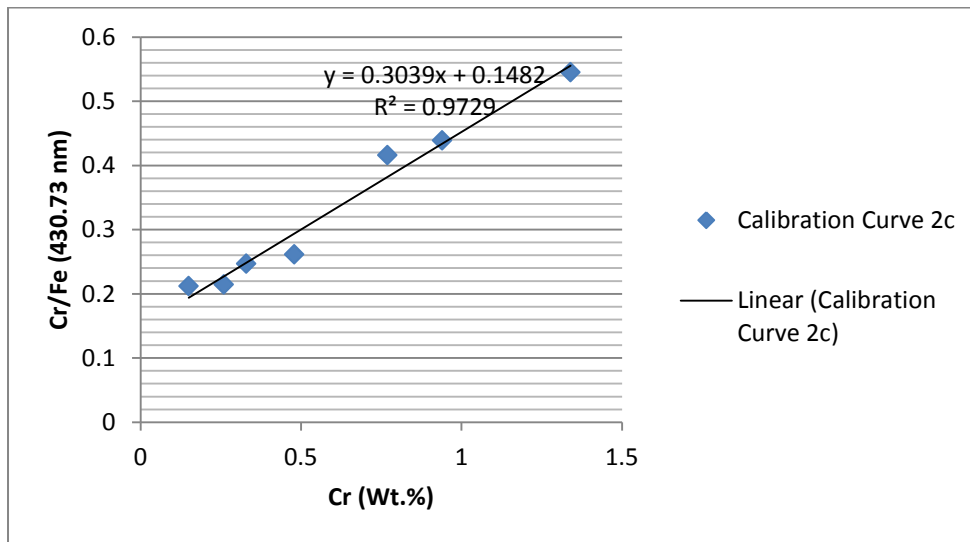


Fig 2.9 Calibration curve for chromium from a set of standard reference steel samples

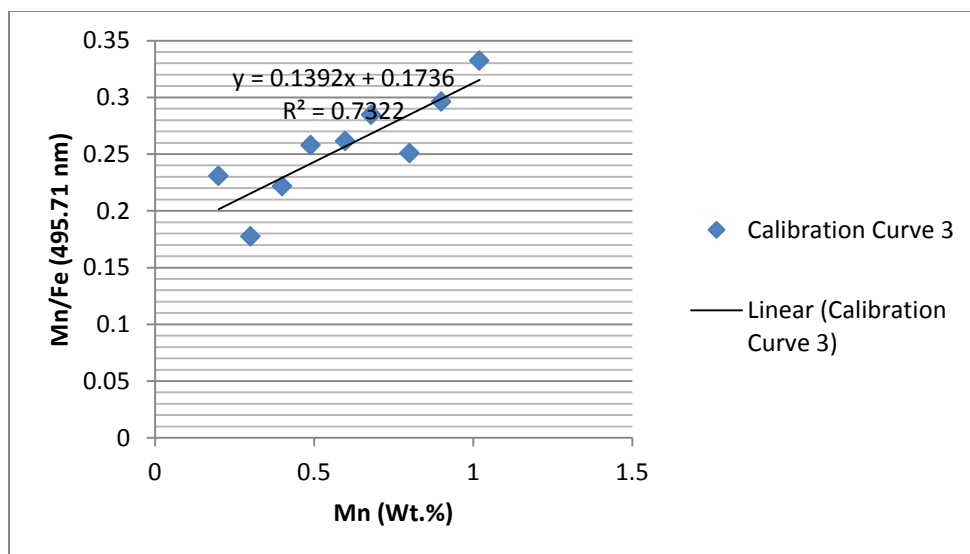


Fig 2.10 Calibration curve for Manganese from a set of standard reference steel samples

Table 2.1 Concentration prediction for blind samples

Element	Blind Sample	X_{pred} (Predicted Concentration) (Wt.%)	Actual Concentration (Wt.%)	S_y (Residual Standard Deviation)	S_{x0} (Standard Deviation of Procedure) (Wt.%)	V_{x0} (Relative Standard Deviation of Procedure) (%)	Accuracy Error (%)
Cr	1	3.36	3.95	0.299	0.48	5.45	15
Cr	2	11.19	11.93	0.299	0.48	5.45	6
Cr	3	0.2	0.21	0.024	0.078	12.57	5
Mn	4	0.92	0.64	0.025	0.17	29.1	44

2.1 COURSES ATTENDED

- PhD Essentials (PGRS Level 1)
- Exploring and Developing Entrepreneurship Competency for PhDs and Early Career Researchers – Building Your Business Model, How Does the money Flow?
- Advanced Presentation Skills
- Critical Appraisal of the Literature
- Invigilating Exams Training
- Science Communication
- Managing References: Refworks Part 1
- Managing References: Refworks Part 2
- Literature Searching Part 2: Web of Knowledge and Scopus Databases
- Literature Searching Part 1: Essential Skills for Success
- Corrosion Awareness Day

2.2 PRESENTATIONS

- *“Laser Induced Breakdown Spectroscopy for Identification and Quantification of Elemental Composition of Subsea Structures”*, Poster Presentation, European Optical Society Annual Meeting (EOSAM) Conference, 25-28 September, 2012.
- *“Laser Induced Breakdown Spectroscopy for Identification and Quantification of Elemental Composition of Subsea Structures”*, Poster Presentation, Engineering Symposium, University of Aberdeen, 28 February, 2013.

2.3 CONFERENCE AND JOURNAL PAPERS

- *Laser Induced Breakdown Spectroscopy for Identification and Quantification of Elemental Composition of Subsea Structures* (In Preparation). I intend to publish a technical paper on initial results from underwater LIBS experiments in due time. Setting up a suitable apparatus to carry out detection of submerged samples has encountered some difficulties.

3. RESEARCH SCHEDULE

My intended work plan for the remainder of the PhD programme will be outlined in this chapter. Table 3.1 represents a combination of the degree of accomplishment and a realistic research plan for the final year of study.

Table 3.1 Planned Programme of Research

Action		Status
<p>Qualitative and Quantitative LIBS analysis of steel samples in air. The latter will involve using internal standardisation method to plot calibration curves and predict with suitable precision and accuracy, the concentration values of analyte elements of interest from blind samples.</p>		Complete
<p>LIBS analysis on corroded steel samples in air. Spectral results obtained will be compared to initial results from reference steel samples without corrosion defects.</p>		In progress
<p>Qualitative and Quantitative LIBS analysis of submerged steel samples. Set-up suitable LIBS apparatus that can carry out underwater detection. These series of experiments conducted and the preliminary results obtained will be used to publish a technical research paper (journal/conference). Temperature and electron density measurements of plasma underwater. LOD and concentration prediction measurements from a set of reference steel samples and blind samples respectively.</p>		In progress
Month	Week	Action
24 - 26	69-80	Based on previous results, conduct more experiments and obtain useful results relating to underwater LIBS. Conduct preliminary experiments to analyse corroded steel samples underwater. Publish a journal/conference paper.
27-28	81-88	Set up a high pressure chamber target sample container to reconstruct similar depth related pressures experienced in a subsea environment. Study the effects of pressure on LIBS signal intensity. Publish a journal/conference paper if not already achieved.
29-31	89-100	Repeat previous experiments at extended pressures.
32-36	101-120	Obtain final precise, accurate measurements. Gather results, write and complete thesis

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