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Executive Summary

Within HYDROPTICS a range of photonic technologies will be developed and combined for realizing advanced sensing strategies for on-line detection of relevant impurities in process water streams such as residual oil content and particles. HYDROPTICS also puts emphasize to relate the results provided by the on-line analyzer to available process data of the industrial cooperation partners at their pilot sites to gain an in-depth understanding of the processes, mainly water purification processes, under investigation. Based on this understanding improvements to the overall process shall be suggested. Likewise, chemical engineering know-how will also be used to optimize sample preparation as required in the on-line analyzer platforms.

By means of the research effort within HYDROPTICS the quality of process water shall be improved by optimization of the overall process in the water treatment plants, with focus on key processing steps.

This deliverable breaks down the planned research into its core developments. These will occur at different TRLs and consist in envisioned advances regarding photonic components, modules, subsystems and use of the combined on-line data of oil-in-water and particle type and content in the context of process optimization. D3.1. also details the different methodologies required, the respective expectation regarding possible results and metric put in place to judge the progress in the respective developments.

If possible, reference will be made to existing standards, test methods and norms.

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1. Introduction

Water is not only an important resource for the environment and all life on the planet but also indispensable for the economy and industry. Due to the rapidly progressing industrialisation and the rising use of resources, contaminations of water systems are a matter of concern. As a result, water quality monitoring and water purification strategies are steadily gaining importance. To also guarantee a sustainable supply and availability of fresh water in the future, it is of utmost importance to refine and develop future-orientated innovative technologies for the monitoring of water.

Focusing on industrial water streams (process water streams and purification plants), on- or inline sensing concepts are greatly preferred due to better automatization and a larger margin of error to react in case of too high or low (for additives in process waters) contaminant concentrations. HYDROPTICS plans to develop and supply a versatile platform focused on the use in the oil industry by combining optimisation for state-of-the-art technologies with novel advances in sensing and fluid dynamics.

2. Improved Sensing Concept Using Advanced QCL Sources

The research to be conducted within HYDROPTICS regarding mid-IR sources aims at achieving the following goals:

- **Improving the long-term stability of an on-line oil-in-water analyser**
- **Improving sensitivity of mid-IR based sensing schemes**
- **Extending the spectral range covered by frequency combs by combining two comb sources**

2.1. Motivation: Improving the long-term stability of an on-line oil-in-water analyses

Quantification in absorption spectroscopy is based on Lambert-Beer´s law, which requires recording of two intensities, IR (cm-1) and IS (cm-1), from which the absorbance A(cm^{-1}) is calculated:

$$A(cm^{-1}) = log\left(\frac{I_R(cm^{-1})}{I_S(cm^{-1})}\right) = \varepsilon \cdot c \cdot d \qquad \text{(eq. 1)}$$

Using a calibration function the concentration is determined from the calculated absorbance value. This fundamental approach for quantitative analysis can be employed for transmission measurements as well as for measurements using the attenuated total reflection technique.

This general principle of quantitative spectroscopy is employed in HYDROPTICS and particularly used for the determination of oil-in-water. According to the ASTM 7678-17, a standard test method developed by the project partner QuantaRed Technologies, transmission measurements in a flow cell configuration are performed. In this test method oil is extracted from the sample by a liquid-liquid extraction step using cyclohexane as extraction solvent and the extracted oil is quantified in the extraction solvent. For measurement, a single DFB-QCL is used emitting at a single wavenumber within the wavenumber range from 1370-1380 cm^{-1}.

For determining I_R (1375 cm^{-1}), the transmission cell of the ERACHECK analyser by QRT is filled with cyclohexane used for extraction and the corresponding reading is taken and stored. Subsequently, the transmission cell is filled with the solvent, after performing the liquid-liquid extraction step, and I_S (1375 cm^{-1}) is recorded. From those two readings the absorbance is calculated, and the concentration of oil in water determined using a previously established calibration function.

This method works fine if the cyclohexane used for extraction is the same solvent as the one employed for recording I_R (1375 cm^{-1}). This condition is fulfilled in off-line analysis where fresh, unused cyclohexane can be used for each single analysis (liquid -liquid extraction). However, in case of an on-line analyser the employed cyclohexane needs to be recycled. As a consequence, traces of other molecules are slowly enriched in cyclohexane, leading to a slightly increase in water being also present in cyclohexane. The accumulating traces of water interfere in the accurate

analysis, a problem which manifests itself as trending baselines drift over prolonged use of a recycled cyclohexane solvent.

Within HYDROPTICS, strategies are proposed to overcome this problem based on both

- **a dual-DFB-QCL and**
- **frequency combs**

instead of a single DFB-QCL.

2.1.1. Dual-DFB-QCL source: Methodology

The mid-IR spectrum of oil extracted into cyclohexane shows a band resulting from the deformation vibration of the methyl-groups which is centered around 1375 cm-1, with hardly any absorption at 1400 cm-1. Increasing water traces lead to a rather unstructured, flat shift in background absorption across the spectral range extending at least from 1450-1100 cm-1. Therefore, in a first approximation, this influence in the background absorption will affect the absorbance at 1375 cm-1, where quantification according to ASTM7678-17 has to be performed, in the same way as the absorbance at 1400 cm-1.

In the dual-DFB-QCL approach of HYDROPTICS, quantification will be based on readings obtained from the cyclohexane after extraction using one DFB QCL providing a reading at 1400 cm-1 (IR) and another one at 1375 cm-1 (IS).

2.1.2. Frequency combs: Methodology

Based on the broad spectral coverage of combs it will be possible to measure the area of the absorption peak related to the deformation vibration of the methyl-groups which is centred around 1375 cm^{-1}. By applying an appropriate integration method it is expected that, as in the case when working with dual DFB-QCLs, improved ruggedness of the on-line oil-in-water analyser can be achieved as baseline shifts due to increasing water traces in cyclohexane can be compensated.

2.1.3. Attenuated total reflection (ATR): Methodology

Upon total reflection of an incident radiation at an interface between an optically dense and an optically thin layer, an evanescent wave is formed. In ATR spectroscopy, this wave interacts with the sample and is partially absorbed. Thus, absorption spectra can be recorded, for which two measurements are needed. In the first measurement, which serves as reference (background) measurement, typically only the solvent, without the target analyte, is placed in contact with the ATR element and the light intensity reaching the detector is recorded yielding the single beam spectrum I_R (cm^{-1}). In a second experiment the solvent is replaced by the sample yielding I_S (cm^{-1}). From both single beam spectra, the absorbance spectrum described by (eq. 1) and used for quantitative analysis.

Using quantum cascade lasers as light source, which provides polarized light, a new variant of ATR spectroscopy becomes feasible and will be explored in HYDROPTICS. The new concept is based on the fact that p-polarized and s-polarized light show different effective depths of penetration, with values for p-polarized light about twice as large as for s-polarized light. This will be exploited to allow for performing reference and sample measurement without the need to exchange the sample. Another possible effect of this measurement approach is the reduction of noise caused by eventual impurities at the ATR crystal-enrichment layer interface. To do that, two approaches will be considered:

- **Adding an additional active optical component for changing the polarization of the QCL source by 90°. For instance, this can be achieved using a photoelastic modulators (PEM) or acousto-optic modulators (AOM).**
- **Applying a fixed polarization aligned at 45° for measurement. The incident light will have equal contributions of p-polarization and s-polarization. After interaction with the sample the two polarization directions will be separated and simultaneously detected by two different detectors.**

2.1.4. Expected Results / Validation / Impact Assessment for 2.1.1, 2.1.2 and 2.1.3

It is expected that the long-term stability of an on-line oil-in-water analyser based on working with recycled cyclohexane can be significantly improved.

For assessing the performance of the new sensing concepts ASTM D7678-17 will serve as a reference for the new methods to be developed according to 2.1.1 and 2.1.2.

The analytical figures of merit of the new, improved methods will be established following ISO 8466-1.

Both, ASTM 7678 and ISO 8466-1 do not consider the effect of long-term drifts due to impurities accumulating in the background solvents. Therefore, in addition to quality control as outlined in section 12 of ASTM 7678-17, long term stability tests will be carried out to determine and validate the applicability of the developed approaches. For that purpose, measurements over a prolonged period of time will be conducted and evaluated using trending charts for recording (I_R), (I_S) as well as corresponding absorbance values, and performing variance and trend analysis.

Similarly, long term stability will also be evaluated using Allan-Werle[1,2] plots.

Regarding 2.1.3 it is planned to benchmark the stability of the new, polarimetric approach against a standard ATR approach where only one polarization is used for data evaluation.

We expect that two positive effects can materialize from application of balanced polarimetric detection.

First, in short term (analysis time less than 10 minutes) this approach will be able to minimize pulse to pulse intensity fluctuations of the employed DFB-QCL. Here, it can be expected, that by implementing the balanced polarimetric approach, the noise level as calculated from RMS values of repeated detector readings can be improved by at least a factor of 5. Second, we also expect that the balanced approach will improve the long-term stability of the sensing system. Similar to 2.1.1 and 2.1.2. Allan-Werle variance for the RMS noise of a blank medium (uncoated ATR element) and trending charts will be recorded over time to assess the improvements made.

2.2. Improving sensitivity of mid-IR based sensing schemes

2.2.1. Enrichment layers: Methodology

To further optimize the sensitivity of the ATR method, a surface modified mesoporous layer will be applied on the ATR surface with the following purposes:

- **excluding water reaching the evanescent field and**
- **enriching target analytes out of the aqueous phase.**

Adsorption of molecules at high-surface area mesoporous materials is used in established solid-phase extraction for separation of target analytes from their matrix, which in most cases also leads to analyte pre-concentration and subsequently to more sensitive measurements. Based on the research conducted in AQUARIUS a new sensor concept based on mesoporous silica and miniaturized ATR elements has been developed. This concept allows for tailoring the surface chemistry of the porous silica layer as required for the intended analysis and in-situ observation of the enrichment process in the evanescent field of the employed ATR element. The mesoporous material is

[1] Werle, P., Mücke, R. & Slemr, F. The limits of signal averaging in atmospheric trace-gas monitoring by tunable diode-laser absorption spectroscopy (TDLAS). *Appl. Phys. B* **57,** 131–139 (1993). https://doi.org/10.1007/BF00425997

[2] Allan, D. Statistics of Atomic Frequency Standards, pages 221–230. Proceedings of the IEEE, Vol. 54, No 2, February 1966.

produced via sol-gel process involving surfactants and applied to the ATR element by spin-coating. Using CTAB as surfactant pore sizes of approx. 4 nm were obtained which is enough for allowing the enrichment of small molecules such as hydrophobic substances into the mesoporous film. The pore size has further been found to be dependent on the used surfactant template. Here we plan to tune the selectivity of the sorbent layer to enrich corrosion inhibitors out of the aqueous phase. This will be done by tailoring the pore sizes and surface modifications on the pore surface for the analytes of interest.

Another approach in this direction will be the implementation of new mesoporous materials for sensor applications, with the goal of better IR-transparency in lower wavenumbers. Here a first focus will be laid on mesoporous titania layers, which show promise in that direction, with the same route of synthesis applicable as for mesoporous silica.

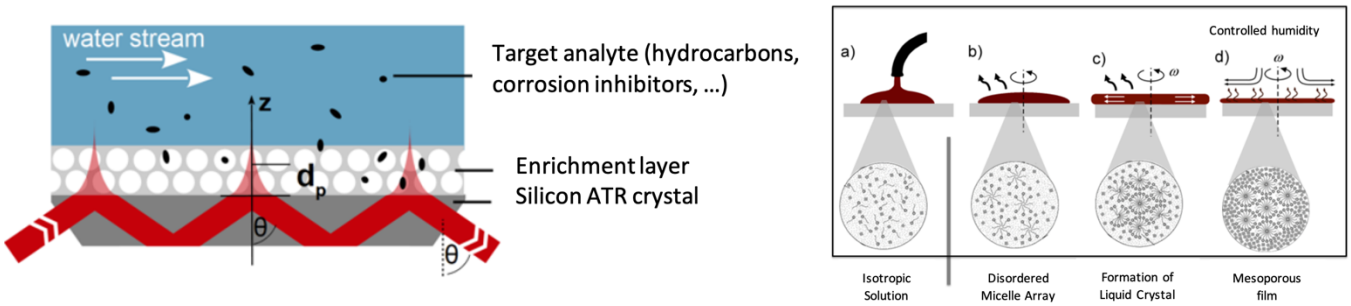

Fig. 1: Left: ATR sensor concept employing an enrichment layer. Right: Schematic of the individual steps for producing mesoporous layers by spin-coating.

2.2.2. Expected Results / Validation / Impact Assessment of enrichment layers

Expected results

We plan to build on previous experiments using mesoporous silica to enrich analyte molecules from aqueous solutions into the evanescent wave of an ATR element. The use of enrichment layers for sensing of small quantities of target analytes delivered a significant uptick in the sensitivity of the method.

In this project mesoporous layers different from silica will be investigated. Results using mesoporous titania and zirconia are expected. We expect increased chemical stability at extreme pH values and a larger optical window for measurements in the important fingerprint range.

Regarding the enrichment time, due to the nature of the absorption process relevant for the enrichment process, a slightly longer loading time is to be expected than without using enrichment layers, making the loading time a very important criterium for the evaluation of the sensing layers performance. Similarly, reversibility of the enrichment process is of relevance. In case enrichment is not reversible, concepts for rapid sensor replacement will be investigated.

Validation

The main criteria for the validation of the enrichment layers are:

i) **high affinity towards target analytes (enrichment factors >25)**

ii) **high selectivity (little to no enrichment of unwanted contaminants, >20 times higher for target analytes)**

iii) **fast enrichment (enrichment times <10 min, ideally in the range of 1 min)**

iv) **Determination of analytical figures of merit based on ISO 8466-1**

v) **IR-transparency in the region of interest. In addition, to be transparent in the spectral range from 1300 cm^{-1} to 1550 cm^{-1}, as required for sensing aliphatic and aromatic hydrocarbons, transparency also at longer wavelength (smaller wavenumbers) is needed. As a minimum these layers shall allow measurements at 1000 cm^{-1} (10µm), which is a region of interest for the analysis of corrosion inhibitors.**

vi) **adhesion on substrate material (robustness, long term stability of layer in continuous measurement >1 day)**

vii) **film thickness > d_p for exclusion of water (depending on the specifications of the ATR crystal, 250-500 nm is preferable)**

Impact Assessment of enrichment layers

For the optimisation of i), ii) iii) and v), absorption/desorption profiles will be determined using an automated flow system. Analytical figures of merit (iv), including sensitivity and linearity of the calibration curve, will be determined according to ISO 8466-1 and compared with the metrices obtained when using state-of-the-art offline methods for quantification of the target analytes used in industrial settings. These are the oil in water analyser ERACHECK from QuantaRed Technologies following ASTM D7678-17 and wet chemical methods for quantification of cationic surfactants or phosphates used as corrosion inhibitors.

Spectral transparency (v) will be assessed by broad band FTIR spectroscopy.

Physical properties (e.g. layer thickness, porosity, wetting angles) of the enrichment layers will be determined using universally applied methods (small angle x-ray diffractometry, grazing incidence small angle x-ray scattering, ellipsometry, profilometry). Practical properties such as stability over time (durability), reusability (regeneration capability) will be determined experimentally using dedicated experimental protocols. In a similar way the efficiency of chemical modification of the enrichment layer will be tested in dedicated sensing experiments. Different layers (zirconia and titania) and their surface modification will be assessed again by experimental evaluation.

2.2.3. Moving towards Mach-Zehnder-Interferometers: Methodology

As the results of the previous H2020 AQUARIUS project showed that the signal to noise ratio of liquid phase sensors based on a pulsed QCL IR-source is still subject to optimization, new sensing schemes need to be brought in to tackle that issue.

In a first iteration signals from thermoelectrically cooled MCT detectors, simultaneously measuring the laser beam passing through the sample cell I_S (sample and solvent absorption) and the reference beam IR (only solvent absorption), are combined in a ratiometric amplifier, where the respective signals are subtracted or divided.

A second step and more relevant step will be the implementation of a Mach-Zehnder interferometer for further improving this balanced detection scheme, which is designed to utilize the coherent nature of the emitted laser light alongside with its high emission intensity. In an MZI, the reference and sample cells are placed into its two arms. The emitted QCL beam is divided into two by the first beam splitter, one beam being directed through the reference cell (I_R) while the second beam passes through the sample (I_S). At a second beam splitter the two beams interfere and are recorded at two detectors. By placing the mirror in one arm of the MZI on a piezo element, the optical path difference between the two arms can be actively adjusted. Introducing a sample in one arm of the MZI will lead to a phase difference causing an increase and decrease in intensity at the two detectors. This will be detected using the balanced detection schemes to account for small fluctuations in laser intensity during pulsed operation. It may be expected that by means of this set-up highly sensitive refractive index spectra of the sample can be recorded, which can be converted to absorption spectra following the Kramers-Kronig transform.

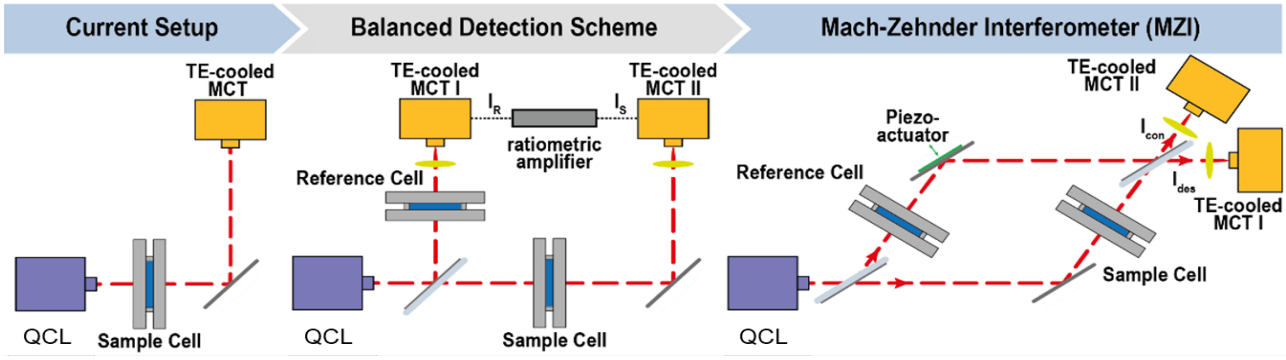

Fig. 2: Suggested evolvement of experimental set-ups for improved transmission measurement.

2.2.4. Expected Results / Validation / Impact Assessment of Mach-Zehnder-Interferometers

As the main objective of the efforts of employing the aforementioned improved detection schemes is the optimization of the signal to noise ratios in liquid phase sensors, the validation of the technology will be focused on the improvement of these parameters.

The criteria for the validation of the progress and improvement for this effort will be the comparison of noise levels (RMS noise of 100 % line) and LODs in the target regions for the single channel and balanced channel detection schemes. It can be expected that an improvement of the RMS noise by a factor of ≥20 can be achieved, with a consequence of a significantly lower LOD for the analytes of interest, compared with the single channel approach.

2.3. Motivation: Broadband mid-infrared spectroscopy by integrating two QCL frequency combs on a Si chip

For dual comb spectroscopy, two frequency combs have to be combined on a detector to be able to detect the multi-heterodyne signal. Until now, the combination of the beam of each frequency comb was done by using a series of mirrors and beam splitter which require thorough optical alignment and are very bulky. One effort conducted in HYDROPTICS will be to integrate two QCL frequency combs and combine their beams (using a Ge waveguide) on a single Si chip to drastically simplify, miniaturize and lower the cost of the dual QCL combs sources. This approach will be applicable as well for on chip combining of two single mode QCL DFBs.

2.3.1. Methodology

When integrating two QCLs on a Si chip for beam combining, several technical challenges have to be tackled:

- **good performances for QCL soldered on Si chip (heat dissipation, electrical connection)**
- **individual control of each QCL (current and temperature)**
- **precise alignment of both QCLs with the Ge waveguide**
- **broadband waveguide beam combiner**
- **low optical feedback towards the lasers**

In order to accelerate this development, a parallel approach is being conducted in the project. The first step consists of:

- **QCL soldering on Si wafer with performances similar to conventionally mounted QCLs**
- **simulation and fabrication of different options for Ge on Si waveguide beam combiner (including anti-reflectivity coating)**

- **setup development for coupling QCLs beams to Ge on Si waveguides with lenses**

Once those building blocks will be delivered, the following steps will be to develop a robust technique for QCL alignment with respect to the Ge waveguide for butt coupling and iterative improvement of the waveguide geometry for beam combining. This will allow to have a functional final device delivering state of the art quality frequency comb with a footprint reduced many folds.

2.3.2. Expected Results / Validation Scenarios / Impact Assessment

To evaluate the progress of the various developments needed in this part of the project, it is important to have clear key metrics to validate or not each step.

The QCL soldering on Si should allow to reach at least 100mW optical power in CW at temperatures above -20C. This will be validated by measuring the output power of a QCL mounted on a Si wafer in a conventional laser package of IRsweep.

The beam combiner should allow to get at least 5mW of optical power at the output of the device. This will be validated by measuring the output power from the beam combiner using a conventional QCL either with lens or butt coupling.

The integrated QCLs on Si chip coupled to Ge waveguide beam combiner should still be able to operate in the comb regime. This will be validated by measuring the beat note of each QCL and by performing a dual comb spectroscopy measurement.

The impact of this task will be to improve the performance of the dual comb setup by delivering perfectly overlapping combined beam from two independent QCL frequency combs. It will as well strongly reduce the footprint of the laser sources and beam combining setup and simplify the alignment procedure of the system.

2.4. Frequency comb stabilization using RF electronics

2.4.1. Methodology

The current dual-comb spectrometer technology utilized two frequency combs that operate in the so-called free running regime. In this operational regime, the lasers are highly susceptible to many different sources of noise and fluctuations, e.g. noise of the laser driver, temperature fluctuations, optical feedback. Hence, the lasers must be protected and shielded from such source with an extensive effort. As an example, in such a system not only the lasers themselves are temperature stabilized, but also the entire optical setup and surrounding environment. Also, the demands on the laser driver noise are extremely high. Despite these large efforts that are put on reducing these sources of noise, the frequency combs still experience a significant drifts and fluctuations that are limiting the overall sensitivity of the dual-comb sensing instrument.

As an alternative strategy to further push the sensitivity and to relax the constrains on noise reduction, a new laser stabilization scheme will be implemented using RF electronics.

Frequency combs are characterized by their equally spaced laser that can be described by just two frequencies, namely the repetition and the carrier envelope offset frequency. If both frequencies are stable, all comb lines and thus the entire frequency comb will be stable. Recent scientific work of TUW revealed that the first, the repetition frequency, can be stabilized using RF injection locking.

In the first step, this technique is currently being applied to the lasers provided by Alpes Lasers using laboratory equipment. Using this gained knowledge an electronic RF module will be developed to stabilize this frequency in both combs. The second frequency, the carrier envelop offset frequency will be stabilized using a phase locked loop (PLL). The first PLL prototype module is currently being tested using two single mode DFB lasers and then will be implemented to stabilize the carrier envelop offset frequencies between the two combs. This relative stabilization will effectively stabilise the dual-comb RF spectrum. Using exchangeable loop-filters on PLL board allows to quickly

adapt and optimize the module to different laser, laser drivers or other changes and thus will allow a rapid joint development of the stabilization by TUW and IRsweep.

2.4.2. Expected Results / Validation Scenarios / Impact Assessment

The electronic RF modules will be first tested using laboratory instruments. This will allow to acquire the exact specifications of the stabilization measures, such as locking range, loop-filter bandwidth etc. The same RF module will then be implemented directly into the dual-comb sensing instrument, which allows for a direct evaluation of the performance benefit due to laser stabilization. This performance benefit will be directly visible through the signal processing chain and thus allow the direct validation of the expected higher efficiency of the averaging and signal post-processing unit.

3. Particle Sensing

3.1. Motivation - Methodology

The only particle sensing schemes employed at the sites of our project partners are optical systems, which are limited to image acquisition and processing by algorithms, only looking at the shape of the particles to discriminate between emulsions and dispersed particles, which are further subject to fouling of optical windows by films of oil and particles. An example for such a system is the Jorin ViPA, which is shown in Fig. 3. The need for novel approaches proposed to be developed in Hydroptics was also confirmed by the external advisor Matthias Busch (Wintershall Dea), as to his knowledge as well, no comparable system is commercially available so far.

The hypothesis made and the motivation for the development of new sensing schemes is that by measuring particle load as well as its chemical composition, important information on the actual status of the water purification plant can be obtained. Furthermore, in case this turns out to be the case, it is expected that this information can then be also used for process control.

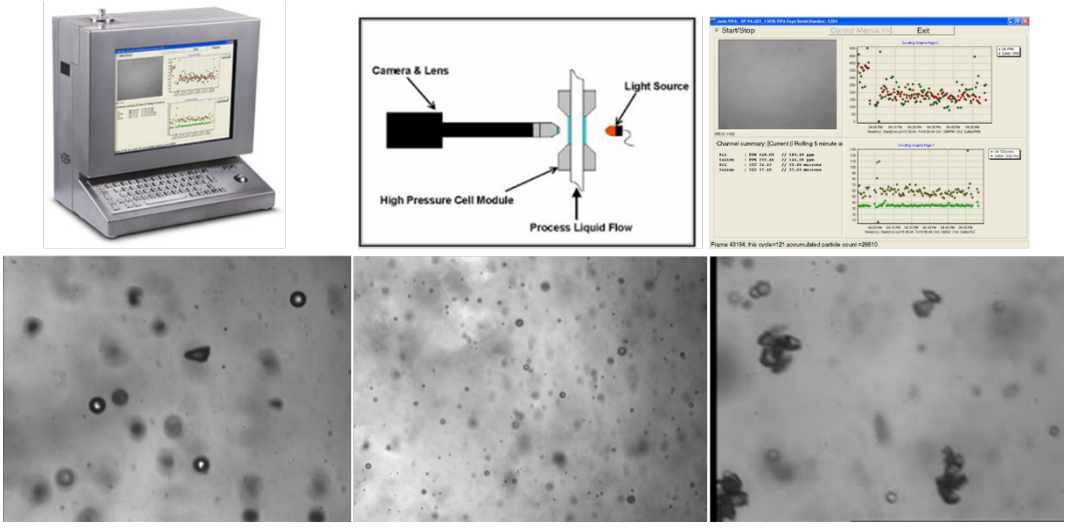

Fig. 3: Particle measurement using the Jorin ViPA.

Regarding the size of the particles, we target a particle range between 1 and 100 µm, with slight adjustments possible pending an exact characterisation of the particle system in later tasks. The upper size limit of the particle sensing scheme will be determined by hard-capping the particle distribution with a mesh filter, and the lower size limit will be determined by the resolution limit of the optical analyser.

State of the art systems and difficulties: Detection of suspended particles (size range >1 µm, solid or suspended droplets plane-focused imaging systems in process pipes or, more often, bypass lines (optionally complemented by

light scatter-based optical counting sensors) are utilised. A volumetric quantitative analysis is done by standard image processing (particle detection/tracking, coupled to a counting algorithm). The overall particle load is calculated from this data assuming a given flow profile and monitored over time. However, some problems stem from this approach:

- **A first problem of this method is the often-poor contrast, in particular of suspended droplets. This negatively affects the reliability of the measurements and may result in an estimated particle load lower than the actual amount, which in turn poses a problem for process control.**
- **Additionally, the algorithms attempt a semi-qualitative analysis by trying to distinguish between solid particles and droplets based on the acquired shape (solid particles are more likely to have sharp edges, liquid droplets assume various rounded shapes). Apart from the low selectivity of the approach, the reliability is also limited.**
- **Another encountered challenge in current sensing schemes for particles in process water is achieving long term stability of the optical system, which is often impaired by formation of deposits on surfaces. These deposits form when particles approach these surfaces.**

To increase both the contrast and the selectivity, HYDROPTICS will attempt to employ spectrally encoded multi-/hyperspectral imaging. Inherently limited by practical applications to transparent regions of the process solutions, and thus the UV/VIS and possibly some parts of the near-IR region, both approaches with broadband illumination and wavelength-selective imaging (using imaging spectrographs or tunable filters) and such with narrowband illumination, will be pursued. The research will also include fluorescence imaging, which is attributed a high potential to be able to both selectively and sensitively detect oil droplets (and other aromatics) within relevant time frames.

To mitigate the problem of deposits on the optical systems, ultrasound particle manipulation will be employed. Ultrasound particle manipulation can be used for the controlled movement of particles larger than 1 µm in a suspension. By applying a standing sound wave field, particles agglomerate in nodal planes spaces at half of the applied sound wavelength. Using 2 MHz sound waves nodal planes are formed approximately every 375 µm. A dedicated flow cell, protected by a mesh filter of 50 µm will be produced which will allow only one nodal plane to be formed, thus particles to be analysed will be concentrated and thus easier to be captured by the hyperspectral imaging system and, additionally, kept away from the sensitive optical windows, thus improving long-term stability.

As so far, no data on particle content and composition are recorded on-line at the industrial cooperation partners OMV and TUPRAS, off-line laboratory-based instrumentation will be used for obtaining qualitative reference information. It is planned to use fluorescence imaging, single point Raman scattering as well as scanning electron microscopy with element specific detection for providing elemental and molecular information on the particles under investigation. For quantitative reference analysis sampling and gravimetry will be employed.

For calibration of the on-line particle sensing system validation of the data processing efforts, classical deterministic chemometric and imaging approaches will be used and benchmarked against machine learning / AI concepts in both terms of performance and practical applicability (runtime complexity of the trained model, compatibility with process-defined real-time requirements etc.).

3.2. Expected Results / Validation / Impact Assessment

Expected Results

- **First time realisation of an experimental approach combining ultrasound particle manipulation to emulsions carrying particles for enhanced spectroscopic characterisation of the oil and particle load.**

The use of image processing algorithms in multi-phase systems can lead to several issues, which our approach is targeting to tackle:

- **Deliver material analysis by use of spectroscopic (mainly NIR and fluorescence) methods**
- **Offer a more reliable distinction between dispersed solids and oil droplets**
- **Potential to analyse even more complex systems (oil droplets covering solid particles)**

Validation

As currently no comparable alternative particle sensing scheme delivering both size and chemical information of oil and particle composition is commercially available, any progress in that matter is new and welcome for our project partners.

Results on total oil content will be compared to laser based mid-IR analysis (ASTM 7678-17).

To validate the obtained on-line data at the industrial partners OMV and TUPRAS, sampling and off-line analysis in the laboratory will be performed.

Impact Assessment

It may be expected that the new, real-time information on the chemical composition of particles will be of added value compared to the state of the art which lacks such information in any case. The actual impact on process monitoring will be assessed with plant engineers of the respective partners.

4. Computational Fluid Dynamic (CFD) Simulations

The research to be conducted within HYDROPTICS involving advanced CFD simulations concerns the two main aspects:

- **Optimization the automated liquid-liquid extraction process**
- **Optimization of key process steps in the water purification plant**

4.1. Motivation: Optimization the automated liquid-liquid extraction process

4.1.1. Methodology

Within HYDROPTICS project (with connection to task given by T5.3) the process of liquid-liquid extraction will be investigated. One of the focus points of this work is to minimise the amount of extraction solvent (cyclohexane) needed and its losses into the water phase. This complex process, having two involved unit operations – extraction and phase separation will be investigated and optimised for its purpose. Figure below shows the workflow regarding the optimisation of liquid-liquid extraction process.

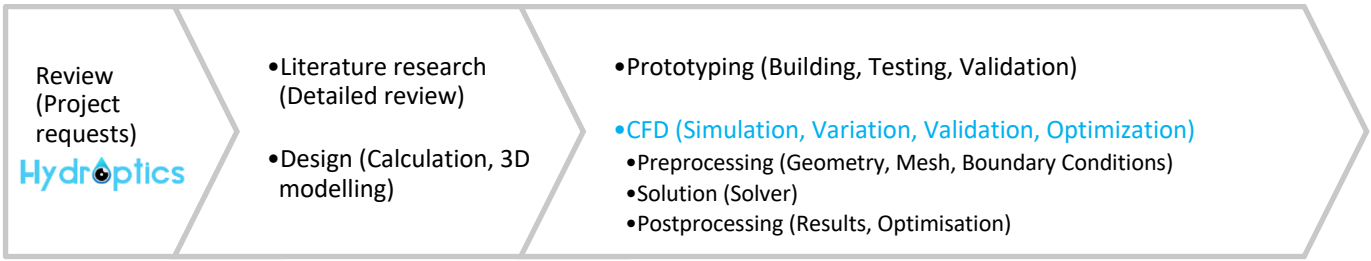

Fig. 4: Workflow of optimization of liquid-liquid extraction process.

Based on previous research it is known that 3-phase decanter centrifuges and 3-phase separator designs can be applied in large scale industrial processes. For these applications, many devices exist, however, if the density difference between phases is high enough, the application of centrifugal force gives by far the best separation results. Thus, one of the main challenges is to downsize and/or miniaturise the equipment and have a final selection

of possible and suitable designs. The selection will be made in order to meet requirements for such purpose. Benchmark parameters are:

- **Throughput and solvent/water phase ratio**
- **Total hold-up and phase hold-up**
- **Size and energy requirement**

The design step will be supported by Computational Fluid Dynamics (CFD) methods in order to derive a digital twin. CFD knowledge will be deepened and the suitable multiphase solver for modelling will be selected. Such approach will allow variation of throughput and solvent/water ratios and further support optimization process.

4.1.2. Specifications

The separator will be designed based on specified properties. TUW and QRT are cooperating regarding this task and detailed planning on specifications will be carried out.

4.1.3. Expected Results / Validation Scenarios / Impact Assessment

It is expected that selected design will be capable to handle multiphase systems which means successful process of extraction and phase separation of such systems.

The designated model will be built for purpose of testing and validation. In parallel with building of a prototype the process of CFD will be performed. Prototyping, testing and simulation will be applied hand-in-hand to use the experimental results for CFD model calibration and validation; CFD parameter variations will allow to optimise the geometry and operating conditions according to design specifications.

4.2. Motivation: Optimization of key process steps in the water purification plant

For the efficiency of gas and oil production, the treatment of the emerging water is a major challenge. The simulation of such processes leads to a more precise understanding of the procedures within the plants and is therefore an important step towards increasing efficiency. A major problem with the simulation of these facilities is the dynamic behavior of many plant components in the overall process. The aim is to simulate overall test facilities (as of partner OMV) and to generate a digital twin of this process, which includes the dynamic behavior of relevant components, to gain an in-depth understanding of the process. Furthermore, through digital twinning of the process and data analysis of critical process parameters, process optimisation strategies can be applied (e.g. debottlenecking, improvement of the dynamic system response to feed quality/quantity fluctuations etc.).

4.2.1. Methodology

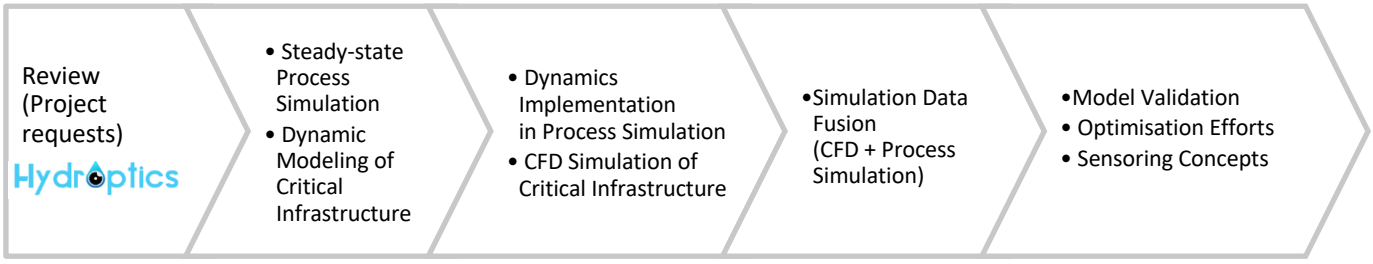

Fig. 5: Workflow for the optimisation of key process steps

The procedure for the digitalisation of the system can be divided into 2 main areas:

i) **Simulation of the overall process using process flowsheeting and grey-box models:** Using existing data of the test facility, dynamic models of the components are developed and implemented into the overall model to provide a basis for the simulation of process parameters. Also, the dynamic effects of the components

will be taken into account. In the end, the established digital twin offers the possibility to help optimising the system by implementing different efficiency algorithms and the fusion with field sensor data.

ii) **Computational Fluid Dynamics simulation of critical plant infrastructure:** Process simulation carried out in i) will provide an adequate overview of the overall process and allows the identification of the most relevant plant components, which influence the process parameters the most. Therefore, the transient behavior of the relevant infrastructure is evaluated through CFD simulation to gain a more precise understanding of the effects within these components. Subsequently, simulation data achieved from CFD simulation are merged with the established digital twin to enhance the precision of the overall dynamic simulation.

4.2.2. Specifications

The characteristics of the created models is meant to be direct representations of the real-world test facilities. Therefore, data sets of the test plants are used in the configuration of the dynamic modelling concept. The gained data from the simulations will be validated by existing measurement data.

4.2.3. Expected Results / Validation Scenarios / Impact Assessment

It is expected that a fully functional model of the overall process will be generated, which is able to fuse both chemical process simulation and computational fluid dynamics to achieve maximum precision in the simulation aspect. This will allow an in-silico evaluation of the plant infrastructure for the purpose of future process optimisation and training. Also, for the implementation of the sensor equipment, predictions of the hydrocarbon fraction and flow rates based on the dynamic behavior of the components will contribute to enhance the sensing concepts.

Conclusions

The definition of metrics for the system validation scenarios was done based on the features of the involved subsystems, integrated sensing platforms, data evaluation and compression algorithm in collaboration with technical partners involved in the development.

Further, test criteria (pass/fail) were devised for the hardware components at a basic level, while at high level metrics were defined for the operational requirements of all modules.

Finally, evaluation metrics were devised for the operability of the on-line sensing systems in the process environments of the end users as well as the specific cases of the real industry settings validation in the pilot sites. To validate the system measurement performed by the platform, procedures and comparisons with existing instrumentation and golden standards were discussed.