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Laser induced breakdown spectroscopy (LIBS) efficacy in hydrogen quantification in metal hydrides

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ABSTRACT

Metal hydrides are often used in pyrotechnics, catalysis, and hydrogen storage, among numerous other applications. The properties of the metal hydride are strongly correlated to the composition of the material, specifically the amount of hydrogen present within the solid. However, few techniques allow one to reliably detect and quantify hydrogen, and fewer still provide results rapidly (within seconds to minutes). Laser induced breakdown spectroscopy (LIBS) is a versatile technique for determining the elemental composition of nearly any material, including metals, alloys, semiconductors, soils, and coatings. In this study, we analyze a variety of metal hydrides with LIBS to investigate the feasibility of using this method to rapidly quantify hydrogen in said materials.

INTRODUCTION

Metal hydrides have maintained continued interest as fuels in pyrotechnic and propellant formulations to improve performance and handling characteristics. For example, the addition of metal hydrides to solid and liquid rocket propellant has been shown to improve specific impulse performance by 4% to 17% depending on formulation [1,2]. Alternatively, titanium subhydride-potassium perchlorate (THKP) has a long history as an electrostatic discharge (ESD) insensitive pyrotechnic composition [3]. Successful use of metal hydrides in pyrotechnic and propellant formulations requires precise hydrogen compositional control to ensure repeatable mixture performance. Precise hydrogen quantification methods are needed to meet these demands.

Hydrogen being the lightest element is not easy to measure. However, recent advances for quantitative measurements have been developed in large part due to the increased interest of hydrogen as an alternative fuel. Traditionally, volumetric, and gravimetric approaches have been used, each of which have advantages and disadvantages. In several techniques the hydrogen is thermally desorbed and then subjected to analysis. Volumetric methods quantify gas content by measuring changes in pressure within calibrated volumes, however, such methods are not specific to hydrogen and are affected by the presence of other gases. Mass spectrometry (MS)-based methods such as; temperature programmed desorption mass spec (TPD-MS), address the issue of specificity by analyzing molecules of desorbed gases. . Occasionally, some of these techniques can be coupled with a measurement of another physical quantity, for example the TPD-MS can also be coupled with a pressure-volume measurement in which a calibrated volume reservoir is used to capture and count the moles of desorbed gas, while the MS provides insight into the composition of the desorbed gas. Similarly, thermogravimetry mass spec (TG-MS) records mass loss as the sample is heated, and the MS signal again quantifies relative amounts of different desorbed gases. While it is possible to directly correlate MS signals with desorbed gas quantities, quantitative MS remains challenging due to difficulties in controlling variables like gas injection rate, ionization efficiency, and detector response. Spectroscopy is generally a reliable and accurate technique, but various factors can introduce errors or uncertainty into the results such as sample preparation or data collection and interpretation. Generally, simple spectroscopic techniques are not used by themselves directly on solid materials and desorbed hydrogen due to the lack of reliable standard methods and references materials and corresponding large errors associated with the measurement. While not spectroscopy-based, Nuclear Magnetic Resonance (NMR) and X-ray diffraction (XRD) are promising but suffer from similar issues. One exception is the use of so-called elemental analyzers (LECO) which apply thermal desorption methodologies, and then chemically convert hydrogen to water prior to detection by Non-Dispersive InfraRed (NDIR). Laser Induced Breakdown Spectroscopy (LIBS) is promising, as small amounts of solid material are desorbed and analyzed in the gas phase, which circumvents the difficulties in measuring hydrogen in solid compounds. In this paper the uses and limitations of the LIBS technique in quantifying hydrogen in metal hydrides is explored. Focus will be given to titanium hydride and its subhydride family of compounds, TiH_x ($x \leq 2$). However, the discussed methodologies can easily be adapted to measure hydrogen content in other metal hydrides.

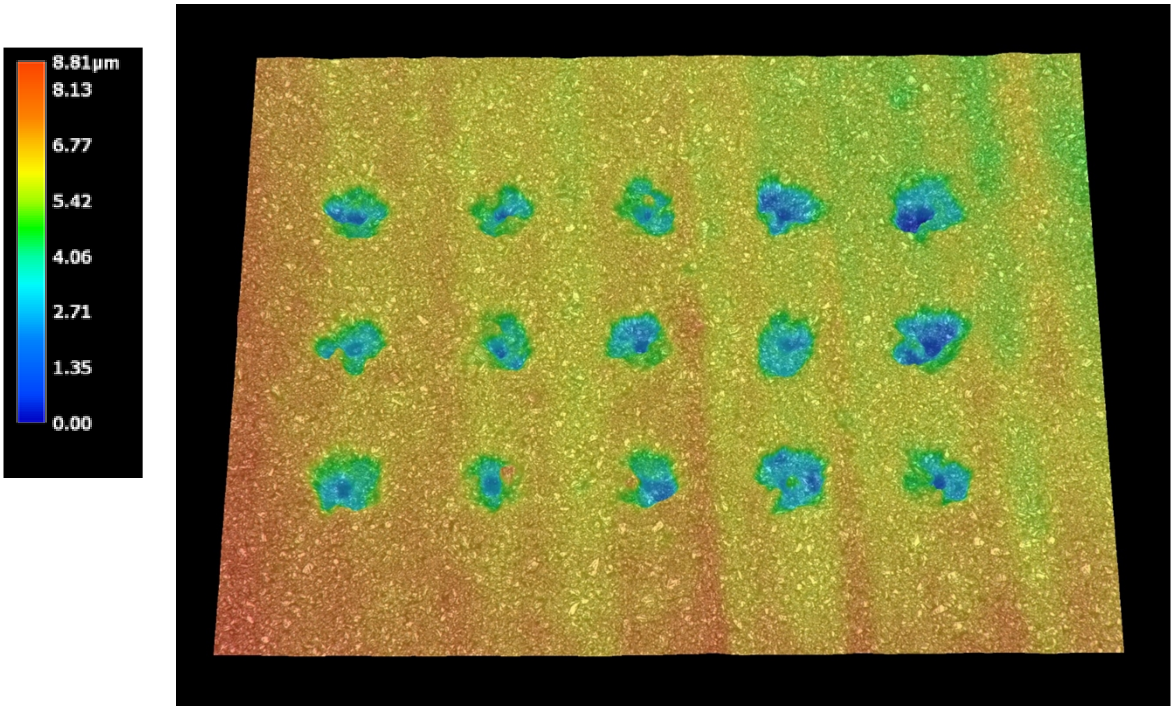
Although not a new technique, LIBS has attracted renewed attention since it can characterize nearly all environmental chemical species with distinct spectral signatures. The analysis with LIBS for hydrogen in metals or other solids is more difficult than for other elements because of severe emission diminution or even disappearance of its spectral lines. The first application of a laser induced shock wave plasma (LISPS) was in 2004 by Kurniawan, to detect a hydrogen emission line at 656.28 nm in a zinc plate, a glass slide and a zircalloy tube. Since then, the application has been developed by multiple manufacturers (notable for the purposes of this paper are applications developed by Keyence and SciApps) to make it available for research and industrial applications and improve elemental detection capability [4–12].

EXPERIMENTAL

The data presented here were collected using Keyence HX-7000N system with EA-300 Nd:YAG 355 nm instrument lasers, and constitutes the first time titanium subhydrides have been evaluated using LIBS. The samples were prepared in-house from commercially available TiH_2, or Ti via a proprietary technique. Samples of commercial, TiH_2, −325 mesh, 98%, powder, Ti <45 µm avg. part. size, 99.98% trace metals basis and TiO_2 powder, <5 µm, ≥99.9% trace metals basis, were acquired from Sigma-Aldrich and used as received. Approximately 0.5 grams of each sample was pressed into pellets with a 13 mm diameter for analysis. The powders were mixed in a mortar and pestle prior to pelletizing to ensure sample homogeneity. The Ti and TiO_2 samples were used as references to calibrate the LIBS signals and, in some cases, used as standards to build a calibration curve from which hydrogen quantification can be performed. For these measurements the laser spot size was approximately 10 µm, and samples were taken from 15 locations on each cylinder face. The spacing between individual analysis points were selected so that they were spaced far enough to avoid overlap and interference of material. Sampling was performed in air which can influence measurements on metals, alloys, oxides and other materials known to interact with oxygen or be oxygen and/or air sensitive.

RESULTS AND DISCUSSION

The pellets of several titanium hydrides and subhydrides were measured by the Keyence LIBS. Upon application the laser vaporizes material leaving aa crater of 6-7 µm in size. The material that occupied this crater is turned into a plasma which is analyzed by the detector. An array of 15 such craters in a pellet sample is shown in Figure 1 below. Additional detail on the sample and crater size after laser ablation is presented in Figure 2.


8.81µm
8.13
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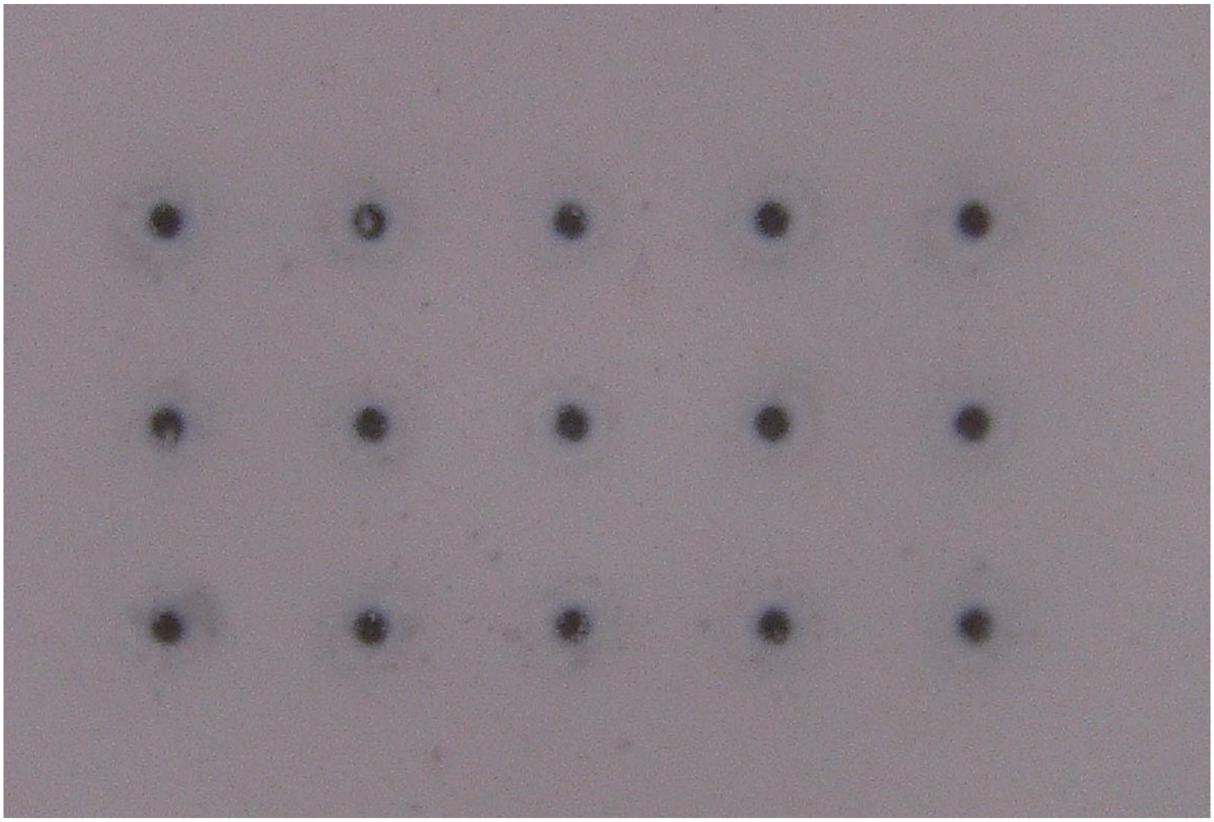
5.42
4.06
2.71
1.35
0.00



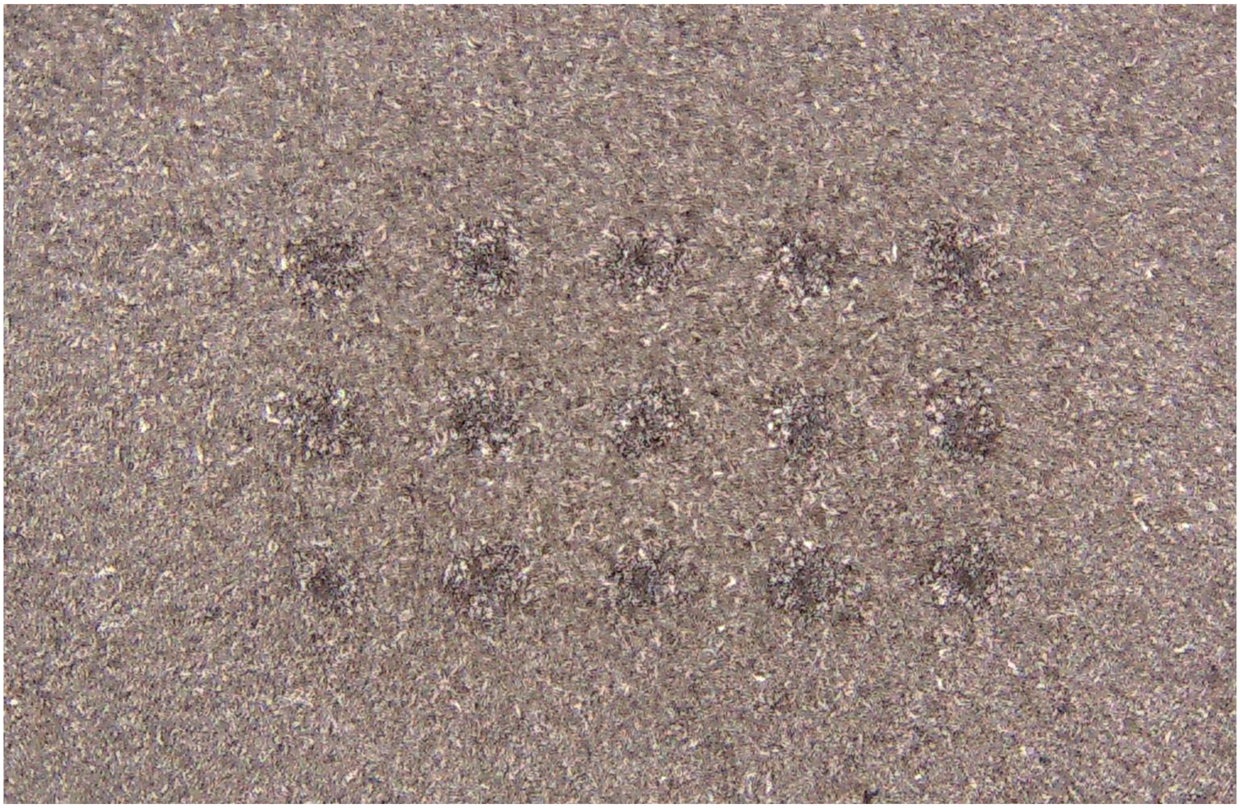


Figure 1. LIBS craters left after the laser ablation of the sample. TiO_2 and TiH_2 sample areas after laser ablation.

LIBS spectra data collected on Ti, TiO_2, and TiH_2 was used to compare and calibrate the LIBS spectra signals measured here. The data collected on these “standard” samples is shown in Figure 4. The 15 data points presented on the sample picture represents a quantification in atomic percentages of individual elements present in the sample. The data is also summarized in Table 1. It was observed that the atomic percentages for TiO_2 are lower than expected for a 33.33 at. % Ti and higher than expected for a 66.67 at. % O content. It is believed these deviations can be attributed to (1) air interaction with the measurement, (2) the lack of developed standards, and (3) compositional irregularities in the TiO_2 powder. The primary issue with performing measurements in air is interaction of the air with the generated plasma. Here measured atomic percentages are consistently biased towards higher oxygen atomic percentages indicating a higher oxygen content which suggests air interaction. One way to mitigate this interaction would be to perform the measurements in an inert atmosphere such as under argon which is currently being explored.

Table 1. Values generated by the Keyence software for titanium dioxide and titanium dihydride. The values are in atomic percentage.

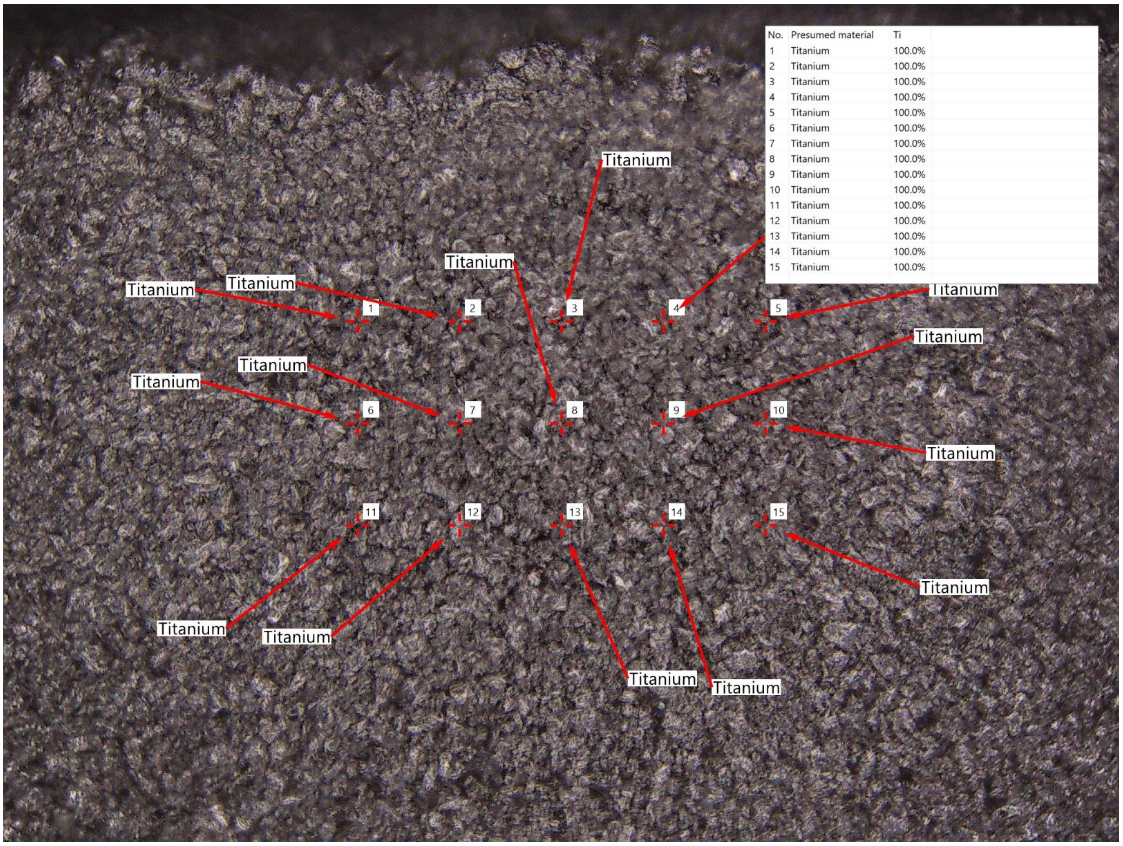
No.	Presumed material	Ti	O
1	Titanium compound	30.9%	69.1%
2	Titanium compound	29.9%	70.1%
3	Titanium compound	29.7%	70.3%
4	Titanium compound	32.1%	67.9%
5	Titanium compound	30.0%	70.0%
6	Titanium compound	30.0%	70.0%
7	Titanium compound	28.6%	71.4%
8	Titanium compound	27.4%	72.6%
9	Titanium compound	27.2%	72.8%
10	Titanium compound	27.5%	72.5%
11	Titanium compound	31.7%	68.3%
12	Titanium compound	29.9%	70.1%
13	Titanium compound	29.8%	70.2%
14	Titanium compound	24.8%	75.2%
15	Titanium compound	32.6%	67.4%

No.	Presumed material	Ti	H	O
1	Titanium alloy	23.0%	59.1%	17.9%
2	Titanium alloy	27.5%	55.3%	17.2%
3	Titanium alloy	19.5%	68.6%	11.9%
4	Titanium alloy	20.0%	67.5%	12.5%
5	Titanium alloy	24.8%	57.0%	18.2%
6	Titanium alloy	20.0%	64.0%	16.0%
7	Titanium alloy	21.5%	62.5%	16.0%
8	Titanium alloy	23.2%	59.4%	17.4%
9	Titanium alloy	23.5%	60.4%	16.1%
10	Titanium alloy	22.3%	61.6%	16.1%
11	Titanium alloy	22.4%	59.6%	18.0%
12	Titanium alloy	21.6%	61.4%	17.0%
13	Titanium alloy	21.0%	63.5%	15.5%
14	Titanium alloy	23.7%	61.2%	15.1%
15	Titanium alloy	25.3%	59.7%	15.0%

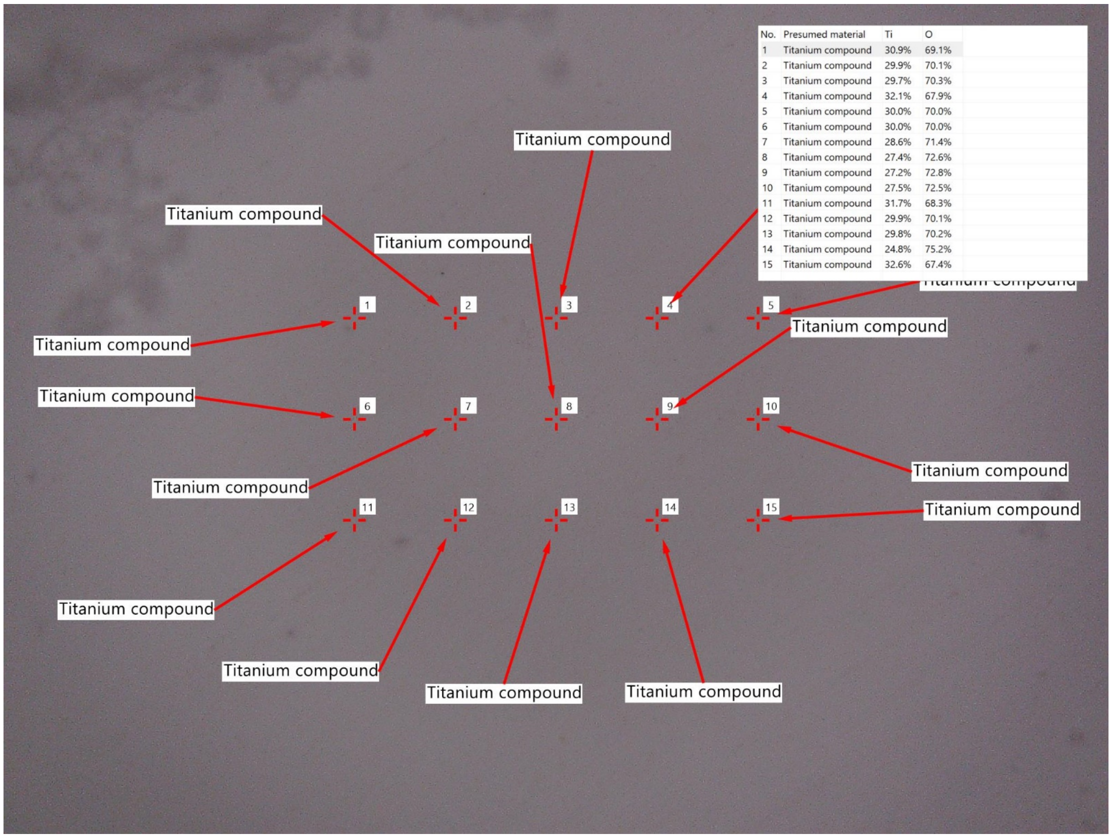
A linear regression was performed using the titanium, titanium dioxide and dihydride spectra as references. The data was fitted in Origin via a linear regression used to combine pure material reference spectrums to fit measured spectra. Regression was done on the entire spectra as the addition of an element like hydrogen doesn't just add hydrogen emission peaks but reduces other peaks due to changes in density. Since the LIBS analysis was conducted in air, the TiO_2 quantity was ignored in the H/Ti ratio calculation. The LIBS spectra for the Ti, TiO_2 and TiH_2 and the linear regression are presented in Figure 5 below. Based on this linear regression the subsequent subhydride samples, $TiH_{1.45}$, $TiH_{1.55}$, $TiH_{1.65}$, $TiH_{1.75}$ were evaluated, and the results are shown in Figure 6 and summarized in Table 2.

The analyzed subhydrides tended to have a lower composition than the anticipated prepared levels, except for the two samples TiH_2 and $TiH_{1.55}$ which are close to their expected composition. While performing analysis in an inert environment would be expected to reduce the measurement uncertainty, it is also a reasonable expectation that the samples have composition variability. Further development of the methodology is expected to reduce the uncertainty in the measurement which would improve the utility of the LIBS method for titanium subhydride characterization. This is supported by previous success in literature using LIBS for characterizing hydrogen content in uranium hydride and titanium hydrides and deuterides [12-14].

All spectral lines displayed in the LIBS output are the Ritz wavelengths which are calculated from the energy levels. The NIST database has the most intense hydrogen spectral lines at 486.1 nm and 656.3 nm. Typically, because the line at 486.1 nm suffers from interference from adjacent Ti lines at 498.173 nm, for quantification purposes the Ti 498.173 nm and H 656.28 nm lines are selected for analysis. [13,14]



No.	Presumed material	Ti
1	Titanium	100.0%
2	Titanium	100.0%
3	Titanium	100.0%
4	Titanium	100.0%
5	Titanium	100.0%
6	Titanium	100.0%
7	Titanium	100.0%
8	Titanium	100.0%
9	Titanium	100.0%
10	Titanium	100.0%
11	Titanium	100.0%
12	Titanium	100.0%
13	Titanium	100.0%
14	Titanium	100.0%
15	Titanium	100.0%



No.	Presumed material	Ti	O
1	Titanium compound	30.9%	69.1%
2	Titanium compound	29.9%	70.1%
3	Titanium compound	29.7%	70.3%
4	Titanium compound	32.1%	67.9%
5	Titanium compound	30.0%	70.0%
6	Titanium compound	30.0%	70.0%
7	Titanium compound	28.6%	71.4%
8	Titanium compound	27.4%	72.6%
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10	Titanium compound	27.5%	72.5%
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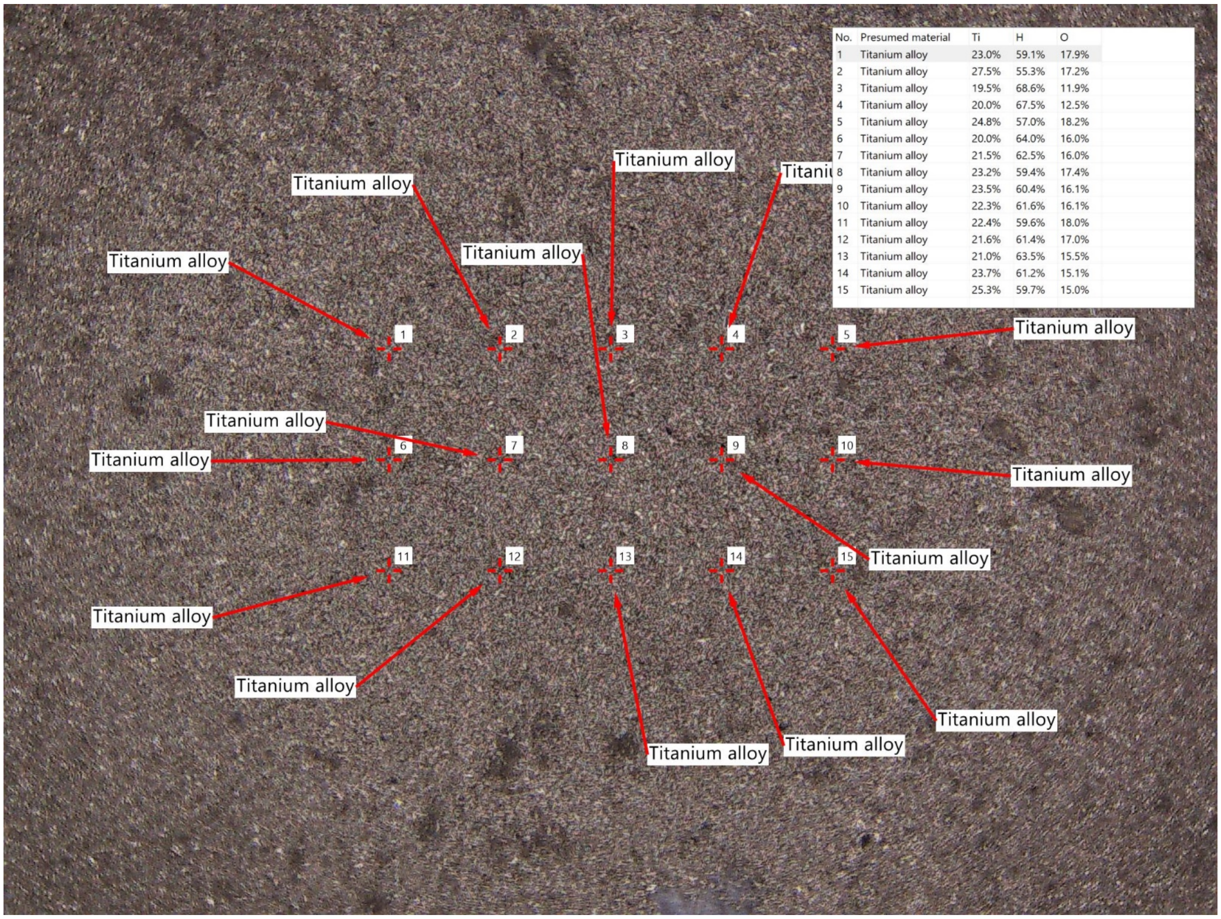

No.	Presumed material	Ti	H	O
1	Titanium alloy	23.0%	59.1%	17.9%
2	Titanium alloy	27.5%	55.3%	17.2%
3	Titanium alloy	19.5%	68.6%	11.9%
4	Titanium alloy	20.0%	67.5%	12.5%
5	Titanium alloy	24.8%	57.0%	18.2%
6	Titanium alloy	20.0%	64.0%	16.0%
7	Titanium alloy	21.5%	62.5%	16.0%
8	Titanium alloy	23.2%	59.4%	17.4%
9	Titanium alloy	23.5%	60.4%	16.1%
10	Titanium alloy	22.3%	61.6%	16.1%
11	Titanium alloy	22.4%	59.6%	18.0%
12	Titanium alloy	21.6%	61.4%	17.0%
13	Titanium alloy	21.0%	63.5%	15.5%
14	Titanium alloy	23.7%	61.2%	15.1%
15	Titanium alloy	25.3%	59.7%	15.0%

Figure 4. LIBS data collected on Ti, TiO_2 and TiH_2, commercial samples from Aldrich. The individual spots analyzed on the samples and the quantification in at. % is presented in the top corner table.

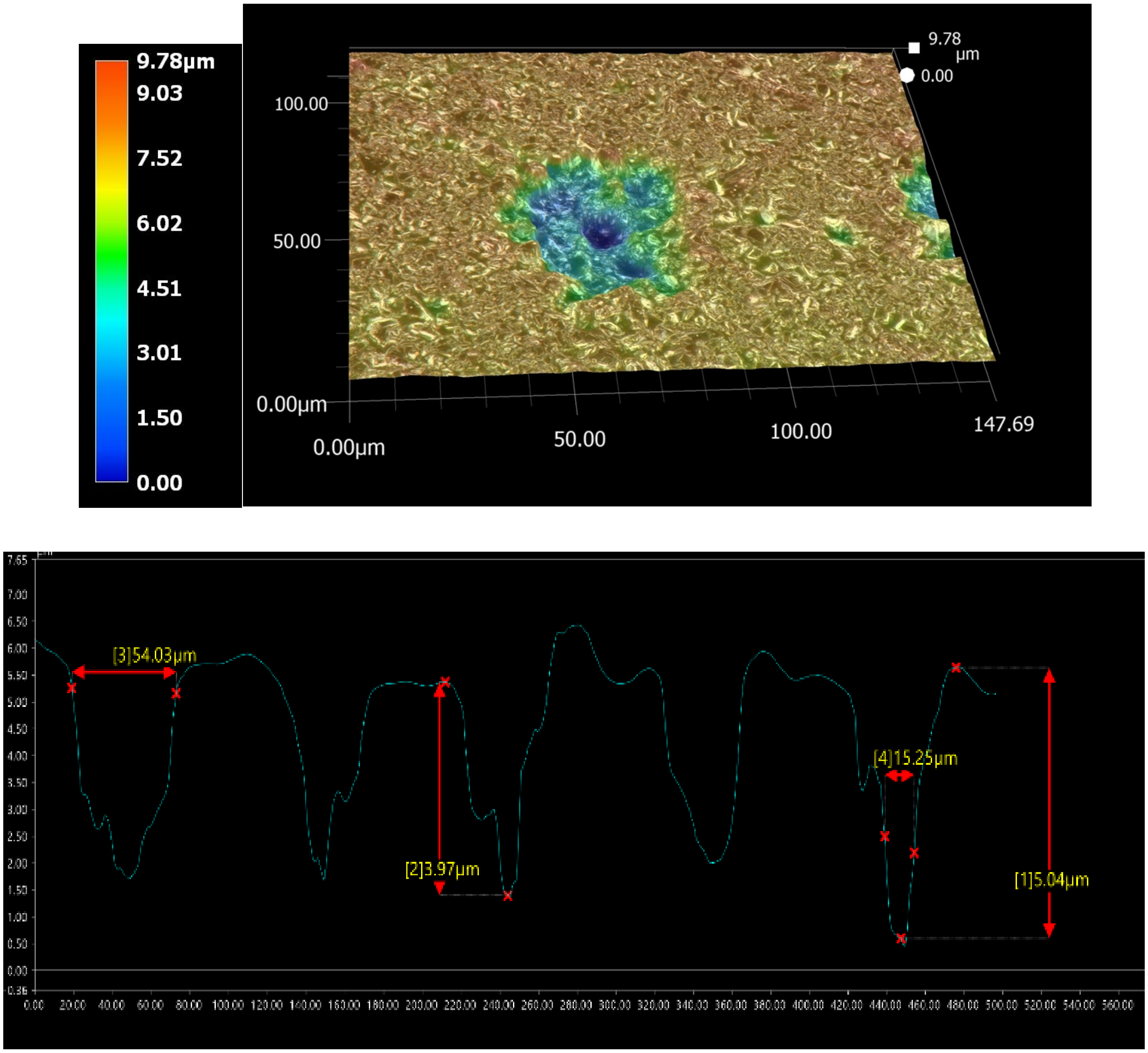

Figure 2. TiH_2 Crater sizes. 10 µm diameter laser spot yields a crater depth of 4 – 5 µm. Affected area on pressed powder wafer was ~50 µm.

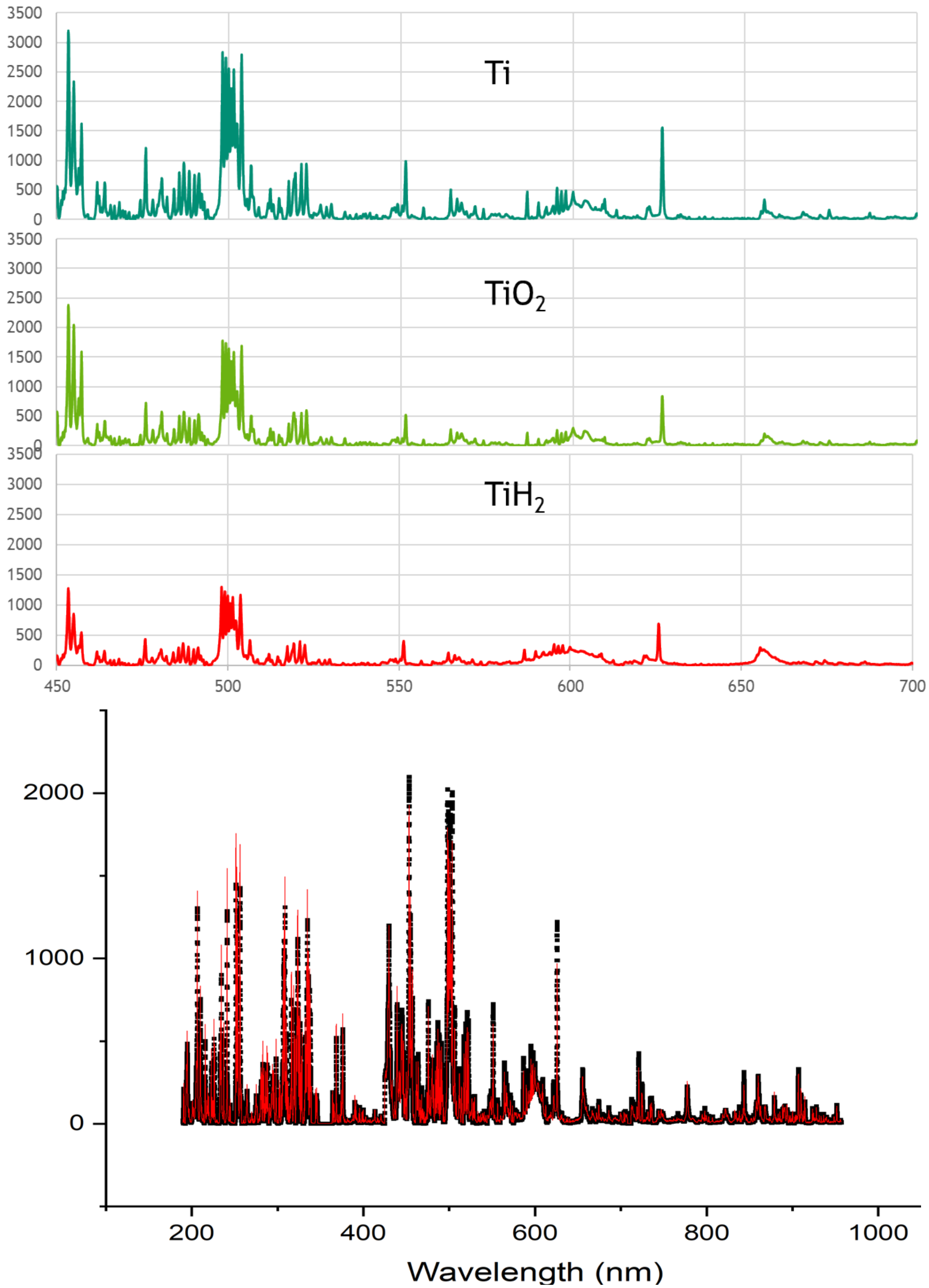

Figure 5. LIBS spectra for Ti, TiO_2 and TiH_2. Origin linear regression example for a single sample point.

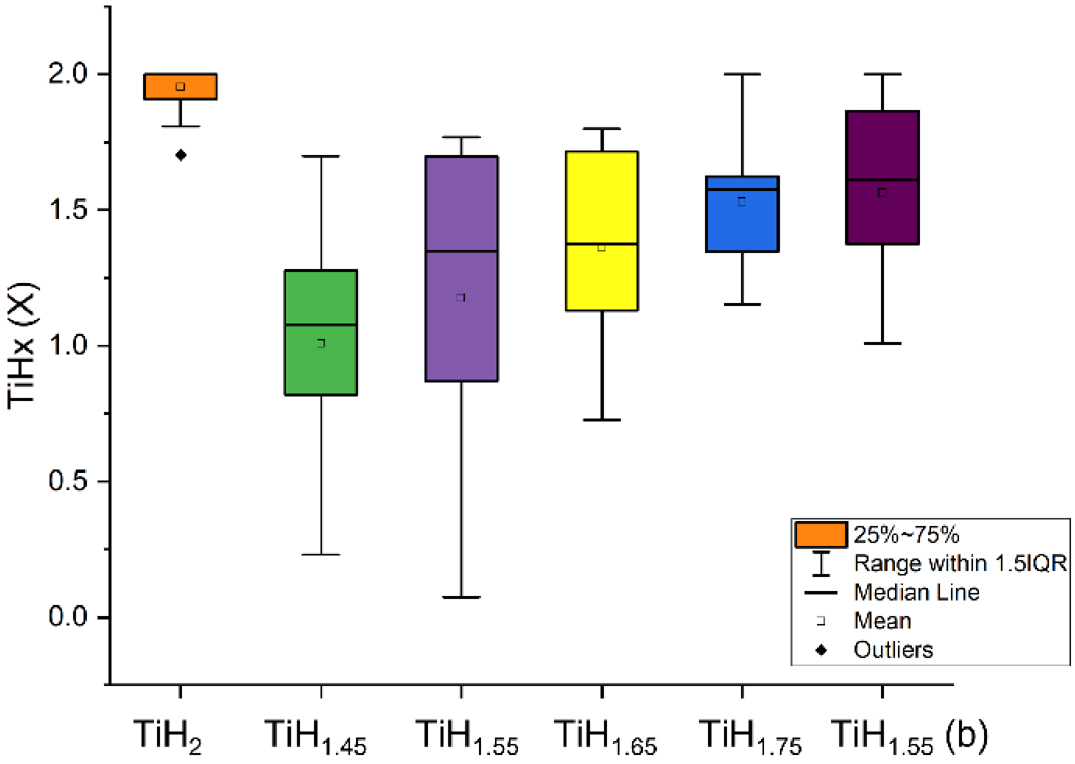

Figure 6. LIBS results hydrogen composition data and respective error bars in the analyzed titanium subhydrides.

Table 2. Data summary for the analyzed subhydrides

Samples	Composition
TiH_2	1.95(+/-0.09)
$TiH_{1.45}$	1.01 (+/-0.40)
$TiH_{1.55}$	1.18 (+/-0.53)
$Ti_{1.65}$	1.36 (+/-0.32)
$TiH_{1.75}$	1.53 (+/-0.22)
$TiH_{1.55}$ (b)	1.56 (+/-0.29)

FUTURE WORK

This works presents the proof of concept of using the LIBS technique for determining hydrogen content, as H/Ti atomic ratios, of titanium subhydride powders. The measurement variability and the lower-than-expected hydrogen content is not yet understood but may stem from variability in the powder composition, variability in the measurement such as how the laser couples with the material, and the presence of air for the analysis. Current work includes the development of an air free sample holder in which the analysis can be performed in an argon environment, from which initial results have shown that the signals improve. The use of standards that can simulate an increasing hydrogen content to obtain a calibration curve is also being explored. Refining of the LIBS technique will permit further assessment of the merit of LIBS for analyzing the composition of metal hydrides and identification of the technique's limitations. Future efforts should look to extend the method to analysis of other simple metal hydrides, such as ZrH_2 or MgH_2, and complex hydrides such as $NaBH_4$.

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