Ultra-broadband infrared gas sensor for pollution detection

TRIAGE project newsletter #4

Mar-2024

Welcome to the fourth TRIAGE project newsletter!

This project has received funding from Horizon 2020, the European Union's Framework Programme for Research and Innovation, under Grant Agreement No. 101015825.

We are approaching the end of the project, and the final demonstrations are being planned. This newsletter gives an update on some of the technology embedded in the TRIAGE system. For more info, please get in touch or join the new LinkedIn group! www.linkedin.com/company/triage-h2020

More information is available on the project website https://triage-project.info

Proof-of-concept demonstration of long-wavelength supercontinuum for gas sensing

NORBLIS has been working on optimising the design and performance of the long-wavelength supercontinuum source (SCS) to make it ready for integration into the second TRIAGE sensor system. Before integration, NORBLIS and DTU decided to perform a proof-of-concept demonstration of gas sensing in the DTU lab. The application was the monitoring of combustion gas emissions from laser removal of protective coatings. The SCS spectrum covered from 2-9.5 μm and was measured using a commercial Fourier-transform infrared (FTIR) spectrum analyser. Spectra were collected with 0.5 cm^{-1} resolution and 1000 averages.

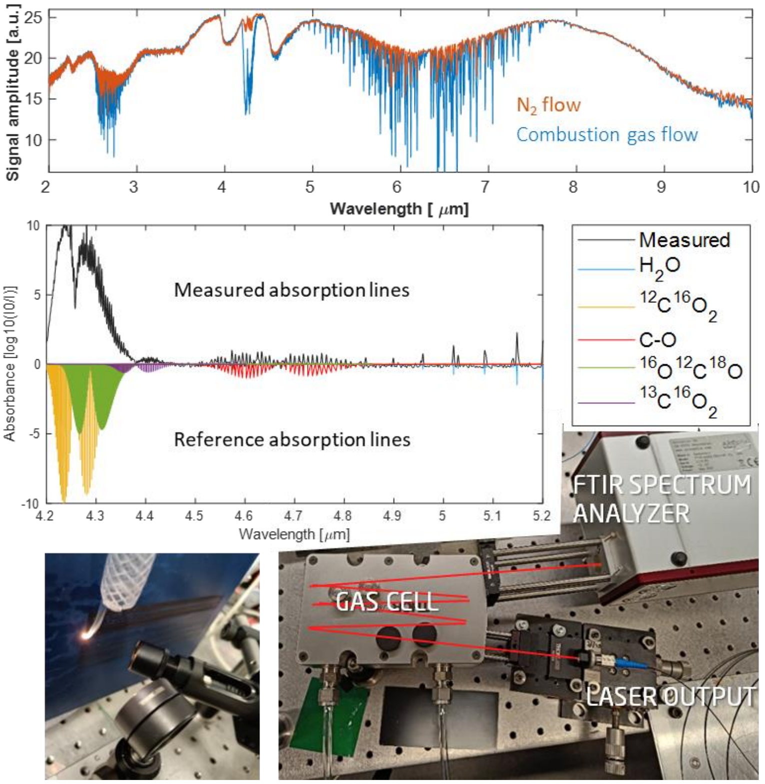

Fig. 1: The lab set-up and results of the analysis of laser ablation gas products.

Consortium

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TRIAGE is an initiative of the Photonics Public Private Partnership.

https://triage-project.info

The protective coating was removed by laser ablation using a 1030 nm laser, and the resulting combustion gas was collected from the laser ablation site by a vacuum pump. 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 combustion 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 H_2O, CO and three different CO_2 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.

Finally, the spectroscopy system was tested on gas samples collected from the exhaust pipe of an industrial laser paint removal system. Similarly to the DTU samples, only CO, CO_2 and water vapour was visible in the absorption spectrum. The spectral data was analysed by CSEM for the presence of sixteen different trace gases using a least-square fitting method based on HITRAN reference spectra. Due to the presence of water vapour, the model for each trace gas included water absorption to improve the fitting parameters. Figure 2 shows the results of the fitting procedure.

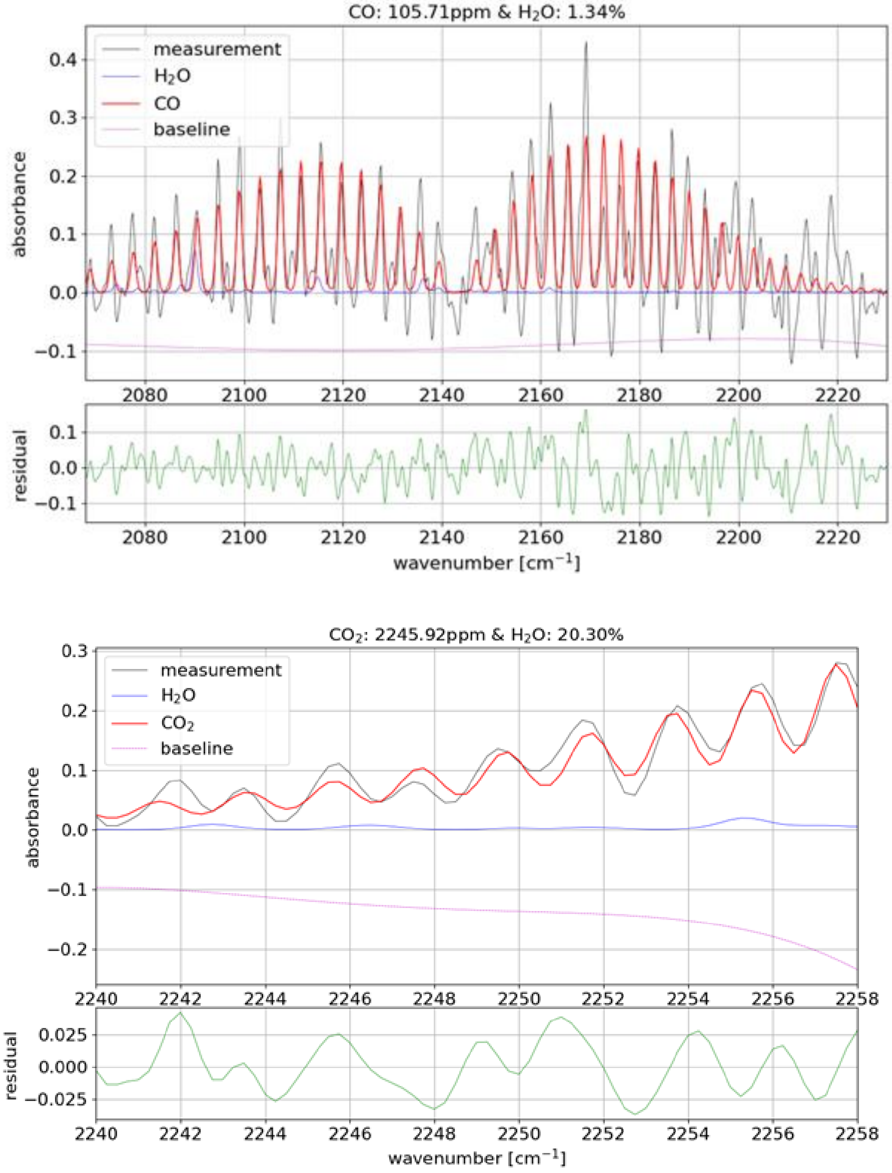

Fig. 2: (Above) Measurements of exhaust gas from ablation of a protective coating with a 1030 nm laser using the TRIAGE SCS. (Below) Fitted parameters from measurements of exhaust gas from industrial laser paint removal system using TRIAGE SCS.

While these results are encouraging, the system was limited to detecting only the most abundant gases expected from such laser combustion. The integrated TRIAGE system is expected to have increased resolution, sensitivity and longer path length, which will enable detection of smaller concentrations of trace gases.

Superlattice-based thermoelectrically cooled photovoltaic VLWIR photodetectors

Building upon the epitaxy technology initially developed for LWIR ~10 µm detectors employed in the TRIAGE system, VIGO Photonics has extended the wavelength capabilities. Taking advantage of the InAs/InAsSb superlattice energy bandgap tunability, the cut-off wavelength has been extended to approximately 14 µm and photodetectors based on this material have been developed. The devices are single-pixel immersed photovoltaic detectors designed to operate without bias. Featuring a wide bandwidth in terms of electrical frequencies and a rapid response time of ~2 ns, these detectors are monolithically integrated with an immersion lens fabricated from the GaAs substrate. This increases the optical-to-electrical area ratio, resulting in a tenfold improvement in Signal-to-Noise Ratio (SNR). Operating without bias leads to reduced 1/f noise. The stacked design, achieved through epitaxially grown tunneling junctions connecting stages, yields a detector resistance of ~100 ohms at the operating temperature. In contrast, standard-design PV or PC devices, optimised for similar wavelengths and operating temperatures, exhibit lower resistances and suffer a bigger performance drop when integrated with a preamplifier. The potential applications of these VLWIR photodetectors include spectroscopy, where, when combined with wide broadband sources, they can function effectively in balanced detection systems, like the ones developed in the TRIAGE project. Scientific institutions, such as Radboud University, are likely to show particular interest in these solutions. These VLWIR photodetectors face competition primarily from liquid nitrogen-cooled photoconductive devices offering comparable parameters but requiring troublesome cooling and a higher price. Widely used pyroelectric thermal detectors, although common, prove too slow to compete in advanced spectroscopic applications.

For more details, you can visit vigophotonics.com and access the datasheet.

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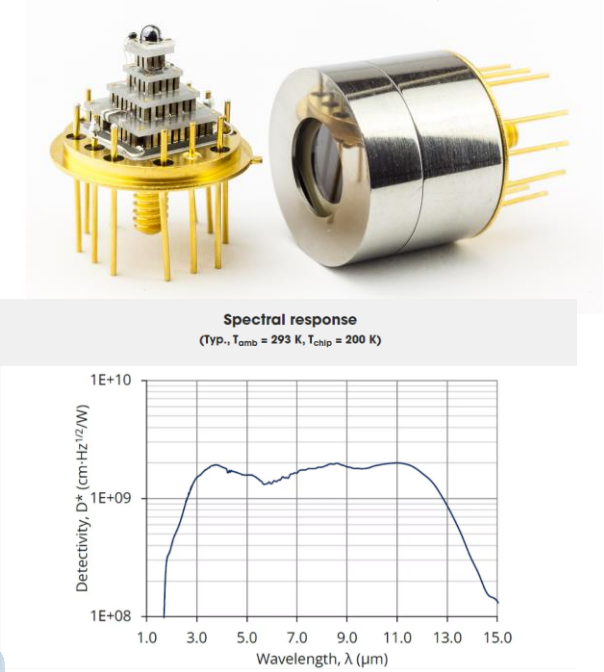

Fig. 3: (Below) Spectral detectivity of PVIA-4TE-13 photodetector; (above) typical cooled detector housing from VIGO Photonics.

Fabrication of chalcogenide fibres at DTU

DTU's role in the TRIAGE project is to design, fabricate, and post-process low optical loss sulfide and selenide-based step-index chalcogenide fibres. These fibres will be incorporated into the NORBLIS 2-10 µm supercontinuum source.

Early work in the project involved optimising the methods used to fabricate the fibre optic preforms such as material purification, glass melting, quenching, and annealing of the glasses. However, producing high purity, amorphous chalcogenide glasses is only the start of the fibre fabrication process.

To draw a small-core step-index chalcogenide fibre at DTU, a rod-in-tube method is used (Figure 4). This is a multi-step process beginning with the fabrication of both: one core glass preform, and one cladding glass preform. The core glass preform is subject to a "preliminary" fibre draw. This aims to reduce the diameter of the preform to around 1 mm, which is then referred to as "cane" or "rod". The cladding glass preform is processed *via* a hot extrusion to a small inner diameter (matching the core rod) tube. The core glass cane is then fitted to the extrude cladding tube, resulting in a rod-in-tube preform. This preform is then inserted into a polymer casing and then finally drawn to a polymer clad, small-core, step-index fibre (Figure 5).

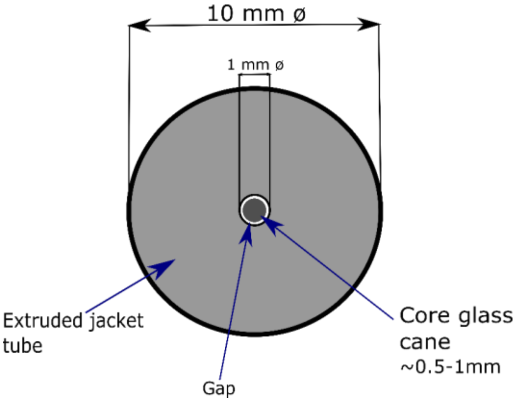

Fig 4: Rod-in-tube preform for small core step index fibres.

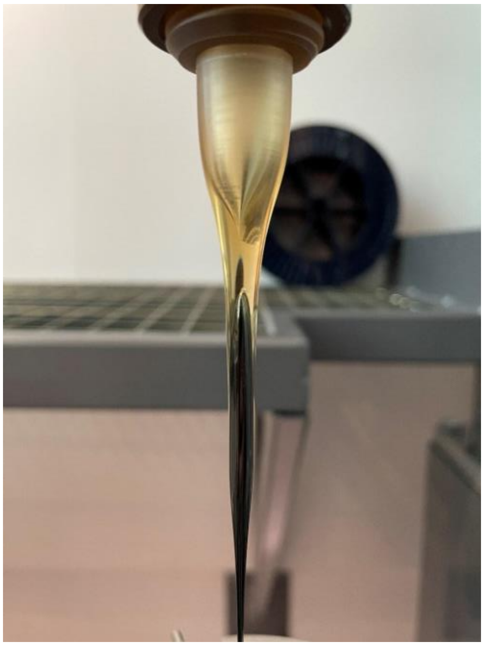

Fig. 5: A fibre drawn rod-in-tube preform in the protective polymer.

A key challenge with this method of step-index fibre fabrication is minimising devitrification (crystallisation) of the glass during each step. Crystallisation of glasses is time and temperature dependent, meaning that each occasion the glass is taken above its glass transition temperature during the (two) fibre drawings and the extrusion, there is a risk of inducing or exacerbating crystal formation in the material.

To minimise the probability of devitrification, there have been two main improvements to the system at DTU. A redesign of fibre draw tower furnace led to commissioning custom furnace inserts which have improved the preform heating efficiency, speeding up the fibre drawing process. Additionally, the extruder parameters, that is, working temperature and force applied to the glass, have been optimised to reduce the process time while also producing a more uniform, symmetrical tube.

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Recent LiU contributions to TRIAGE

LINKÖPING UNIVERSITY

- 1-TRIAGE validation tests – current status and future steps
- 2-Exploring comparative methods for environmental methane monitoring
- 3-TRIAGE participation at EUROSENSORS 2023

1-TRIAGE validation tests – current status and future steps

To develop a robust and reliable instrument for air pollution detection in different outdoor environments, it is necessary to perform different types of tests.

These include the verification of the robustness of the assembled system to physical disturbances (*e.g.* during transportation or under different weather conditions), ease of use of the user interface and basic functionality, response to single as well as mixtures of target gases under controlled lab conditions before moving to the field environment, and evaluation of how different user setting may influence the measurement performance. Furthermore, it is important to test performance and interferences with external changes in temperature, humidity, and pressure in climate chambers as well as in outdoor conditions. Tests at selected TRIAGE-NET end user partners with separate reference measurements are ongoing. Tests will progressively move from sites with higher target gas concentrations to lower concentrations to evaluate optimal use conditions. Long-term tests are desirable to evaluate possible drift or other interfering factors developing over time.

2-Exploring comparative methods for environmental methane monitoring

Reducing emissions of the key greenhouse gas methane is important to mitigate climate change. The LiU team has developed a novel approach to measure methane at atmospheric concentrations by means of a low-cost electronic nose combined with machine learning models for highly sensitive detection of methane down to 33 ppb and coefficients of determination up to 0.91 for *in situ* measurements. These results are useful for establishing a robust and reliable method for complex data analysis.

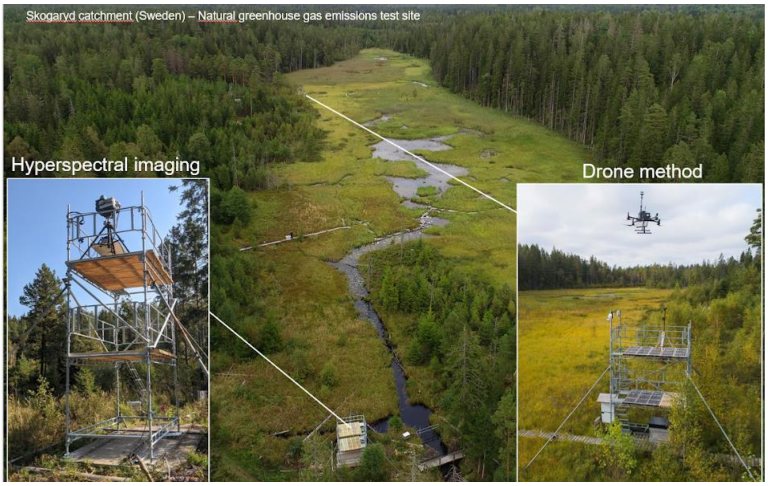

Fig. 6: Validation and demonstration at a selected end-user test site with comparative methods.

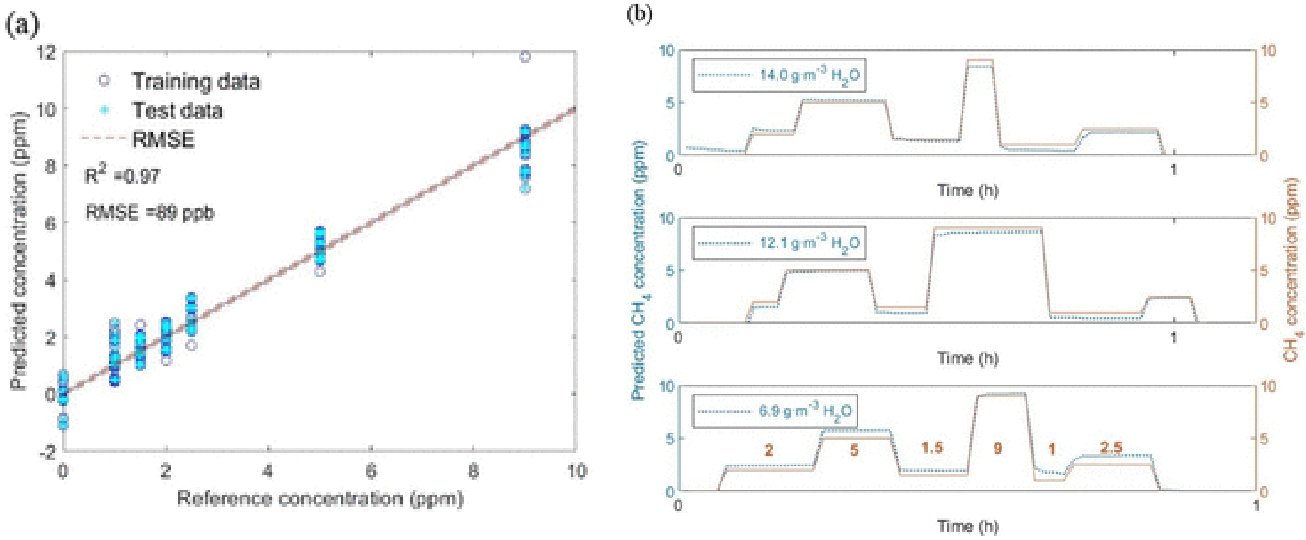

Fig. 7: (a) Results of a partial least-squares regression for methane ranging from 0 to 9 ppm under different concentrations of water vapour ranging from 4.5 to 14.0 g·m^{-3} , and (b) application of this regression to the test data to predict the methane concentration over time compared to the supplied concentration. (From Domènech-Gil et al. 2024)

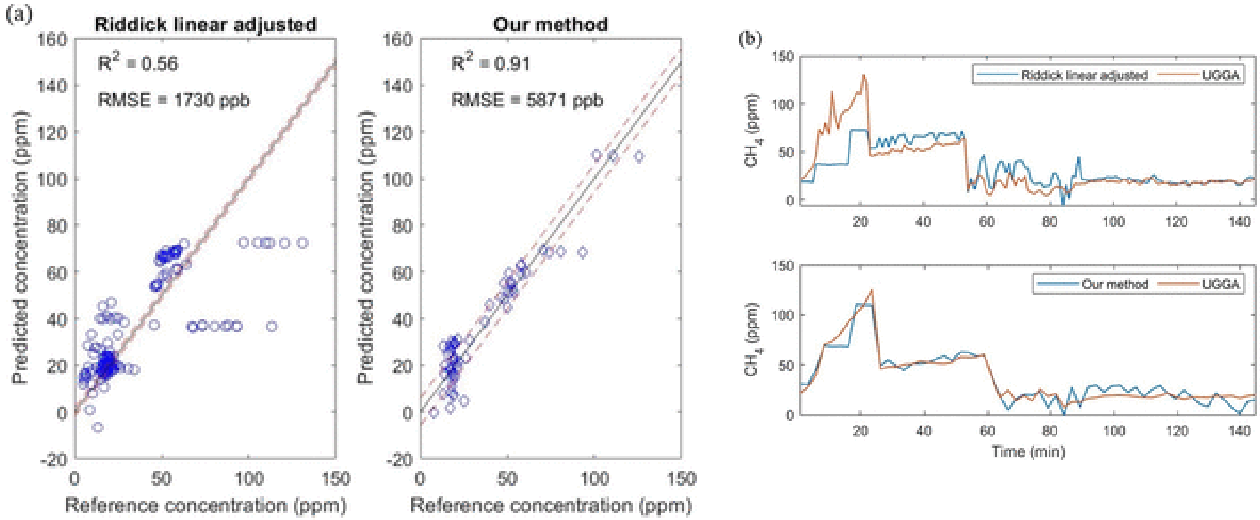

Fig. 8: (a) Comparison between the best results obtained among the previous methods studied when quantifying methane and the LiU method and (b) temporal evolution of (a).(From Domènech-Gil et al. 2024)

This work was recently published in the journal Environmental Science & Technology:

Guillem Domènech-Gil, Nguyen Thanh Duc, J. Jacob Wikner, Jens Eriksson, Soren Nilsson Påledal, Donatella Puglisi, and David Bastviken, *Electronic Nose for Improved Environmental Methane Monitoring*, Environ. Sci. Technol. **58**, 352−361 (2024).

Hyperspectral trace gas analyses was also further developed and applied to sludge storage methane emission assessments as exemplified in Fig. 9. This work was published in Environmental Science and Technology as a collaboration between LiU, TRIAGE-NET partner Tekniska Verken AB, and the research institute RISE:

Fig. 9: Methane emissions from a sludge storage plant from:

Galfalk M, Paledal SN, Yngvesson J, Bastviken D., "Measurements of Methane Emissions from a Biofertilizer Storage Tank Using Ground-Based Hyperspectral Imaging and Flux Chambers," Environ. Sci. Technol. **58,** 3766-3775 (2024).

3-TRIAGE participation at EUROSENSORS XXXV

During 10-13 September 2023, the LiU team attended the EUROSENSORS XXXV Conference in Lecce, Italy, with an oral presentation entitled "Machine Learning for Enhanced Operation of Underperforming Sensors in Humid Conditions". The TRIAGE partner demonstrated the powerful contribution of data treatment to overcome device manufacturing issues on sensor performance.

Multi-pass cell development at Senseair

Multi-pass cells (MPC) task in the TRIAGE project is developing the multi-pass cell, the sub-system that enables guide the propagating mid-infrared beam in a confined space. The multi-pass cell with a total length of about 45 cm dramatically improves the light-matter interaction between the mid-infrared beam and the gaseous analyte to about 30 m optical path length.

Figure 10 shows the evolution of the MPC development steps at Senseair where in the current design version (MPC F), more mechanical stability is demonstrated.

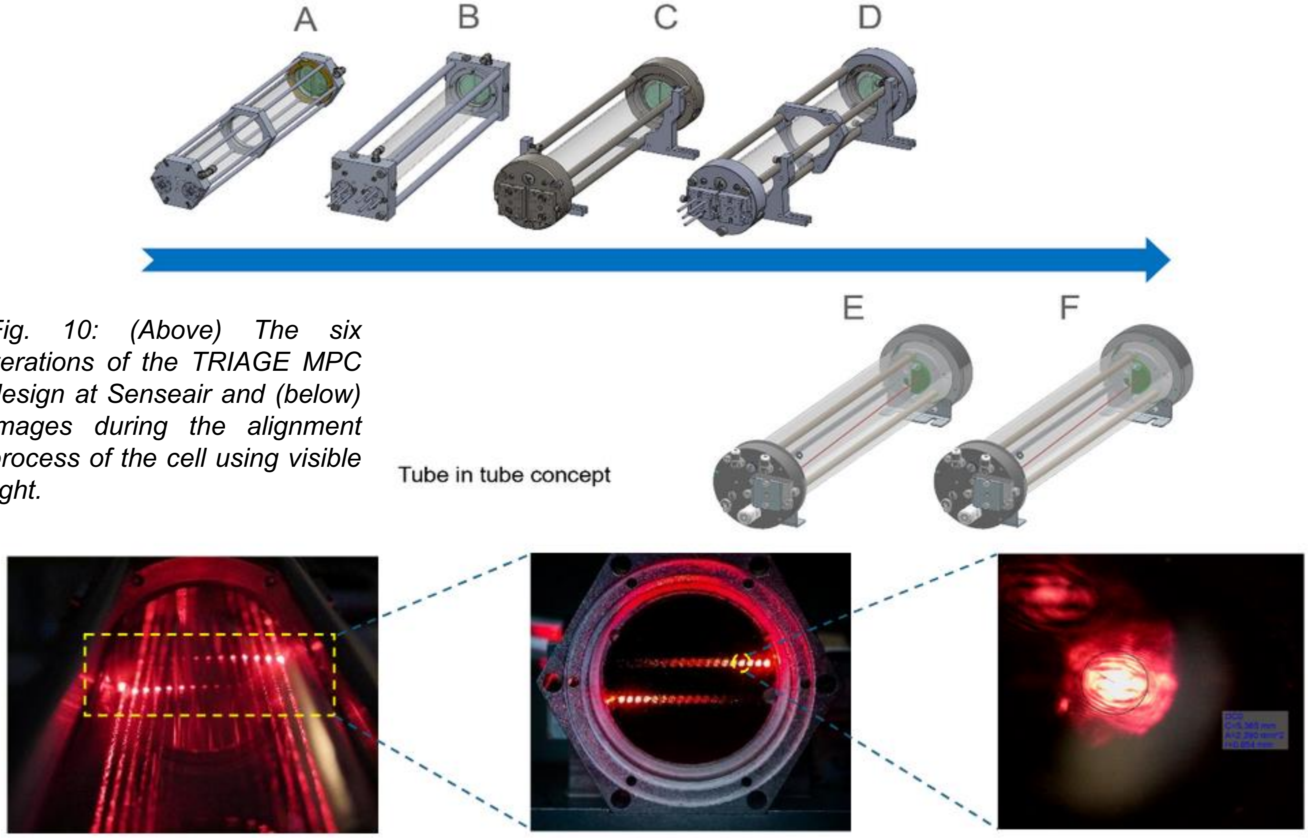

Fig. 10: (Above) The six iterations of the TRIAGE MPC design at Senseair and (below) images during the alignment process of the cell using visible light.

MPC A was the initial concept of the MPC with a linear guide rail. MPC B is the next generation with removed linear guide rail and removable glass tube that makes the MPC more maintenance-friendly. A new revision MPC C redesigned the MPC so that there were only three connection rods, which was expected to reduce the beam shift when different pressure level is applied. It also introduces in- and outlets to increase the system interface possibilities. MPC D used bigger holes in the end cap and introduced the possibility for mirror adjustment in the *x*- and *y*- directions. Next development was the MPC E which was intended to address the beam shift during the pressure changes. The most recent development was MPC F which involved a mirror bracket that could be screwed into the mirror disk. With self-integrated adjustment, MPC F avoids the need for external alignment tools. It will decrease the MPC production time and allow easier maintenance. Moreover, initial tests of MPC F indicate that this design gives more stable outgoing light even within pressure variation.

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