



DTU ELECTRO
Department of Electrical-
and Photonics Engineering



DEN DANSKE
MARITIME FOND

LASER-CLEANR

Laser Ablation and Spectroscopy for Eco-friendly Removal
of Coatings, Lower Emissions, AND Recycling

Technical Project Report

By

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Executive summary

The LASER-CLEANR project set out to investigate the laser ablation technology as a clean alternative to abrasive medium blasting for removal of marine paints from ships. The motivation was clear: Laser ablation not only creates significantly less waste; it also enables recycling of the waste material. As such, the project addresses two of the UN sustainable development goals: (12) Responsible consumption and production, and (14) Life in the sea.

Over the course of 13 months, the LASER-CLEANR team demonstrated:

- ✓ A working hand-held prototype system for industrial laser cleaning, tested at Fayard shipyard at Fyn.
- ✓ That light emitted during laser cleaning can be used to identify the contents of the removed paint and show whether the laser has cleaned all the way down to the steel substrate.
- ✓ Fast laser-based analysis of gas and particles from the ablation process. Only CO, CO₂ and H₂O was found in the exhaust gas, while particles collected showed signs of volatile organic compounds (VOCs) with possible hazards to human health.
- ✓ That Powell lenses are not suitable for laser cleaning, and that most likely the easiest way to increase speed is to have more laser power and do faster scanning or have multiple scan heads in parallel.

More work is needed to e.g. test the influence of fouling and corrosion, improve methods for gas/particle sampling and analysis, and improve the scanning speed/range to make laser cleaning a viable alternative to abrasive medium blasting.

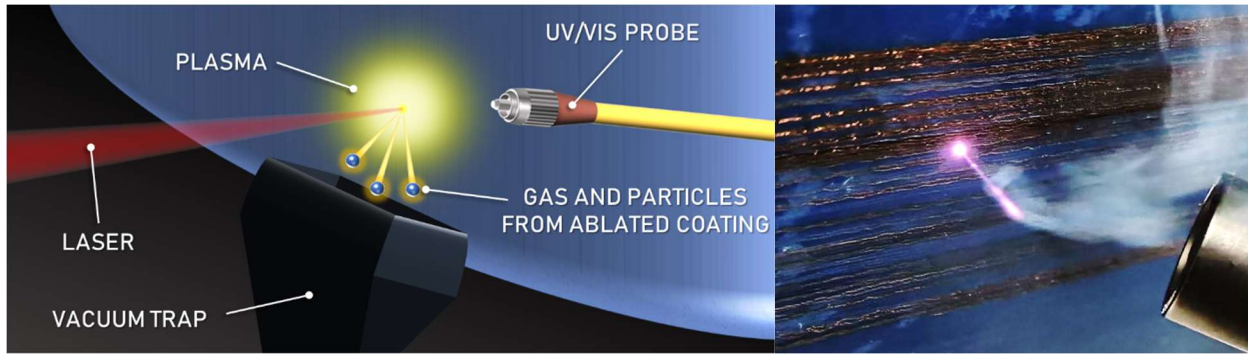


Figure 1. (Left) Concept illustration. A laser beam is ablating paint on a ship hull creating a bright plasma that is monitored using an optical fiber probe. Gas and particles from the ablation is collected for further analysis and potential recycling. (Right) Photo from the experimental lab setup.

Introduction

Project description and motivation

Protective coatings are essential in many industries for maintaining performance and integrity of various components and structures. Marine structures and vessels in particular depend on protective coatings to minimize the exposure to sea water and organic growths (fouling). Without protective coatings, organic fouling would cause increased drag on ships resulting in increased fuel consumption, meanwhile the salt water would cause the hull to corrode, compromising the structural integrity of the ship. In order to maintain the protective properties of the coating it must be reapplied regularly, but not before removing the old coating. The golden standard for paint removal on marine vessels is by abrasive medium blasting, i.e. sand- or water blasting. However, this method is extremely toxic and polluting to the environment, which is why it is typically performed in developing countries and countries without strict environmental regulations. To bring the paint removal process back to Danish and European shipyards would require a completely different process that not only significantly reduces environmental pollution, but is safe and compatible with existing drydock processes. One technology that can satisfy this is laser ablation.

Laser ablation is a well-known technique within industrial cleaning, which involves scanning a high power laser beam across a component or structure to completely vaporize any contaminants or surface layers from metallic substrates. In contrast to abrasive methods, laser ablation does not produce additional waste so the smoke and ablated material can therefore easily be collected by a vacuum system. In this way, laser ablation not only reduces the environmental impact of paint removal, but can also makes the production of paint more sustainable by enabling ablated material to be recycled. It is with this goal in mind that the project will study laser ablation of paints and develop a prototype laser ablation system that allows for the collection of ablated material.

Relation with UN Sustainable Development Goals

The project is related to responsible consumption and production (goal 12) in the sense that it seeks to not only reduce the amount of waste material generated during paint removal, but also capture any harmful gases or particles and recycle the collected waste material. This leads directly to the goal of improving life in the sea (goal 14) by reducing the amount of waste from paint removal that ends up in the oceans and ultimately in the food chain. Increasing the knowledge and awareness of laser ablation for marine paint removal may eventually lead to changes in regulations and ultimately cleaning practices at shipyards, which would help protect marine and coastal ecosystems where the ship yards are located. This is summarized in Figure 2.

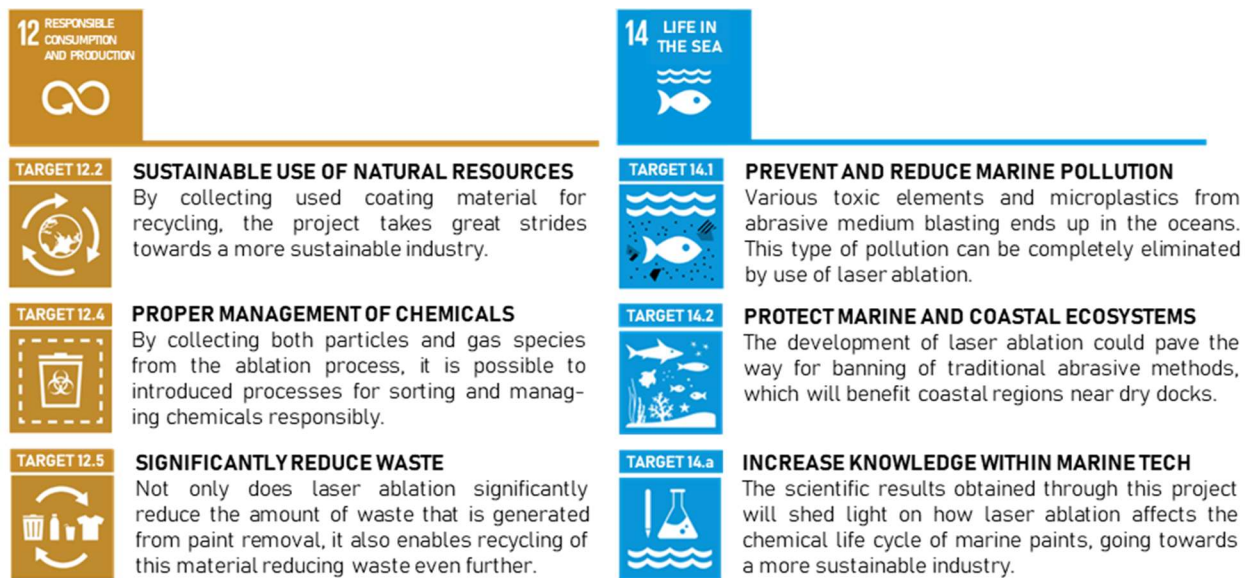


Figure 2. Overview of UN Sustainable Goals that are addressed by the LASER-CLEANR project.

Project structure and milestones

The project is divided into five activities as outlined in Figure 3. In A1, the light emitted from laser ablation of paints due to generation of plasma is investigated using ultraviolet/visible (UV/VIS) spectroscopy. In A2, a system for collecting and separating gas from particles is developed. In A3, different methods for improving the ablation speed is tested. In A4, the gas and particles collected during ablation is analyzed using mid-infrared (MIR) spectroscopy. Finally, in A5 the prototype system is demonstrated.

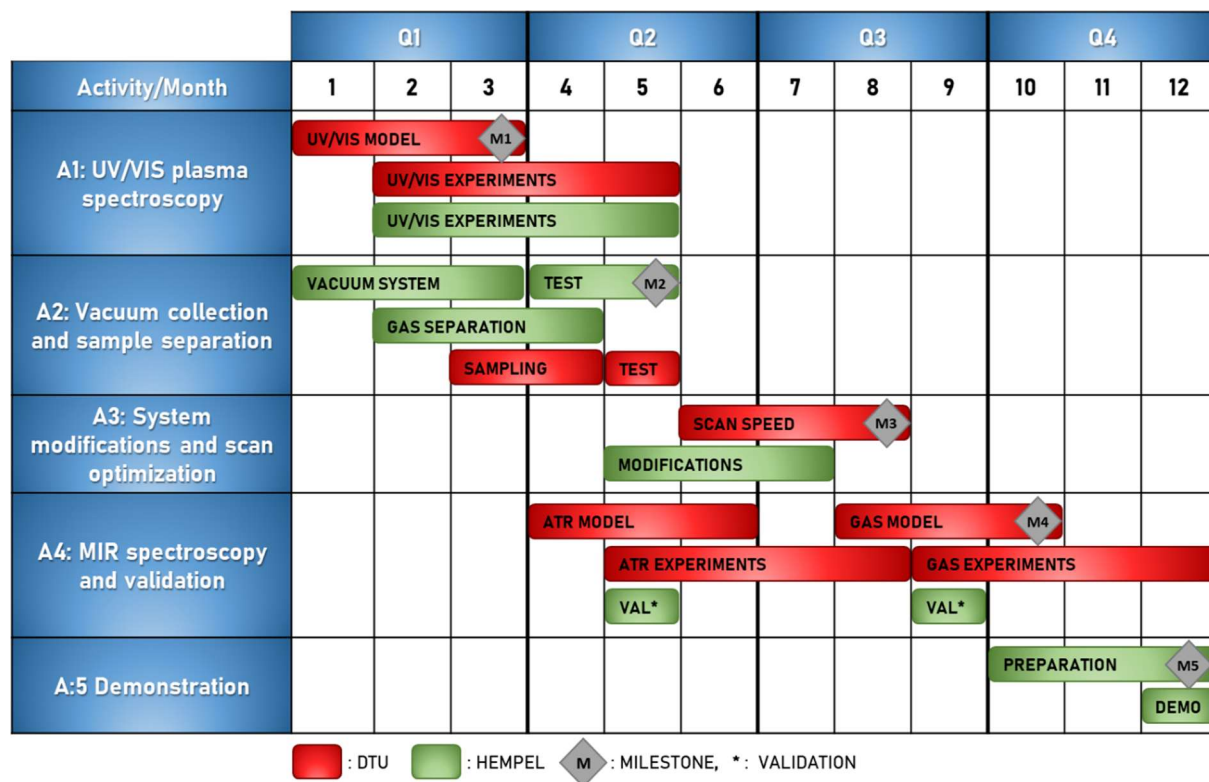


Figure 3. Gantt chart overview of the project activities and milestones.

In addition, each activity has a corresponding milestone:

- ✓ M1: Model for interpretation of plasma emission data tested for various laser/coating parameters.
- ✓ M2: Vacuum separation of gas and particles demonstrated.
- ✓ M3: Scanning speed/range increased by factor x2
- ✓ M4: Calibration models for determination of gas/particle chemistry based on MIR absorption data validated
- ✓ M5: Prototype system for laser ablation and waste collection demonstrated in an industrially-relevant environment

About the team

The project was carried out in collaboration between DTU Electro, Department of Electrical and Photonics Engineering, and Hempel Growthub, Hempel A/S.

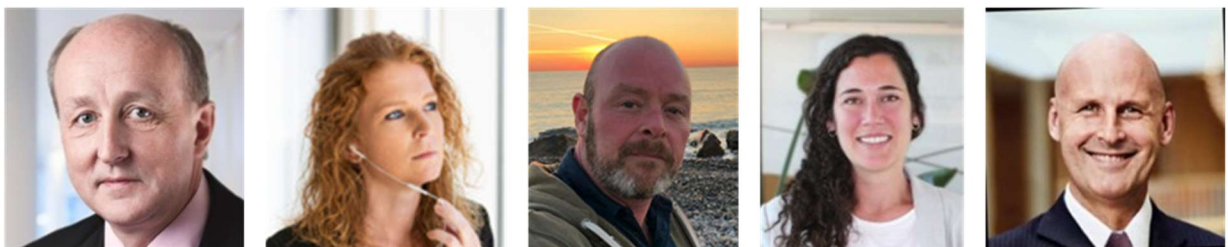
DTU ELECTRO



Left: Christian Rosenberg Petersen (senior researcher). Right: Doyinsola Simbiat Sonoiki (PhD student).

Christian and Doyinsola is part of the Fiber Sensor and Supercontinuum group at DTU Electro. The group is primarily focused on developing optical fiber sensors and optical fiber lasers that cover a wide range of colors (supercontinuum) for use in non-destructive imaging and spectroscopic sensing. Christian has more than ten years of experience working with high-power lasers and has successfully demonstrated the use of these lasers within imaging and spectroscopy. Doyinsola has a background within spectroscopic data analysis obtained during her international M.Sc. program at Aarhus University and Ghent University, Belgium.

HEMPEL GROWHUB



Left to right: Kim Scheibel (customer futurist), Amalie Trige Pedersen (senior project manager), Morten Schnohr (technologist), Lucia Villaverde (innovation designer), Mark Terrell Sutton (executive manager).

Hempel GrowHub is an internal incubator within Hempel with the primary goal of developing products and services adjacent to the paint in the can. The team is small, but with a wide array of competencies within the team.

Mark Terrell Sutton is the Manager of the department. He has over 15 years of experience within Hempel and has an entrepreneurial and digital background.

Amalie Trige Pedersen is the Project Manager of the project. She has 7 years of experience in the field of project management, and 5 of those years within Hempel.

Kim Scheibel has worked at Hempel for over 40 years and brings to the project a vast amount of industry knowledge alongside his innovative mindset.

Morten Schnohr has worked at Hempel for over 15 years and has a thorough understanding of various technologies. He is curious by nature and excels at understanding the things the other team members are not specialists at.

Lucia Villaverde is a relatively new addition to the team and has worked at Hempel for approximately a year. She is the industrial designer of the team, responsible for carrying projects from conceptualization to product development. She brings ideas to life through 3D modeling and rapid prototyping.

Briefly about the science

Laser ablation

Laser ablation is the general term used for controlled material removal using lasers. However, the physical processes by which the material is removed vary significantly depending on the laser parameters. In the Hempel system, the laser operates in a modulated continuous wave (CW) mode, which means that the laser power switches between a constant power level (P_ON) and zero (P_OFF) with a given modulation frequency (time between one P_ON to the next P_ON) and duty cycle (ratio between P_ON time and P_OFF time). This results in relatively long square pulses of light on the hundred microsecond time scale (0.0001 s) with a very high pulse energy on the mJ level. When these pulses are focused onto a paint sample, the energy is gradually absorbed over the duration of the pulse and converted into heat, which leads to not just evaporation of material, but also heating and even melting of the surrounding material. In contrast, the DTU system operates in an ultrashort pulsed mode with ~300 femtosecond pulses (0.0000000000003 s) having significantly lower pulse energy on the μ J level. Because the energy is absorbed in a very short amount of time, the material is not able to convert the energy into heat, causing a thin layer of material to practically explode and evaporate in a plume of plasma. For this reason, femtosecond laser ablation leads to

smaller and much more well-defined ablation craters with less debris and damage to surrounding material. However, this also means that it is much less effective for removal of large quantities of material. The difference between the two cases is illustrated in Figure 4.

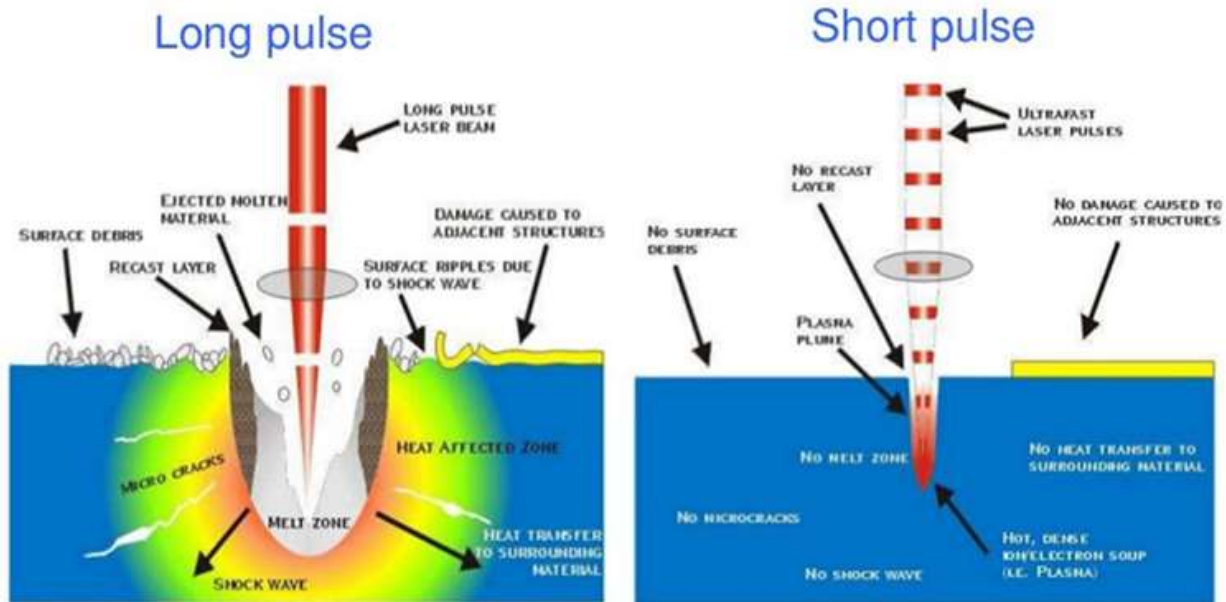


Figure 4. Illustration of long vs. short pulse laser ablation. From: Claverie, F. (2020). Laser ablation. Sample Introduction Systems in ICPMS and ICPOES, 469–531.

LIBS – laser-induced breakdown spectroscopy

As described in the section above, laser ablation inherently creates a plasma of ionized material, meaning that electrons are separated from the atomic nucleus. This hot ionized state of the atoms is maintained only during a short period of time, after which the plasma cools down and the electrons will try to reach a stable bound state by recombining with the nucleus. One possible way to recombine with the nucleus is through radiative recombination, in which a photon with a specific photon energy (color) is emitted. Since electrons can only exist in discrete energy levels dictated by the structure of the nucleus, the color of the emitted photon carries information about the structure of the atom. This principle is used to determine the atomic composition of materials by analyzing the emission spectrum from laser-induced plasma, and the method is known as laser-induced breakdown spectroscopy (LIBS). The concept is illustrated in Figure 5. As with laser ablation, the plasma emission is strongly influenced by the laser parameters, and its influence on plasma heating/cooling and free-free/free-bound electron dynamics. In brief, it affects the amount of continuous background emission that is emitted

alongside with the discrete recombination emissions, which deteriorates the signal and possibly ends up drowning out the atomic signatures. In particular, the so-called bremsstrahlung (braking radiation) is caused by acceleration/deceleration of electrons, e.g. through collisions of charged particles, which is most prevalent at high plasma densities. For this reason, femtosecond lasers are considered beneficial for LIBS analysis because of the reduced thermal effects and plasma densities.

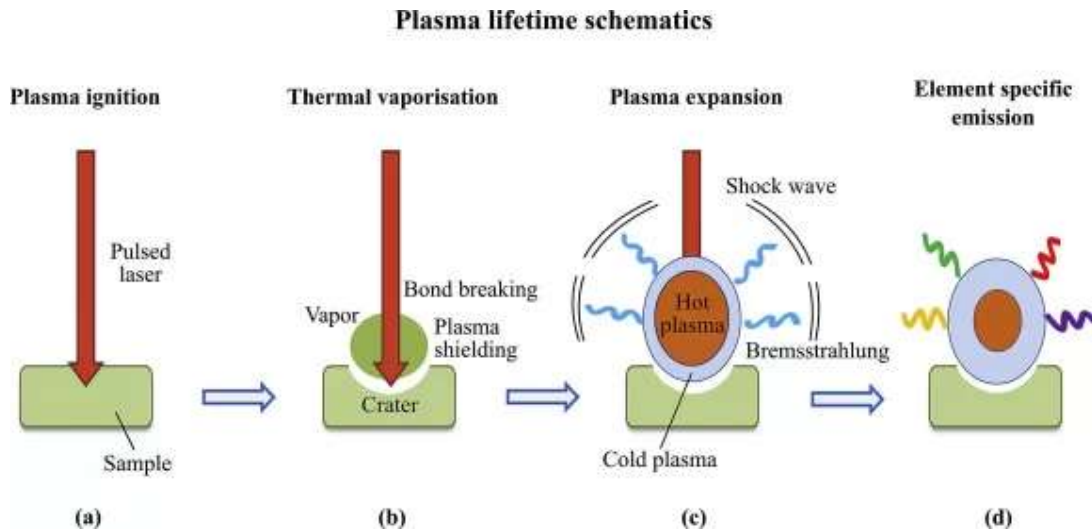


Figure 5. Illustration of photon emission in LIBS. Source: <https://endurancelasers.com/libs-lips-device-explore-the-material-with-a-laser-induced-plasma-spectroscopy/>

Mid-infrared absorption spectroscopy

Absorption spectroscopy is the science of analyzing what colors of light disappear (is absorbed) after interacting with a sample, and by how much. The absorption of light is related to the motion of molecules, which vibrate and rotate (if a gas) at specific frequencies related to the molecular structure. As it happens, certain “colors” of light in the mid-infrared part of the electromagnetic spectrum have corresponding frequencies that match the frequencies of molecular motion, which means they are in resonance (like a tuning fork). A consequence of this resonance is that the photon energy is very efficiently transferred into vibrational/rotational energy in the molecule (heat), effectively depleting the number of photons at this specific frequency. By monitoring a wide range of frequencies in the mid-infrared, it is therefore possible to identify molecular structures.

Results

Activity 1: UV/VIS plasma spectroscopy

The goal of A1 was to monitor the ablation process by looking at what elemental signatures appear in the plasma and determining the plasma temperature, which greatly influences the ablation process and the plasma-chemistry. Figure 6 shows how we collect the plasma light emission with a lens and optical fiber in the DTU lab (top) and the Hempel lab (bottom).

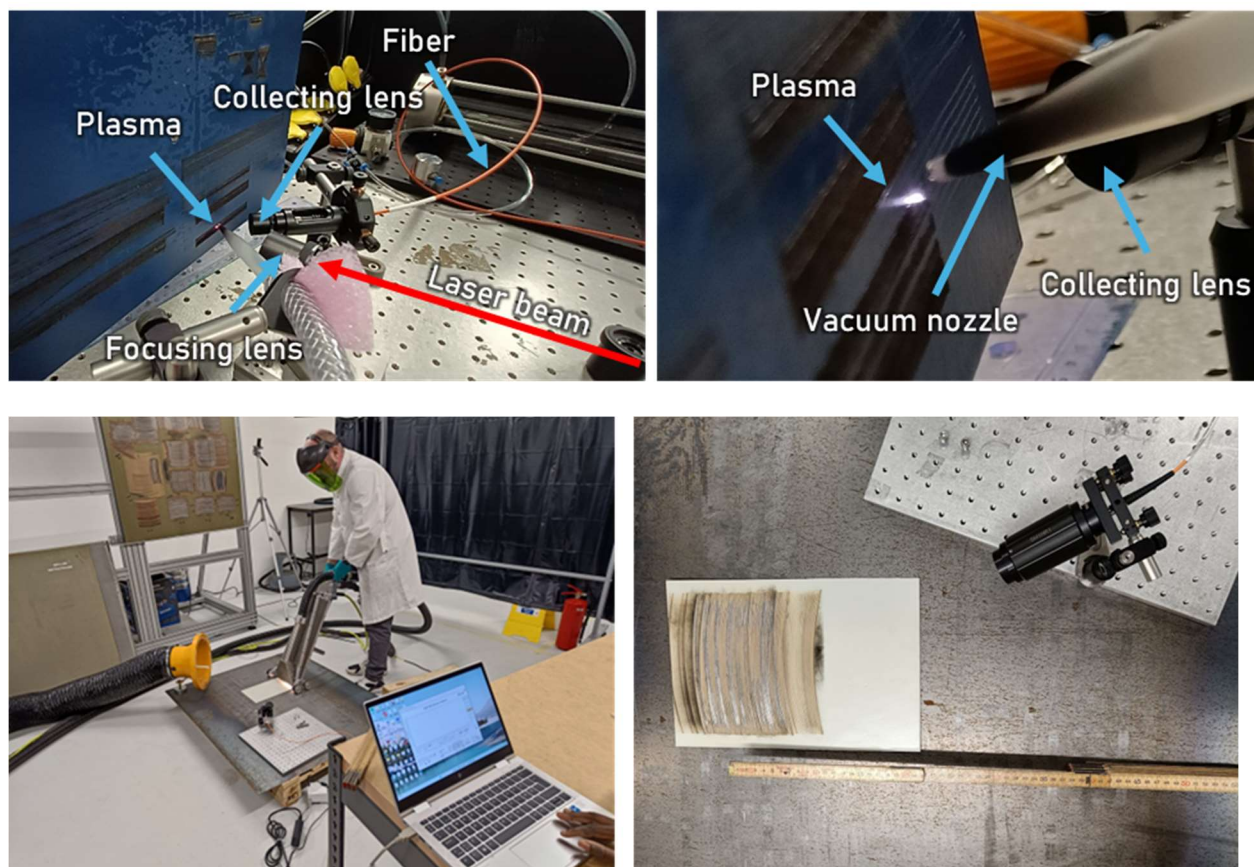


Figure 6. Photographs from the DTU lab (top) and Hempel lab (bottom) showing collection of UV light.

The result of these measurements is a series of optical spectra depicting the light intensity at different wavelengths, as shown in Figure 7. It is clear from the figure that the intensity and shape of the spectrum changes during scanning, but also the intensity of the narrow LIBS emission peaks. These variations are mainly caused by small variations in the paint, particle/smoke interference, and the laser focus during scanning. In the case of the femtosecond pulsed laser, several spectra have strong and narrow emission

peaks with almost no continuous background emission. For the CW laser, there is a significant background emission for all spectra that increases in intensity towards longer wavelengths. This emission is attributed to a combination of thermal radiation from the significant heating of the surface and vaporized particles, and bremsstrahlung.

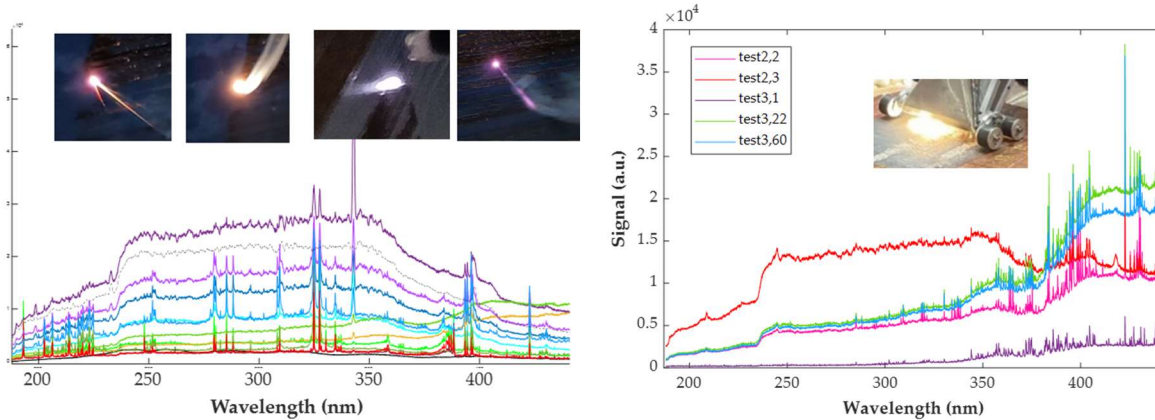


Figure 7. Left: Optical spectra collected during femtosecond laser ablation in the DTU lab. Right: Optical spectra collected during CW ablation in the Hempel lab. Inserts: Photographs of the laser plasma generated during ablation.

At first glance, the spectra from the two systems appear to be very different, but if the background emission is removed in numerical postprocessing the similarities appear. Figure 8 show a comparison between selected spectra collected with the Hempel system (top; orange/black) and the DTU system (bottom; green/blue).

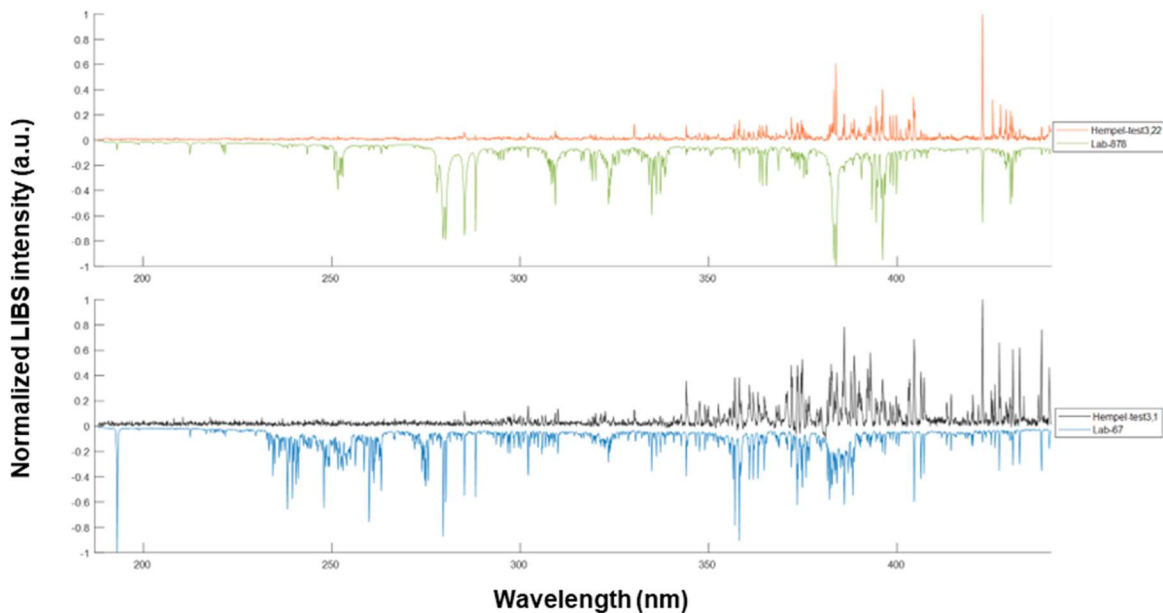


Figure 8. Comparison between selected spectra collected with the Hempel system (top; orange/black) and the DTU system (bottom; green/blue).

The next step in the analysis is to identify the elements causing the individual line transitions visible in the spectrum. To this end, we created a script that uses data from the NIST LIBS database¹ to compare the experimentally obtained spectrum with reference spectra. Figure 9 show an example of this, where lines in the experimental spectra (top) are matched with reference lines (bottom) from NIST. The figure show that the main difference in the two experimental spectra is that the blue spectrum contains more signal from iron (Fe) and carbon (C), indicating ablation of steel, while the yellow spectrum contains more titanium (Ti), sodium (Na), silicon (Si), magnesium (Mg) and calcium (Ca), indicating mainly ablation of the paint. As such, the signal can be directly related to the ablation process.

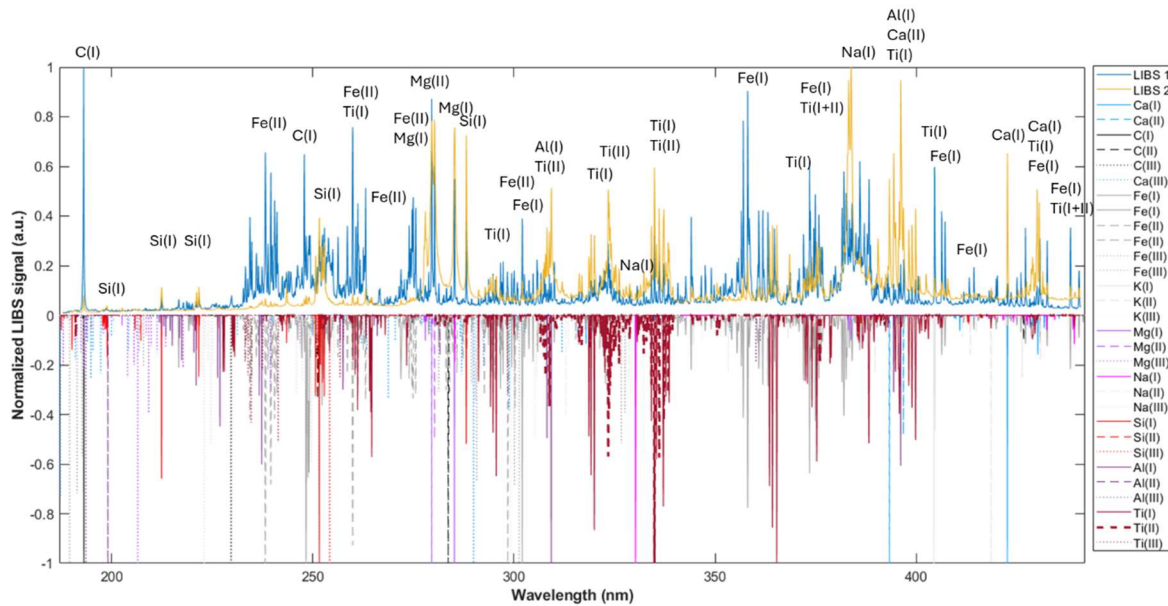


Figure 9. Identification of elements from the LIBS signal. Comparison between experimental spectra (top) and reference NIST spectra (bottom) is together with a numerical algorithm to label the peaks with their respective element(s).

Plasma temperature

From the observed emission peaks it is also possible to estimate the plasma temperature. It is estimated using the Boltzmann plot method assuming an optically thin plasma in local thermodynamic equilibrium, mathematically expressed as below:

$$\ln \left[\frac{\lambda_{ki} I_{ki}}{g_k A_{ki}} \right] = - \left[\frac{E_k}{K_B T} \right] + C$$

¹ <https://physics.nist.gov/PhysRefData/ASD/LIBS/lib-form.html>

Where, λ_{ki} , I_{ki} , g_k , A_{ki} , E_k , K_B , and C are emission wavelength, intensity of emission line, degeneracy of the upper energy level k , transition probability, upper energy level, Boltzmann constant, and a constant, respectively. The term on the left-hand side of the equation is plotted against E_k for six Fe(I) emission lines: 358.12 nm, 371.97 nm, 374.56 nm, 385.99 nm, 404.58 nm and 432.58 nm, as indicated in Figure 10. The linear plot obtained is called the Boltzmann plot and the slope of the fitted line yields the plasma temperature T .

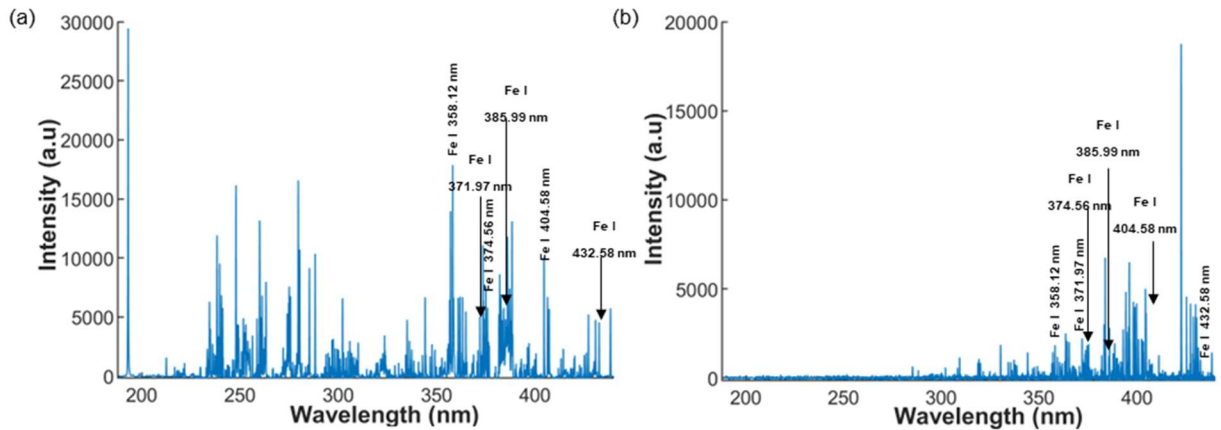


Figure 10. LIBS spectra of epoxy sample showing selected atomic lines of Fe (a) DTU and (b) Hempel.

Figure 11(a) and (b) shows the Boltzmann plots generated using the six Fe I lines of the epoxy sample for the DTU and Hempel systems, respectively. From the slope of the two plots an estimated plasma temperature of $T = 8696$ K and 6824 K was found for the DTU and Hempel systems, respectively. From the linear fits (red curves) it is clear that the estimates comes with a significant uncertainty, yet they interestingly show that the DTU system produces much higher plasma temperatures, which also explains why we see ionic emission lines such as Fe(II) and Ti(II) only in the DTU spectra.

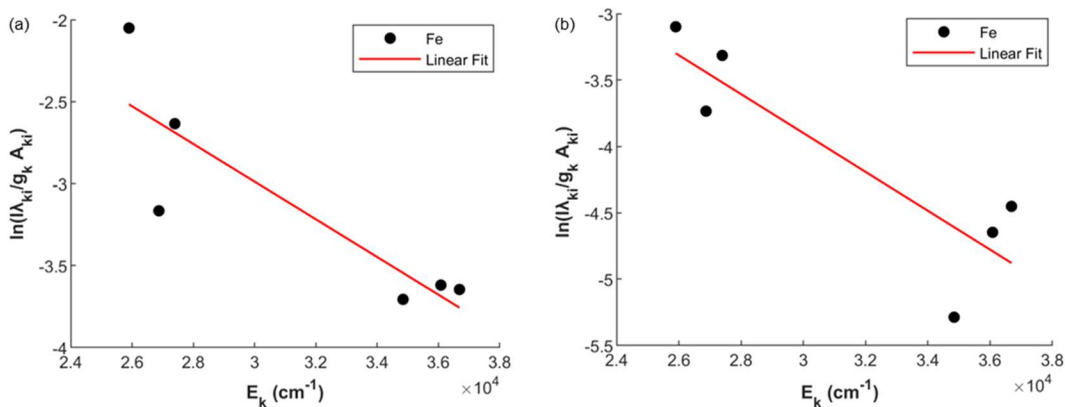


Figure 11. Boltzmann plot made using six Fe I atomic lines. The solid line represents the results of a linear best fit for (a) DTU and (b) Hempel systems. The temperature is equal to 8696 K and 6824 K, respectively

Activity 2: Vacuum collection and sample separation

DTU system

In the DTU system, the gas and particle emissions from the ablation process was collected using a gas sampler (Dadolab QB1) providing a flow rate of up to 75 l/min or 1.25 l/s. Particles were separated out using a particle filter, and the remaining gas was either sent to the lab exhaust or collected using Tedlar gas bags. This is shown in Figure 12.



Figure 12. (Left) Extraction of gas and particles. (Middle) The gas sampling system. (Right) Particle filter filled with particles and soot after a session of ablation experiments.

Hempel system

A Nilfisk industrial vacuum system was mounted above the focused laser spot, which facilitated the collection of the dust particles and the smoke produced by the laser ablation process. To reduce the risk of sparks entering the vacuum, a separator was introduced into the system before the vacuum. This separator can catch any potential sparks before they go into the filter of the vacuum.

The dust collected from the process was analysed by the internal analytical lab at Hempel, which showed that it primarily consists of the inorganic raw materials of the original coating (>90 % inorganic pigments), and a few percent of epoxy fragments and soot from incomplete combustion. The soot was removed by thermal processing, which turned the dust from black into a light gray.

The gas produced by the process was also collected and analysed. Both by DTU and by an external consultancy firm (HumanHouse), specializing in chemically safe working conditions. This will be discussed in Activity 4.

Activity 3: System modifications and scan optimization

Powell lens

One of the methods that was investigated for increasing the scan range was by stretching the laser spot into a line using a so-called Powell lens. The main issue with this approach is that the power used to ablate the paint is distributed over a line, which means that more power is needed to reach the same results. The lens concept is illustrated in Figure 13.

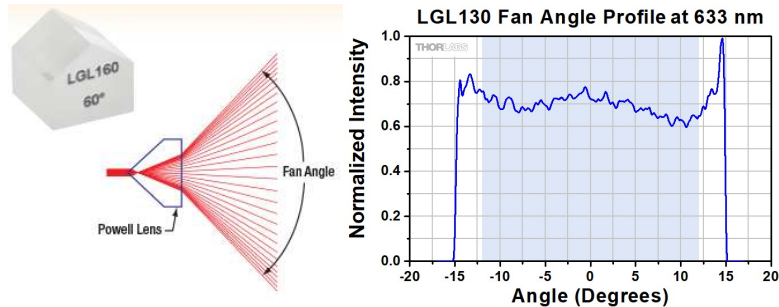


Figure 13. Powell lens concept. Figures from Thorlabs.com.

For testing in the DTU system we acquired a 30 degree fan angle Powell lens, which is the smallest angle commonly available and therefore the one that will lead to the highest intensity during ablation. The lens was anti-reflection coated for the 450-900 nm range, which is a bit shorter than the 1030 nm wavelength of the laser, but close enough that it should still provide lower reflection than the uncoated glass. Figure 14 show a few photographs from the test, which revealed another glaring issue with this approach. Although light was distributed over a line, the intensity was significantly greater at the two ends of the line. As a result, the paint was ablated only at the ends. Moving the lens closer to the paint to reduce the length of the line or changing its position relative to the laser beam also did not improve the results. In fact, with the lens moved close to the focal spot of the laser, the laser beam created a small plasma spot inside the lens. We therefore concluded that this was not a viable solution for laser cleaning.

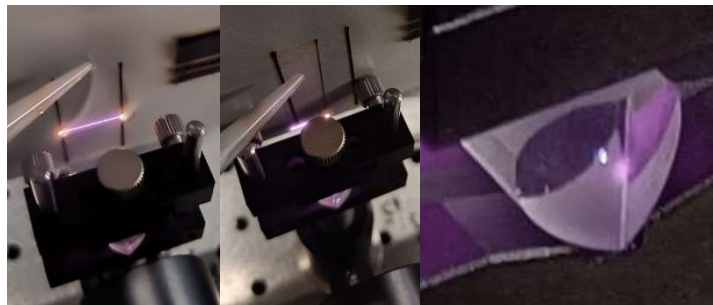


Figure 14. Ablation results with the lens far (left) and close (middle) to the paint sample. At the close position, a tiny white plasma formed inside the lens (right).

Laser window

Hempel reported some issues with the protective windows in the laser head getting damaged after some time. DTU was therefore tasked with investigating this further. First, the window transmission was measured using a halogen lamp and a fiber coupled CCD array spectrometer (see Figure 15). The blue curves show the window transmission, which is very close to 100 % in the 1000–1100 nm region where the laser operates. The measured transmission is slightly above 100 % at the end due to measurement uncertainty and possibly refraction/dispersion (“bending”) of the light from the glass window. The purple, dotted curve shows average transmission from a typical “B-coating” from the supplier Thorlabs, which is very similar. Next, the window was inspected in a light microscope, which revealed a lot of particles, scratches and spots. The coloration of the spots indicate it might be from a solvent or perhaps coating residue. The zoom in shows a ring of tiny dots around the spot, which could indicate that some material was evaporated and then settled as residue (see Figure 16). The conclusion was that the windows, although packaged in sealed plastic bags, require careful cleaning and inspection before they are installed in a laser head.

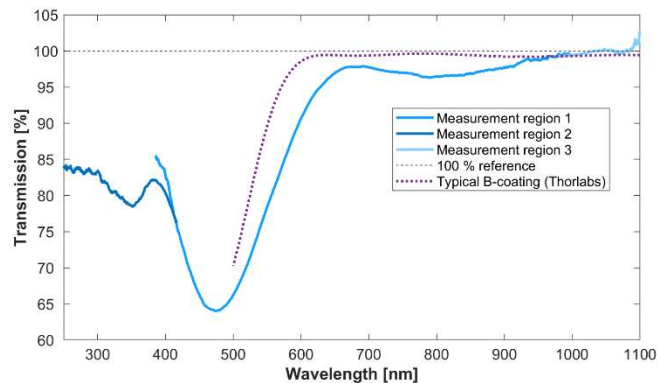


Figure 15. Transmission spectrum of the protective window used in the Hempel system compared to a typical Thorlabs B-coating. Source: Thorlabs.com.

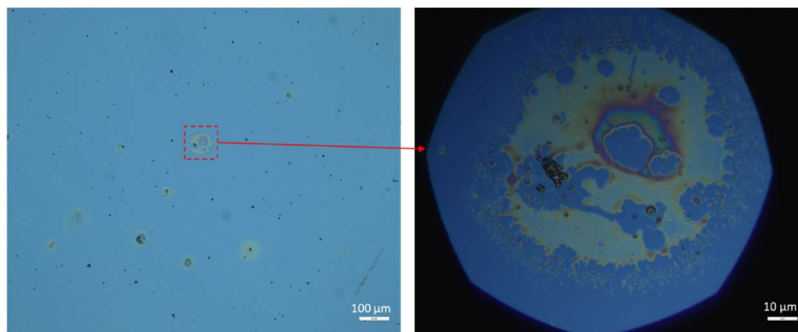


Figure 16. Microscope images of the surface of the window, revealing various spots and residues, which could be from cleaning.

Galvanometric scanning (Hempel)

In an effort to increase the scan size and thereby the speed of removal, a galvanometric scanner was introduced into the laser setup. The scanner can move the single laser spot rapidly from side to side, while the handheld laser unit can be manually moved up and down by the operator. This enables the handheld system to clean a 20 cm wide line with a simple manual movement, imitating the movement of a manual power grinder.

Proto-type system (Hempel)

Hempel designed and built a complete handheld prototype system in collaboration with the DTU workshop. The system consists of the laser gun enclosed within an aluminum chamber, which encloses the whole laser beam all the way to the point of impact (see Figure 17). The vacuum suction is mounted on top of the enclosure with the inlet placed right above the point of impact to extract the ablation fumes. At the other end of the laser fiber cable is the Ground Service Unit (GSU), which is an electrical chassis carrying the heavy equipment as one unit – the laser, the vacuum cleaner, and the separator – which can follow the person operating the handheld unit.

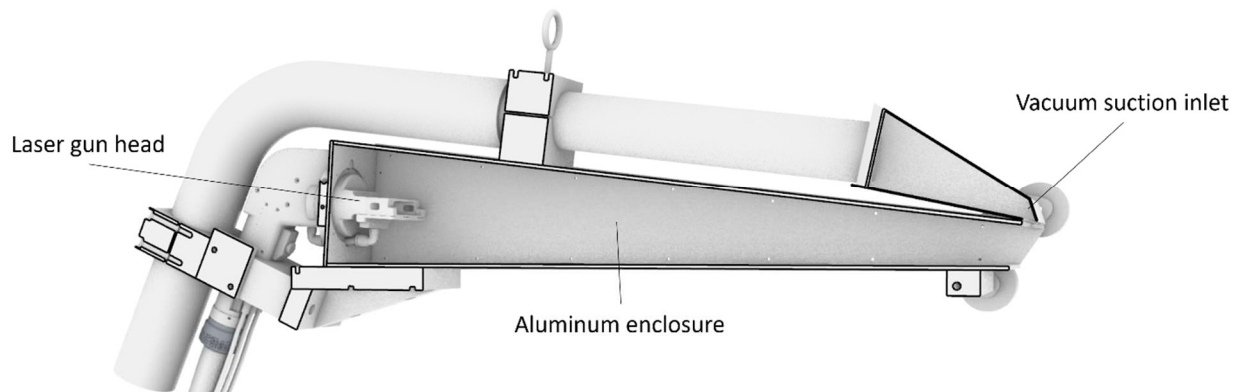


Figure 17. Schematic illustration of the Hempel hand-held prototype unit.

Activity 4: MIR spectroscopy and validation

Particle analysis

It was decided that the particles collected in the filters of the DTU gas sampler was to be analyzed using MIR spectroscopy, specifically attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy. The particle dust was gently scraped from the filters into a beaker, as shown in Figure 18 (top left). The dust was then mixed with a solvent to create a slurry that the ATR probe (PIR fiber loop, art photonics GmbH) could be submerged into, as shown in Figure 18 (right).



Figure 18. Photographs from the particle analysis using ATR-FTIR spectroscopy. (Top, left) Extraction of dust from the particle filter before subsequent mixing with a solvent. (Right) ATR probe submerged into slurry of dust and solvent. (Bottom, left) Setup and raw spectrum recorded.

The best results were obtained using methanol, since it has less overlap with the chemicals in the dust we want to measure. An example of the spectra obtained is shown in Figure 19. The purple dashed line shows the pure ethanol reference spectrum, which does not contain any dust. Interestingly, the blue spectrum of the slurry of methanol and dust is almost identical to the pure ethanol spectrum except for an offset, which is likely due to scattering. However, after allowing the methanol to dry, the molecular fingerprints of the dust became apparent. These are indicated by arrows in the plot.

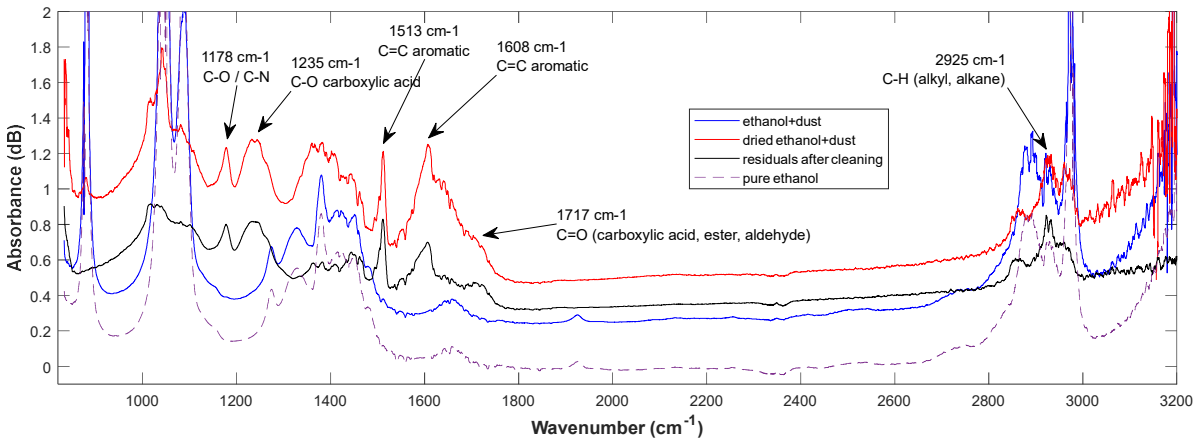


Figure 19. Absorption spectrum from ATR-FTIR spectroscopy of ablation dust in ethanol solution. After evaporation of the ethanol, several absorption fingerprints emerge, which are indicative of aromatic compounds (e.g. benzene, xylene, toluene), alkane compounds (

The ATR spectrum reveals a series of molecular C=C and C-C bonds that are typically attributed to aromatic compounds (1608 cm^{-1} / 1513 cm^{-1}), such as benzene, toluene and xylene. However, aromatic compounds are typically associated with overtone peaks in the $1800\text{--}2000\text{ cm}^{-1}$ region and C-H absorption peaks above 3000 cm^{-1} . Our measurement shows no such overtone and only C-H peaks from $2800\text{--}3000\text{ cm}^{-1}$, indicative of alkane compounds. The C=O peak at 1717 cm^{-1} is indicative of saturated aliphatic ketones, such as acetone, but also overlaps the region of carboxylic acids. The two additional peaks at 1178 cm^{-1} and 1235 cm^{-1} are related to C-O bonds, which are also present in acids. Identifying the exact compounds present in the ablation dust will require rigorous testing and calibration with different reference chemicals, but at this point we can confirm that the dust contains traces of VOCs and soot.

The above analysis is broadly in line with the VOC screening performed at the Hempel lab by the third-party company Eurofins. The analysis was performed using standard analytical thermal desorption (ATD) in combination with gas chromatography and mass spectrometry (GC/MS). The results showed total VOC emissions near the ablation site in the several mg/m^3 range, which is potentially hazardous to human health. The list of identified VOCs includes a number of aromatic compounds, such as toluene, xylene, and various benzenes; a number of alkanes, such as n-dodecane and n-undecane; carboxylic acids, such as acetic acid and derived compounds like butylacetate. None of the measured VOCs were by themselves above the thresholds set by the Danish Work Environment Authority², but e.g. benzene was registered at $0.91\text{ mg}/\text{m}^3$ (limit is $1.6\text{ mg}/\text{m}^3$), so

² <https://at.dk/regler/bekendtgørelser/graensevaerdier-stoffer-materialer-291/bilag-2/>

even with strong vacuum near the ablation site it is recommended to use personal protective equipment such as filter masks and gloves.

Gas analysis

The gas output from the DTU gas sampler was analyzed using an in-house made super-continuum source (SCS). The SCS spectrum covered from 2–9.5 μm and was measured using a commercial Fourier-transform infrared (FTIR) spectrum analyzer. Spectra were collected with 0.5 cm^{-1} resolution and 1000 averages. First, a gas cell with 3.2 m path length was used for the experiments, which was first purged with a nitrogen flow before introducing the gas. Due to the gas collection method, the combustion gas was diluted by ambient lab air, which is evident by the presence of strong water absorption in the measured spectrum. A zoom in of the region between 4.3–5.2 μm show the detailed spectral lines from H₂O, CO and three different CO₂ isotopes. In the region from 2.5–2.9 μm and 5–7.5 μm , only water absorption was identified, and the region from 2.9–4.2 μm and 7.5–9.5 μm was devoid of any clear absorption features. This suggests that any volatile gases produced during ablation has most likely condensed and deposited inside the tubing or the filter.

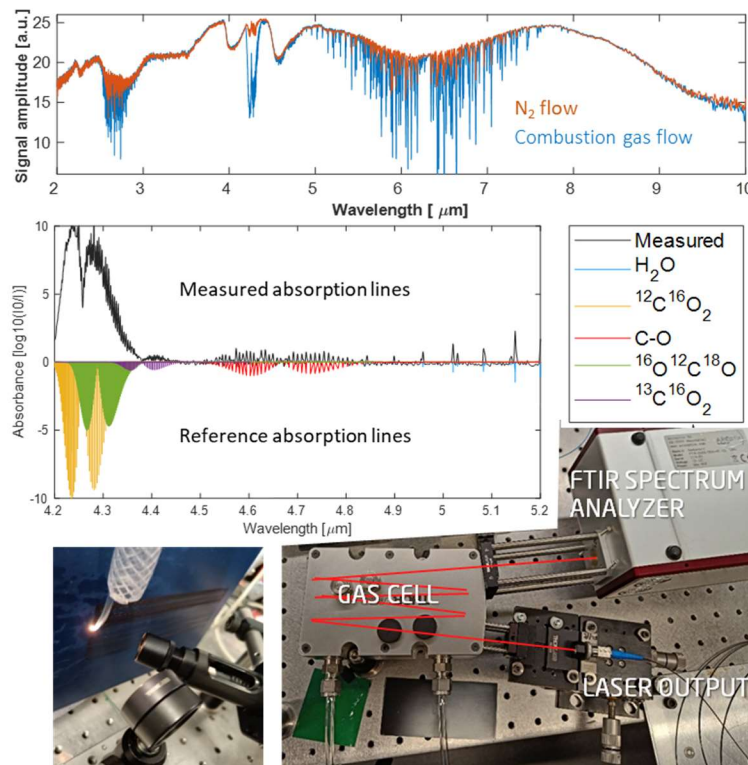


Figure 20. Gas spectroscopy performed in the DTU lab.

The experiment was repeated using exhaust gas collected from the Hempel system using Tedlar bags, as shown in Figure 21. To allow for detection of even smaller amounts

of gas, a 31.2 m Herriott gas cell from Thorlabs was used. The longer path length led to stronger absorption, but no new gas species were detected.

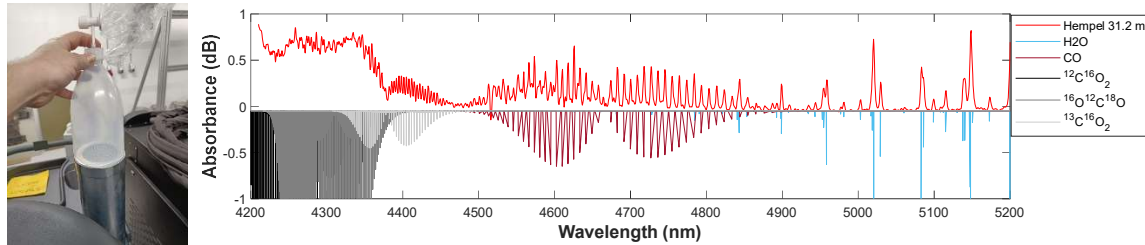


Figure 21. Sampling of gas from the Hempel system (left) and resulting spectrum (right).

Activity 5: Demonstration

In November 2023, Hempel took the prototype system to Fayard (Shipyard at Fyn) to demonstrate the system to key stakeholders. Fayard was very excited about the system, specifically because it does not produce any significant noise or waste, and because of the clean work environment.

The feedback on possible improvements that could be made was in terms of speed of removal and consistency in removal pattern. This feedback has been taken into consideration in the process of developing the next prototype. Figure 22 show photographs from the demonstration.



Figure 22. Photographs from the system demonstration at Fayard in November 2023.

Project dissemination

Conferences

1. Oral presentation at SPIE Photonics West 2024 in San Francisco, subconference “High-Power Laser Materials Processing: Applications, Diagnostics, and Systems XIII”, presentation no. 128780B. Link: <https://www.spiedigitallibrary.org/conference-proceedings-of-spie/12878/128780B/Laser-induced-plasma--and-gas-spectroscopy-from-femtosecond-laser/10.1117/12.2692205.full>
2. Poster presentation at Danish Optical Society (DOPS) National Optics Congress 2024 in Odense. The poster is shown in Figure 23.

Publications

1. (in preparation) Doyinsola S. Sonoiki, Christian R. Petersen, Morten Schnohr, Kim Scheibel, and Ole Bang, “High Repetition Rate Femtosecond Laser Ablation and LIBS of Marine Paints”, Spectrochimica Acta Part B: Atomic Spectroscopy, Elsevier.

Other dissemination


1. Feature article in Electro-Optics Magazine: “Spectroscopy teams up with laser cleaning to remove ship paint”. Link: <https://www.electrooptics.com/article/spectroscopy-teams-laser-cleaning-remove-ship-paint>
2. Presented the project at the DTU Electro department lecture 29/9-2023.

DTU ELECTRO

LASER-ABLATION PLASMA ANALYSIS

C. R. Petersen^{1,2}, D. Sonoiki¹, Morten Schnohr³, Kim Scheibel³, Ole Bang^{1,2}

¹ DTU ELECTRO, ² NORBLIS ApS, ³ Hempel, GrowHub, Hempel A/S



ABSTRACT

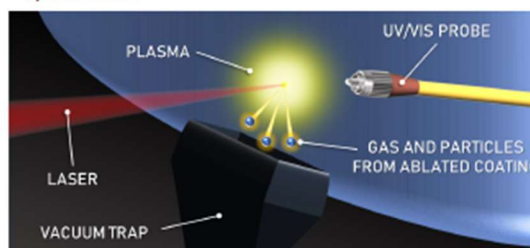
- Abrasive medium blasting is the standard method for removing paint from e.g. ships.
- It **pollutes** the environment and creates tons of **toxic waste**.
- It is not feasible to separate the blasting medium and paint, so there is **no recycling** potential.



- In laser ablation there is no blasting medium so the solid waste can be separated from the fumes and collected for **recycling**.
- Depending on process, **toxic fumes** may be generated.
- A better understanding of the plasma chemistry is needed!

PROJECT LASER-CLEANR

- The first goal of the project is to investigate the plasma emission from laser ablation of paints using laser-induced breakdown spectroscopy (LIBS) to identify the type of paint.
- The second goal is to analyze the ablation fumes using infrared absorption spectroscopy. This is achieved using a gas sampler, a multipass gas cell, a supercontinuum (SC) laser, and an FTIR spectrometer.



METHODS

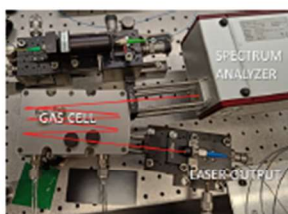
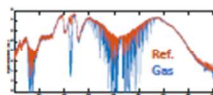
Plasma analysis

- Pump laser: 1030nm, 288 fs, 50 kHz, 80 uJ
- Sample scanning: UR5-e robot arm
- Array spectrometer from 188-440 nm with 0.15 nm resolution



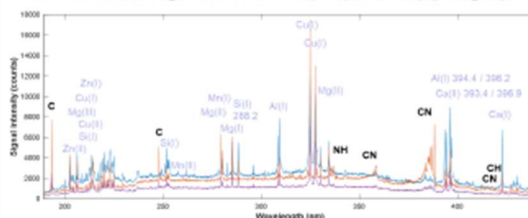
Gas analysis

- In-house built mid-infrared SC laser (2-10 μm)
- 3.2m multipass gas cell (white cell)
- FTIR spectrometer with 0.5cm-1 res.



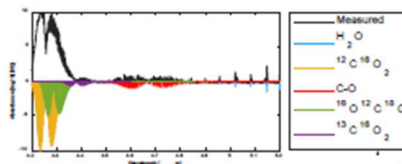
RESULTS

- Plasma analysis shows strong signals from elements like Al, Mg, Mn, Zn, Cu, C, Ca, and Si
- Some spectra collected had elevated levels of C accompanied with molecular signatures from NH, CH, and CN (cyanogen)



- Gas analysis did not find signs of CH, NH, or CN, only CO₂, CO and H₂O. Maybe a longer gas cell or less diluted gas needed.

- More work needed to investigate gas emissions from different paints.



FUNDING

This work was funded by The Danish Maritime Fund and Hempel GrowHub.



CONCLUSIONS

- LIBS can be used to identify elements present in the paint and what molecules are forming during the ablation process to better understand the plasma chemistry, which may be relevant to the recycling process.
- IR gas spectroscopy was used to measure CO₂, CO, and H₂O from the ablation fumes. CH, NH, and CN compounds were not detected.

Figure 23. Poster presented at the DOPS National Optics Congress 2024.

Conclusions and perspectives

In terms of milestones, the project overall was a success (see table below). We managed to set up a test bench for studying laser ablation and LIBS at DTU, as well as a handheld prototype for industrial laser cleaning, which was showcased at a Danish shipyard. We confirmed that it is possible to use LIBS to determine the paint contents and monitor the ablation process, also in an industrial setting. We demonstrated proof-of-concept analysis of gas and particles from the ablation process using infrared spectroscopy, and compared with a standard air quality analysis performed using a third-party consultant. The only milestone that was not achieved is related to increasing the speed of laser cleaning. However, we have identified a path forward for reaching this goal and therefore believe that it is possible to make laser cleaning practically viable for surface cleaning of ships and other large marine structures.

Future work will focus on increasing the cleaning speed by utilizing more powerful lasers with optimized parameters, investigating how to quickly analyze and reduce particle/gas emissions using laser technology, and optimizing the yield of material that can be recycled for use in new paints.

Milestones

Milestone text	Goals reached?
M1: Model for interpretation of plasma emission data tested for various laser/coating parameters.	YES: Using the elemental signatures we were able to distinguish different types of paints, and by scanning laser parameters we could identify the best operating regime for maximum LIBS signal.
M2: Vacuum separation of gas and particles demonstrated.	YES: Both DTU and Hempel systems implemented particle separation.
M3: Scanning speed/range increased by factor x2	NO: The Powell lens was not suitable for improving scan speed. Only solution we could think of is to use higher power and either scan faster or split the beam into smaller beams that can be scanned separately, but this was not implemented during the project.
M4: Calibration models for determination of gas/particle chemistry based on MIR absorption data validated	IN PROGRESS: It was found that the gas samples collected both at DTU and Hempel did not contain gases other than CO, CO ₂ and H ₂ O. Therefore, the results could not be used to verify the GC/MS reference measurements. Subsequent particle analysis at DTU did reveal traces of VOCs, but further work is needed to validate the results.
M5: Prototype system for laser ablation and waste collection demonstrated in an industrially relevant environment	YES: The system was demonstrated at Fayard shipyard on Fyn in November 2023.