

# **D3.5 FIWARE-enabled Water Quality** Sensors

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### Executive Summary

This deliverable (D3.5) contains part of the work done within Work Package 3 (WP3) 'Smart Applications and Devices', specifically Task 3.5 'Advanced Water Quality Sensors', aiming at developing smart devices that improve Urban Water Supply monitoring and infrastructure management. In this task, three actions have been executed: i) develop advanced water sensors to improve the data gathering of water quality, ii) increase the reliability of the raw data using intelligent processing, and iii) demonstrate the integration of the extracted data into data management platforms.

The document reports the development of two different sensors. First, the development of the 'Nanosensor' sensor, a device that detects multiple chemicals dissolved in water, temperature and conductivity, with a perfect size to be used in water loops, and second, the development of a printed device that consists in a free chlorine electrochemical sensor and temperature sensor platform with a wireless compact autonomous electronic control unit (ECU) and software for data acquisition into a remote computer.

The Nanosensor development is reported describing all the steps carried out, starting with the theoretical concept behind the sensor, involving the concept, the multi-parameter strategy, the working principle, and the fabrication process. It is followed by the resistance study of the sensor under water conditions to ensure a minimum time of data gathering until failure, the software developed to improve in raw data acquisition by reducing signal noise, and the laboratory sensor testing, which encounters several problematics that are addressed, identified, and improve afterwards.

The printed sensor is explained in a similar manner, starting with the theoretical concept behind it, the sensor design, the fabrication route, and a theoretical description of the electronic control unit encapsulating it, which enables the connection of the printed sensor with external devices. The development involved the creation of a desktop application to configure and visualize the sensor readings.

The further development of hardware/software components is necessary to integrate the data extracted from these sensors into the FIWARE ecosystem of the project, properly named FIWARE4Water architecture. This deployment is demonstrated within the Cannes Demo Case #2 (France) and detailed in the deliverable 4.2 "FIWARE4\_Leakage Management", and the technical development of the software is explained in deliverable 2.3 "Extension of FIWARE for supporting water management and quality monitoring use-cases". Furthermore, the intelligent processing of raw data extracted from sensors is technically explained in D4.3 "FIWARE4\_Water Quality Monitoring and Pollution Response", and tested under practical conditions.

### European added value (EAV) and upscaling

The European Added Value of deliverable 3.5 has multiple aspects: (i) showcasing the fabrication and implementation of two different multiparameter sensors as advanced water quality sensors, (ii) the methodology on how to validate sensor behaviour and localize the errors, and (iii) the development of FIWARE components to export the raw data to remote systems. All these actions can be reimplemented across Europe since the theoretical knowledge can be learnt from and future recommendations can be extracted from it. Furthermore, software development requires design and implementation time. The component developed is integrated with the FIWARE ecosystem, which means that the adaptation of the FIWARE architecture already solves the principle of sensor integration and deployment.



## **Related Deliverables**

**D2.3** – "Extension of FIWARE for supporting water management and quality monitoring use-cases", reporting the connectors implemented to enable the integration of sensors.

**D4.2** – **"FIWARE4\_Leakage Management"**, where the deployment and end-testing of the developed smart solutions for the French demo case are described.

**D4.3** – **"FIWARE4\_Water Quality Monitoring and Pollution Response"**, where the raw data improvement algorithms and the sensors are tested under practical conditions.



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## List of Acronyms/Glossary

Acronym	Description		
BIXX	Business Issue, one of the four French Business issues (BI01 to BI04)		
CIRSEE	Centre International de Recherche Sur l'Eau et l'Environnement (in		
	English, International Centre for Research on Water and Environment),		
	partner in the F4W project		
CNRS	Centre National de la Recherche scientifique (in English, National		
	Centre for Scientific Research)		
EGM	Easy Global Market, partner in the F4W project		
EUT	Eurecat, partner in the F4W project		
F4W	Fiware4Water project		
NGI	Next Generation Internet		
	The Next Generation Internet (NGI) initiative, launched by the European		
	Commission in the autumn of 2016, aims to shape the future internet		
	as an interoperable platform ecosystem that embodies the values that		
	Europe holds dear: openness, inclusivity, transparency, privacy,		
	cooperation, and protection of data.		
PLC	Programmable Logic Controller		
RTU	Remote Terminal Unit		
SCADA	Supervisory Control And Data Acquisition		
SUEZ	Parent company of 3S and third party of 3S in the F4W framework		
TZW	DVGW-Technologiezentrum Wasser, partner in the F4W project		
WPL	Work Packages Leaders		
3S	SUEZ Smart Solutions, subsidiary of the worldwide group SUEZ, and		
	partner in the F4W project		
GA	Grant Agreement		



### Introduction

Advanced sensor technology is widely used in water quality monitoring, providing real-time information on the water status and raw data to be processed afterwards. Nanosensors research contributes heavily to self-sustainable sensing systems, and the addition of artificial intelligence as low-level analytics improves the extraction of raw data, reducing the final economic cost of implementing later post-processes.

The Nanosensor is a device previously investigated in the H2020 PROTEUS project (GA No 644852), where it was able to measure physical and chemical parameters such as conductivity, temperature, flow rate, pH, total chlorine, hardness, and nitrate. The main feature of the sensor was the merge of physical and chemical sensors to build a multi-parameter sensor (multiplexing). During the Fiware4Water project, the reliability and lifetime of the sensor were studied to bring the sensor into TRL 8. However, the results of the testing phase of the sensor indicated a malfunction within it that made the raw data gathering impossible, impacting not only the main objective to achieve a high TRL, but the implementation of software to filter the gathered raw data and the planned deployment of the sensor.

To address the issues, the printed sensor and the nano::stations were introduced. The printed sensor consists of a free chlorine electrochemical sensor and temperature sensor platform with a wireless compact autonomous electronic control unit (ECU) and software for data acquisition in a remote pc. The key technological advantage of this multiparametric sensor is its reliability at a low cost enabled by fabrication through printing technologies. The introduction of this sensor into the project enabled the generation of low-level raw data filtering processes, which are detailed in D4.3 "FIWARE4\_Water Quality Monitoring and Pollution Response".

At the beginning of the project, the French demo case decided to install four multiparameter probes, named nano::stations, to begin the water monitoring as soon as possible and gather enough water quality measurements to develop the Smart solutions properly explained in D3.2 "FIWARE-enabled applications for Water Distribution". These two reasons already secured the implementation of the French demo case in case of problems with the Nanosensor. Therefore, the nano::stations were further focused after the problems were encountered, and all the actions planned for the Nanosensor were rejected. This document reports the main points of the implementation, but a further explanation on the installation is reported in deliverables D4.2 "FIWARE4\_Leakage Management" and D4.3.

### Document structure

The deliverable is structured in two big chapters: The Nanosensor and the remediation plan with the Printed sensor and the nano::stations.

The Nanosensor actions are split into different sections: The theoretical concept behind the sensor, the development to improve the lifetime of the sensor and raw data extraction, the development of the FIWARE component to integrate the sensor data, and the validation stages out and within the testing facility, and the remediation plan carried out to solve the problems encountered during the validation stages.

The remediation plan starts with the general changes within the French demo case, focusing on the nano::stations installation and connection. Afterwards, the Printed sensor is introduced, with the fabrication route, the theoretical concept, the data transmission protocols and the user interface to configure and visualize the data.



### I. The Nanosensor

### I.1. Concept

The Nanosensor aims at performing multiple detections of chemicals dissolved in water networks in addition to measuring temperature and conductivity. It is based on the device investigated in the previous H2020 PROTEUS project for which a single electronic chip contained all sensing elements. The size and shape of the Nanosensor are such that it can be inserted into water loops for allowing online and real-time analysis of water networks.

#### i. The multi-parameter sensor

The action of CNRS in FIWARE4WATER was initially based on the results claimed at the end of the former H2020 Proteus project, where a sensor was able to measure both physical (conductivity, temperature, flow rate) and chemical (pH, total chlorine, hardness, and nitrate) parameters were reported. One of the achievements done during PROTEUS was the co-integration of physical and chemical sensors on the same chip to yield a multi-parameter sensor (multiplexing). The objective was to improve the readiness level of the sensor during the Fiware4Water project.

#### ii. Working principle of the chemical sensors

CNRS is the only organization developing this chemical sensor. They are elaborated by depositing the sensing material (also called the "active material") between two metallic electrodes. The resistance of the active material is expected to be modified when interacting with chemicals, and the variation of the resistance is supposed to be related to the concentration of the chemicals.

The working principle of the chemical sensors that CNRS is developing is based on a synergetic effect occurring between carbon nanotubes (CNTs) and organic polymers. CNTs were chosen for their interesting electrical properties of conduction which appeared of interest for designing resistive sensors, while conjugated organic polymers were used to both electronically interact with carbon nanotubes and with some specific chemicals thanks to a proper chemical functionalization. The expected working principle of such systems is shown in Figure 1 and is the following one:

1) The chemical groups (binding sites) grafted onto the polymers can recognize some chemicals (called the analytes), giving rise to *specific recognition* of the targeted analytes by the probes, and thus possibly yielding *selective sensors*;

2) Thanks to their conjugated backbones, the polymers can interact via  $\pi$ - $\pi$  interactions with the external walls of the CNTs, thus acting as a relay between the recognition sites and the CNTs, and ensuring *electronic communication* between the binding sites and CNTs and *transferring the recognition event to the CNTs*;

3) Efficient transduction of the signal by CNT whose conductivity should be modified when electronically interacting with the polymers.





- Specific recognition of the targeted analytes by the probes 
 - Electronic communication between binding sites and CNT
 - Efficient transduction of the signal by CNT (conduction properties)

Figure 1 Working principle of CNTs/conjugated polymers as active materials in sensors.

At the end of the PROEUS project, it was concluded that the chemical sensors could effectively be sensitive to several chemicals depending on the organic polymer used in the CNT/polymer system: chlorine, chloride, nitrates, pH and hardness.

Based on these outcomes, it was proposed to further develop these sensors to reach a high TRL value at the end of Fiware4Water. We initially chose to focus on the development of the integration of two chemical sensors to the chip to measure pH and chlorine, in addition to conductivity and temperature sensors which technology was developed within the framework of the Proteus project and which are bought with the chips at ESIEE Paris. In parallel to this, it was also anticipated to start to develop the detection of further analytes.

#### iii. Fabrication of the chemical sensors

Electronic chips with conductivity and temperature sensors are bought at ESIEE Paris. They also contain 20 pairs of interdigitated metallic electrodes for elaborating chemical sensors. An electrical contact is created between two metallic electrodes by depositing suspensions of CNTs in a solvent, 1,2-dichlorobenzene, in between. For fabricating CNT/FFUR-14 sensors, a solution of the polymer dissolved in 1,2-dichlorobenzene is added to the pristine CNT suspension prior to deposition between the electrodes. Deposition of the suspensions is effectuated with the help of an ink-jet printer.

#### I.2. Development

#### i. Presentation of the Nanosensor

The project started with a newly designed sensor. The sensing chip comprised 20 chemical sensors, 2 temperature sensors, and 3 conductivity sensors. Each chemical sensor was defined as a pair of interdigitated electrodes. This geometry was chosen to improve the sensitivity of the sensors. Also, the sensor chip was positioned in such a way that it will be perpendicularly positioned to the flow thanks to the bevelled shape. This was expected to determine (if any) the influence of sensor positioning on measurement quality. Three positions of the sensor could be envisaged: direct inflow, parallel to the flow, and opposite to the flow.

The general physical aspect of the sensor is a 19 cm-long PVC tube with a 3.5 cm diameter which can be fitted into a drinking water loop. It comprises two main parts: the sensor head and the sensor body (see Figure 2). The head is the sensing part of this multi-parameter Nanosensor. It holds a PCB (Printed Circuit Board) with an electronic chip on which are deposited the chemical and physical sensors. The head housing is designed with a bevelled shape to accommodate the chip on its PCB. It can be oriented in different positions concerning the water flow for potentially optimized sensitivity and resilience.

The sensor body comprises another PCB that is connected to the head *via* a flat cable and to a computer via USB. It is called the AFE (Analog Front End) as it carries out all low-level signal processing required to read data from the sensors. The AFE core components are a PSOC (**P**rogrammable **S**ystem



**o**n **C**hip) component coupled with several multiplexers to manage the large numbers of sensors in the chip.

Fiware4Water prototypes are to be operated through a Python-based acquisition and data processing code that interrogates the AFE through C-based libraries. Data can be stored in both local and cloud-based MongoDB databases. Data can also be collected through USB or UART to a dedicated connection box managing wireless communication, energy supply and data formatting into a Fiware compatible format.

The development of such devices involves a wide variety of fields, including chemistry, physics, electronics, computer sciences... The different actions taken within the framework of Fiware4water are from now on described in chronological order.



Figure 2 Detailed design of the Nanosensor studied in Fiware4Water.

#### ii. Improvement of the lifetime of the chemical sensors

One of the first actions undertaken was to investigate the possible ways to improve the stability of the chemical sensors. When immersed into water and activated, the sensors were dying within (at best) a few days (Figure 3). Work on the improvement of the lifetime of the sensor was thus firstly conducted.





Figure 3 Increase in the resistance value of a chemical sensor immersed in water with time.

Analysis of the active material by microscopy revealed that a part of the sensing material was lost (and so released into water, Figure 4, top). This was confirmed by a second analytical technique. A chip was studied by Raman spectroscopy. After 5 days of immersion in water, the signals due to the CNTs could not be found at certain places between the fingers of the electrodes, showing that there were no more CNTs on the chip at that place (Figure 4, middle).

We thus developed a process that was intended to decrease the loss of the active material by protecting it with a polymeric membrane. This membrane should allow the active material to keep being in contact with water. We went for the deposition of a commercial organic polymer by the so-called Non-solvent Induced Phase Separation (NIPS) process. This process consists in creating pores into a non-dried layer containing an organic solvent by exposing it to water.

Another cause of the fast ageing was identified as the nature of the resist (gloptop) used to protect the metallic contacts. It was found at the end of 2020 that the material that had been used since the beginning of the project was not waterproof. It was degrading in water, allowing water to come in contact with the metallic parts of the sensors, killing them (Figure 4, bottom). Also, some of the gloptop was covering some parts of the sensing material, thus avoiding any contact between the active material and water.

Finally, a combination of the deposition of the polymeric membrane with the use of a waterproof gloptop allowed to obtain chemical sensors showing an almost stable resistance when activated in water for a period up to >2 months. Note that these results were obtained on chemical sensors immersed in water and continuously activated for the whole period.





Chip wirebonded to PCB

Figure 4 Visible degradation of the sensing parts: top: loss of the active material (in green); bottom: degradation of the gloptop.

#### iii. Characterization

#### • Response to a sodium hypochlorite solution

Following the results obtained within the framework of the former PROTEUS project, we have first focused on the detection of "chlorine". The response of a representative CNTs sensor upon increasing amounts of NaOCl is shown in Figure 5. It shows that the sensor was responding in a concentration range [0.05, 3.75] mg/L, which comprises that advised by World Health Organization ([0.2, 0.5] mg/L).



Figure 5 Response with time of a chlorine sensor upon addition of various amounts of NaOCI.



Ageing studies and responses to chlorine over a period of 5 weeks were performed on the 20 sensors of the same chip that were protected with the porous membrane. Results reported in Figure 6. show that *i*) sensors are responding after each addition of NaOCl, and *ii*) a drift of *ca.* 30% was observed. However, it was believed that this drift could easily be managed through software means afterwards.



Figure 6 Response to additions of NaOCI (5 mg/mL) of sensors on a same chip over a period of 5 weeks.

The above-reported experiments show that single sensors fabricated with the same material (pristine CNTs which are CNTs without any polymer) deposited on a chip are responding similarly to the addition of chlorine.

In February-March 2021, to evaluate if any difference was obtained when combining the FF-UR14 polymer that was described as sensitive to chlorine during the Proteus project with CNTs, chips were fabricated with 10 (pristine CNTs) sensors and 10 (CNT/FF-UR14) sensors. Figure 7 shows the response of two single sensors of each type deposited on two chips to the addition of a solution of NaOCI as representative examples. These tests were also performed in the lab. It can be observed that both pristine CNTs and CNT/FF-UR14 sensors are responding in a very similar way to the addition of chlorine.





Figure 7 Response of pristine CNTs (green) and CNTs/FF-UR14 (yellow) sensors of two chips to the addition of a chlorine solution (red arrows). The 2 pictures are taken from two separated experiments.

These tests, unfortunately, demonstrated that the response of sensors fabricated with different active materials was not selective to chlorine.

#### • Measurement of pH

The response to a pH change was monitored both in the presence and absence of chlorine.

In presence of chlorine, pristine CNTs and CNTs/FF-UR14 sensors were sometimes found to respond quite similarly (Figure 8, top and middle), sometimes not (Figure 8, bottom). The concentration of total chlorine and pH were determined with external sensors.







Then, the response to pH of both types of chemical sensors was probed in the absence of chlorine. Figure 9 shows two separated experiments on both types of sensors. The experiment on top shows that both sensors from a same chip respond in a very similar way, while the other experiment (middle and bottom curves) show that, sometime, the response of the sensors is different.





Figure 9 Top: response to pH changes of pristine CNTs and CNT/FF-UR-14 sensors from the same chip; middle: response of a pristine CNTs sensor to pH changes; bottom: response of a CNT/FF-UR-14 sensor from the same chip than the middle one to pH changes.

Characterization of the sensors reported above shows that:

• pristine CNTs and CNT/FF-UR14 sensors respond similarly and in a reproducible manner to the addition of a solution of sodium hypochlorite in the range [0, 1] mg/L;



• the response of sensors to pH changes in the presence or absence of "chlorine" looks quite random.

#### iv. Improvement on the software side

In parallel to lab testing, developments on the software side have been started. In fact, once the sensors met the conditions to be inserted into a water loop, they were expected to be sent to TZW for being tested in their water loop in the so-called "realistic conditions". A necessary condition to provide partners a convenient device was to provide it with a friendly user interface. The description of the software part about the Nanosensor done in the Introduction part is schematized on Figure 10.



Figure 10 Simplified representation of the software chain for the Nanosensor.

#### • Improvement of the quality of the raw signal

The signal of a single sensor used to appear as « dissociated signals » (see Figure 11). It came out that the frequency used by the PSOC (AFE) was not adapted resulting in a problem with communication between the PSOC and the PAC codes. In fact, the number of data sent by PSOC was different from the number of data acceptable by PAC. This resulted in the presence of outliers (which were data from the previous sensor included in data from the analyzed sensors).



Figure 11 Representation of a "dissociated signal".

Once this first issue was solved, the signal obtained was relatively "noisy", as can be seen in Figure 12. Using a current of 5  $\mu$ A instead of 1  $\mu$ A to activate the single sensors improved the signal/noise ratio and led to an acceptable signal with a relatively low noise level.





Figure 12 Signal obtained with a current of 1 🛛 A (blue trace), and signal obtained with a 5 🖾 A current (red trace).

#### v. New molecules for multi-parameter sensing

This work was started in parallel to the development of the sensors initially chosen in order to be ready to add the possibility to detect other parameters once the issues of ageing were solved.

#### • Design of the molecules

While we were tackling some issues concerning the ageing of the sensors and the treatment of data described above, and for the sake of rapid development of the Nanosensor, we anticipated the detection of other species and the measurement of other parameters than pH and chlorine. Within these lines, new molecules were synthesized to get selectivity to chemicals of interest. The general design of these compounds is as follows. They contain aromatic systems that can potentially interact with the walls of CNTs by p- p stacking and there are further possibilities to functionalize them with chemical groups that can make them interact specifically with some chemicals. Their molecular structures contain electron-rich parts (for instance N and O atoms) that can interact with positively charged species, especially metal ions, or electron-deficient compounds. In addition to that, their structure defines a pre-formed cavity that can accommodate ions depending on their size. This is of great interest given the selective recognition of species. Also, the presence of protons than can form hydrogen bonds is well-adapted for interactions with anionic species.

#### Preliminary sensing tests by emission spectroscopy

A fast way to test the ability of the newly synthesized molecules to interact with chemicals and validate their further use in the design of sensors is to record their emission spectrum in presence of these species. Any change in the spectrum will be indicative of an interaction between the molecule and the targeted species. Thus, emission spectra of the four molecules designed previously were recorded in presence of various analytes dissolved in water. It was found that the emission of **A** was sensitive to the presence of fluoride, that of **B** was sensitive to aluminum, that of **C** was sensitive to a widely used herbicide in Europe, glyphosate, and its main metabolite, aminomethylphosphonic acid (AMPA), while the emission of **D** was found to be impacted by the presence of zinc and aluminum. The emission spectra of the four molecules in presence of these species are reported on Figure 13. As can be observed, we can clearly see either an increase or a change in emission wavelength upon addition of the species to a solution of the molecules. The chemical structure of **D** is also shown as a representative one.





Figure 13. Top, left: emission spectra of **A** and **A** + fluoride; top, right: emission spectra of **B**, and **B** + aluminum; bottom, left: emission spectra of **C** and **C** + glyphosate, and **C** + AMPA; bottom, right: emission spectra of **D**, **D** +  $AI^{3+}$ , and **D** +  $Zn^{2+}$ .

These results are encouraging given further use of these molecules to fabricate selective sensors.

#### • New molecule for pH measurement

As described earlier in this document, no clear response of the sensors to pH could be obtained. A possible solution to improve the response to pH was to design a molecule that is pH-sensitive to use with CNTs to further design a new electrical sensor. A molecule, labelled **E**, was synthesized. Preliminary investigations on the sensitivity of **E** to acids were performed by adding various amounts of a 0.1M solution of HCl to a solution of **E** (Figure 14). As can be observed in Figure 14, the emission spectrum of **E** is impacted by the addition of the acidic solution. Note that methanol was used as a solvent as its chemical structure is close to that of water, and **E** is not soluble in water.





Figure 14. Emission spectrum of a solution of **E** in MeOH upon addition of increasing amounts of a 0.1 M HCl solution.

#### I.3. Nanosensor integration in a FIWARE environment

EGM made use of its EdgeSpot hardware<sup>1</sup> to integrate the Nanosensor with a software environment. The EdgeSpot is a derivative work exploiting the results of the H2020 LOTUS project. It has been designed to allow the connection of any sensors and actuators through all types of telecommunication networks for a wide variety of use cases. Its capabilities allow edge processing and control algorithms to be run on the field while maintaining a low energy footprint. It can be powered by a battery, solar energy, or an electrical network to adapt to a variety of situations encountered in the field. The architecture of the Software Development Kit (SDK) developed to ease the programming of the EdgeSpot is largely inspired by the other SDKs available on the market for other platforms. However, it had to be made different due to the number of specific hardware components used in the board and the need for flexibility we need to have.

The connection between that board and the Nanosensor is described as follows: The testing of AFE connectivity to the EdgeSpot uses a 5V UART interface. A programming interface based on AT commands is supplied with the AFE of the Nanosensor. To test the EdgeSpot with the AFE, the test procedure was:

- Connect the AFE (power and serial bus) to the EdgeSpot.
- Power on the EdgeSpot.
- Connect an FTDI (USB to UART converter) cable between the laptop and the EdgeSpot.
- Run a python script that allows you to read the data from the EdgeSpot RS232 monitor port and store it in a .csv file. This code also displays the curves of these measurements.
- Collect results as a .csv file containing the data of all the sensors.

The acquisition process from the AFE is as follows Figure 15: a read command is sent with the duration N of the reading window as an input parameter. During that time, measurement points are pushed over the UART interface. The AFE currently limit the reading window N to about 1s. The number of measurement samples sent during that period depends on the queried sensor: the temperature sensor would send 112 samples whereas the conductivity one would send 13 samples.

<sup>&</sup>lt;sup>1</sup> https://www.egm.io/wp-content/uploads/2021/08/fiche-EGM-EdgeSpot-2-EN-3.pdf





Figure 15 : acquiring data from nanosensor through the EdgeSpot showing (a) the stabilisation period (b) and possibility to repeat measurements through a periodic activation of the AFE (ON/OFF) showing reproducible signals.(from LOTUS project)

From this work, we evolved the EdgeSpot embedded software to make it compliant with a FIWARE environment. Using previous results, sensors are read sequentially. To improve the stability of the measurements, the first 30 data points from the AFE were collected and the first 25 ones were ignored; then a mean is performed with the remaining data points to provide a single value measurement.

Once all the data points are acquired, they are sent by the EdgeSpot to the MQTT broker using a senML<sup>2</sup> format like the following one:

It is a Json formatted string that contains a list of 2 items. The first item provides the identification of the sensor ("bn" field) and the timestamp in the Unix epoch ("bt" field). The latter is computed using the RTC module included in the SensorBox. The second item is a reading of the value of a sensor in which the following information is given: name, units and value (respectively "n", "u" and "v" field).

Figure 16 shows some messages received from this setup using an MQTT client subscribed to the LOTUS topic.

<sup>&</sup>lt;sup>2</sup> IETF RFC8428, https://datatracker.ietf.org/doc/html/rfc8428





Figure 16 : MQTT messages encoded as senML as collect by a MQTT client

On the NGSI-LD context broker side (Stellio was used), a specialized MQTT bridge has been developed to be able to collect senML encoded data over an MQTT connection and map it to an NGSI-LD context. Thus, to ensure the interoperability and genericity of the bridge, it expects data from devices in senML format. SenML is a standardized format for representing simple sensor measurements and device parameters in Sensor Measurement Lists. The bridge disposes also of its mechanism to map and find correspondent CEFACT units (the accepted unit format in NGSI-LD) from senML messages. Examples of senML/CEFACT unit mapping are available in the foot link <sup>3</sup>.

One of the main issues of the received IoT data is the ownership of these data. Data comes with provider ids (device ids, for example), and following the entity model of NGSI-LD, data issued from a device may be stored in the other entity (called context entity).

For these purposes, the process of device provisioning (device registration, device properties definition and defining the correspondent NGSI-LD entity that this device will update) in the MQTT bridge is designed to be an automatic process. The MQTT bridge disposes of its database in which the bridge will try to find the correspondent entity and property that needs to be updated. The Figure 17 details the main components and possible interactions of the MQTT bridge.

<sup>&</sup>lt;sup>3</sup> https://github.com/easy-global-market/ngsild-api-data-models/blob/master/UnitCodes.md





Figure 17 : MQTT bridge architecture

In this case, since we are still in a hardware integration phase, so we are not yet interested to map a complex data model, we kept a very simple one partially shown here:

Use-case example: Let us assume the example of a sensor attached to a Tank. This device will generate values of the Water parameter, such as level, in the Tank.

The NGSI-LD model of this use-case consists of 2 entities Tank and Device where the Entity Tank have a property waterLevel, observedBy (as a Relationship) by the Device. The graphical presentation of this model is depicted in the Figure 18:



Figure 18 : Mapping sensor data to monitored asset

The NGSI-LD correspondent Tank entity stored in the context broker is depicted in Figure 19.

{		
	"id": "urn:ngsi-ld:Tank:01",	
	"type": "serviceRoint",	
	"waterLevel": {	
	"type": "Property",	
	"value": 5.	
	"unitCode": "observedAt": "2021-03-18T09:24:00.00Z" ,	MTR.
	"observedBx": {	

Figure 19 : NGSI-LD representation of water level information

Let us suppose that the device is publishing data over an MQTT broker with the format in Figure 20:





Figure 20 : Example of senML encoding

The main role of the MQTT bridge is to (i) subscribe to these senML data, (ii) check if the correspondent senML device (field bn) is provisioned in a local database and then (iii) Generate updates on the correspondent Tank and its waterLevel property entity with mapping the senML unit (field u) "m" to "MTR" (field unitCode in NGSI-LD) and the timestamp (field bt) to the ISO 8601 format (field observedAt), if the mapping exists in the database.

This MQTT bridge was then used to collect the data from the Nanosensor and feed the Stellio context broker. From that point, it was easy to present the information in a visualisation component such as the Grafana FIWARE enabler shown in Figure 21, thus demonstrating the FIWARE integration of the Nanosensor.





Figure 21 : Nanosensor data collected and presented in a FIWARE dashboard.

### I.4. Preliminary tests at TZW facility

#### i. Timeschedule

For Fiware4Water it was planned that the CNRS Nanosensor should first be tested in the TZW model network for 12 months to evaluate the Nanosensor performance in network conditions. Afterwards an integration of the Nanosensors in the Cannes drinking water network for 12 months was planned to test it under real condition and to collect data for task 3.2 and 4.2.

For the test of the Nanosensor on TZW premises, different preliminary works had to be done. This mainly included the adaptation of the TZW model network to insert the Nanosensor and the installation of various sensors fitted as reference sensors. Furthermore, TZW had to establish an internet connection to the basement the network model is located in. This was not planned originally since the sensor was supposed to function offline, but at the state, TZW was testing the Nanosensor an internet connection was mandatory. Since TZW only rents the basement, this involved considerable technical and organisational effort with the landlord.

The work on the experimental plans started in the summer 2020 together with CNRS and 3S. The delivery of the sensor to TZW was at that state planned for autumn 2020.



During the project, several delays regarding the testing of the Nanosensor occurred. Some of them were correlated with Covid19, and others caused by technical difficulties. Finally, two Nanosensors were delivered to TZW in April 2021. The instruction about the sensor handling had to be done remotely since travelling from France to Germany was not possible due to the Covid19 situation.

Sensor test and data evaluation and assessment were in the spring and summer of 2021 till it was decided to stop experiments cause of fundamental problems with the sensor functioning.

### ii. Laboratory Experiments

To begin with, only the electrical conductivity and the free chlorine were calibrated in the laboratory. The pH value was not to be tested initially because, according to CNRS, there were still problems with the specificity of the sensors.

For chlorine experiments, a model water was prepared that has a characteristic hardness and pH value typical of drinking water (Table 1).

Parameter	Value
Hardness	5 °dH
Chloride	20 mg/L
Bromide	0.1 mg/L
Nitrate	10 mg/L
Sulphate	60 mg/L
тос	1.5 mg/L
рН	8.3

Table 1: Composition	of soft	model	water
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Following the instructions of CNRS bevor starting the experiments, the Nanosensors weere run in a beaker under constant conditions for over 48 h to achieve a stable baseline. Therefore, the 2 sensors were emerged in a beaker with soft model water.

The variation of the conductivity was done by using a concentrated sodium chloride solution (1 g NaCl per litre of deionised water). For the calibration, 10 concentration levels were prepared in the range from 200  $\mu$ S/cm to 2000  $\mu$ S/cm. For each measurement with the Nanosensor, the conductivity was determined in parallel with a conductivity device from the laboratory (WTW inoLab Cond Level 2).

The calibration of the free chlorine was done with a concentrated hypochlorite stock solution (300 mg free chlorine per litre deionised water) diluted in soft model water. For this purpose, 10 different concentration levels in the range of 0.1 to 1 mg/L free chlorine were prepared. For each measurement with the Nanosensor, the concentration of free chlorine was determined in parallel using the DPD method (PERKIN ELMER UV/VIS Spectrometer Lambda20). Since concentration of free chlorine is decreasing over time the reference measurements of the free chlorine concentration were done once at the start of each concentration and once before changing to the next concentration.

The sensors were tested in a large common beaker into which the respective measuring solution was filled. Initially, the measurements were carried out without, later (second free chlorine experiment) with the use of a magnetic stirrer.



#### iii. Results

As sensors could be stabilized when activated in water for at least 2 months and that variation of their resistance was observed upon addition of a solution of NaOCl, two sensors were sent to TZW in April 2021. They comprised 10 pristine CNTs sensors and 10 CNTs/FF-UR14 sensors, 2 temperature sensors and 3 conductivity sensors.

The sensors operated exclusively in an "online" mode. It was therefore not possible to define a specific measurement or "calibration measurement". Instead, measurements of resistance were taken continuously at an interval of approximately 40 seconds. The result of a conductivity calibration is shown in Figure 22.



*Figure 22 : Raw data of the Nanosensor from the electrical conductivity calibration experiment. Blue: CNT sensors, black: conductivity sensors, red: temperature sensors. All units on the y-axis are in arbitrary units (a.u.).* 

Figure 22 first shows the raw data of all individual sensors of the chip (blue = CNT, black = conductivity, red = temperature). The experiment was carried out on 22.04. and lasted from approx. 08:30 to 14:30. During this time, the conductivity was calibrated in descending order (starting with the highest concentration, ending with the lowest concentration).

The following observations can be made:

• A reaction to the NaCl occurred not only on the conductivity sensors (C1 to C3), but also on the CNT sensors (both functionalised and non-functionalised). Meaning the CNT sensors reacted non-specifically.



- Especially the CNT sensors showed a clear increase in noise in the course of the experiment/day. If the signals are still quite stable at the beginning, they suddenly show a strong noise in the course of the later morning (with the exception of sensors 1.E and 2.E).
- The signal-to-noise ratio of the three conductivity sensors seems to remain roughly constant over the entire course of the experiment. A response to the sodium chloride is visible, but could be somewhat more pronounced given the large differences between 250  $\mu$ S/cm and 2000  $\mu$ S/cm.

Each calibration solution was measured with the sensors over a period of at least 20 minutes. As part of the data evaluation, the measured values were averaged over this period and compared with the true conductivity. The result is shown in Figure 23. Except for the temperature, the measured values of all sensors show a more or less strong linear correlation with the electrical conductivity. Each measuring point shown represents the mean value from 20 min of measurement. In addition to the mean value, the standard deviation was also calculated and is shown together with the mean values in Figure 24. It becomes clear that measurement uncertainty is many times higher than the actual measured value and strictly speaking it is difficult to distinguish between different concentrations. This is especially true for the low conductivity recorded in the second experimental section, as the noise is particularly high here.





Figure 23: Relationship between the averaged measurement signals (y-axis) of the Nanosensor and the electrical conductivity. All units on the y-axis are in arbitrary units (a.u.).





Figure 24 : Relationship between the averaged measurement signals of the Nanosensor and the standard deviation with the electrical conductivity. All units on the y-axis are in arbitrary units (a.u.).

The noise of the sensors is examined in more detail using the CNT sensor 1.A and the conductivity sensor C1 with the expected course (true concentration of the calibration standards) in Figure 25. Theoretically, a staircase-shaped curve should be observed in the conductivity sensor C1 during calibration. However, the difference in the type of noise between sensors C1 and 1.A is clearly visible. While C1 shows a normal distributed noise, sensor 1.A basically shows a binary noise around a stable


baseline. There are positive and negative deflections, but they always have the same value. This is an indication of a possible signal processing error.



Figure 25: Detailed view of the Nanosensor sensors 1.A (CNT, top) and C1 (electrical conductivity, middle) with the real course of the electrical conductivity (calibration standards, bottom).

During the free chlorine experiments all CNTs (functionalised and non-functionalised) reacted, but the electrical conductivity did not. The raw data and the correlation between the averaged measurement signals and the true chlorine concentrations are shown in Figure 26 and Figure 27.



Figure 26: Raw data from chlorine calibration (without using magnetic stirrer). All units on the y-axis are in arbitrary units (a.u.).





Figure 27: Correlation between averaged signals and true chlorine concentrations. All units on the y-axis are in arbitrary units (a.u.).

Again, a strong noise was observed in all CNT sensors from the beginning, but as with the electrical conductivity, this was of a binary character.

In preparation for the installation of the sensors in the model network, the chlorine calibration was repeated using a magnetic stirrer in a beaker (to simulate a flow). The relationship between the averaged measurement signals and the concentration of free chlorine looks significantly worse. Only the CNT sensors 2.1 and 2.J show a good correlation, Figure 28.





*Figure 28: Correlation between averaged signals and free chlorine concentration (with magnetic stirrer). All units on the y-axis are in arbitrary units (a.u.).* 

After testing in lab conditions, sensors were placed into a water loop with a flow rate of 0.1 m/s. Chemical sensors were activated and increasing amounts of NaOCI were added in a similar way than described above in lab conditions. Results are shown on Figure 29, top. Chemical sensors appeared highly noisy, to such an extent that it looked very difficult to see any response. Temperature and conductivity sensors were also activated. As can be seen on Figure 29, bottom left, the signal corresponding to temperature sensors was also found to be very noisy.





Figure 29 Characterization of chemical sensors (top) and temperature and conductivity sensors (bottom) in circulating water (0.1 m/s).

# iv. The model network (Loop)

To simulate the conditions of a real drinking water network experiments on a model network scale in  $a \approx 30$  m water loop with DN 50 diameter PVC pipes were followed after lab experiments (Figure 30). In addition to the 2 Nanosensors (Figure 31) the following sensors/measurements were integrated into the model network:

- Pressure sensor (KELLER)
- Flow meter (DIEHL METERING Hydrus)
- Free chlorine sensor (DULCOTEST ProMinent)
- Spectrolyser (S:can)
- Temperature (S:can)
- Conductivity (Endress+Hauser messpanel)
- SAK (Endress+Hauser messpanel)
- Redox potential
   (Endress+Hauser messpanel)
- pH (Endress+Hauser messpanel)
- turbidity (Endress+Hauser messpanel)





Figure 30 : TZWs model network

The 200L reservoir tank of the network was filled with drinking water from the local waterworks and pumped into the circuit with a velocity of approximately 0.1 m/s. Additionally, the possibility to use the network completely in discharge mode (no loop) or to make a partial discharge and constantly fill up the system with fresh water is given. The latter was done when a fast decrease of free chlorine in the network was to be simulated.

Free chlorine was increased by dosing HClO with a dosing pump shortly after the tank. Complete mixing of the water was ensured by a static mixer behind the dosing pump.



Figure 31 : mounting for Nanosensor



The model network experiments were focused on the evaluation of the free chlorine measurement of the Nanosensor. In addition to the permanent data recording by the reference sensors, reference measurements were carried out in the laboratory using the DPD method (PERKIN ELMER UV/VIS Spectrometer Lambda20) to determine the free chlorine concentration.

The experiments were mostly following the same scheme. Hydraulic conditions were kept constant and no chemicals other than HClO were added. The concentration of free chlorine was increased by the dosage of HClO. After determination of the dosing, the free chlorine concentration decreased over time due to the natural reaction and/or the inflow of freshwater. With these experiments, conclusions should be drawn about the value range, the reaction time and the accuracy of the Nanosensor towards free chlorine.



In Figure 32 an overview of some reference data from the model network is shown.

*Figure 32 : reference measurements from the model network* 

The Redox value visualizes all chlorine dosage events. In Figure 12 the chlorine concentration within one experiment is shown exemplified. In most experiments, the chlorine concentration was in a range between 0 and 3 mg/L. After the start of the experiment (dosing chlorine), the concentration dropped to 0 mg/L within approx. 5 hours, caused by the continuous exchange with fresh water.



Figure 33: Chlorine concentration over time within one experiment (10.05.2021).

Due to software errors on the control computer of the Nanosensor, it was not possible for the TZW to export the raw data or measurement data from the experiments in the model network and to statistically evaluate and visualise them at this point. Unfortunately, CNRS was not able to offer



support. Therefore, only a subjective assessment based on the (functioning) display of the measurement data in the software dashboard can be made at this point.

As soon as the sensors were used in inflow conditions, a strong noise was observed. This noise was particularly severe with carbon nanotubes and functionalised carbon nanotubes. During the experiments, it was difficult to identify a trend. Furthermore, it was noticed that the reactions of one type of sensor differed more than they did in lab experiments. In extreme cases, sensors of the same type showed opposite reactions to the same change in water quality.

### v. Conclusions

Based on the available data TZW concluded:

- In conductivity experiments under lab conditions, the conductivity sensor showed a reaction to conductivity changes induced with NaCl dosage. After averaging the conductivity over one conductivity step and comparison to the standard deviation, it was seen that the range of the noise during experiments was higher than the change in resistance which could led back to the changes in conductivity.
- In conductivity experiments under lab conditions the carbon nanotubes (CNT) and functionalised carbon nanotubes, intended to measure free chlorine, react to a change in conductivity induced with NaCl.
- In lab experiments with free chlorine, no reaction of the conductivity sensors was observed.
- In lab experiments with free chlorine, a reaction of all CNTs was observed. The standard deviation overlays the range the sensor was reacting to changes in concentration of free chlorine.
- When a magnetic stirrer was used, the noise of all CNTs became stronger. This might be to the influence of the induced flow or an interaction between the sensors and the magnetic device.
- A final evaluation of the loop experiments couldn't be given at this point since the evaluation
  was based on graphical output and not on analysis of raw data. It seemed that the Nanosensors
  were currently not fit for use in inflow conditions. The scope of the noise overlayed the actual
  reaction to changes in free chlorine concentration, and the reactions between sensors within
  the same type sometimes differ.
- A change of the active material used to measure free chlorine was necessary since it was not just selective to free chlorine.
- By adapting and further developing the algorithm that calculates final values from the resistance raw data, an improvement in accuracy might be possible (especially for CNT sensors).

Therefore, the Nanosensor at that stage was neither suited for the use in a beaker nor in a flow system to determine the concentration of free chlorine or the conductivity.

# I.5. CNRS testing

As of February 2021, based on the results reported above with the addition to CNRS testing, the team figured out that the performance of the sensors in terms of reliability and selectivity to the targeted analytes was not accurate. Several issues have merged:

 it was not possible to define a calibration model that was reproducible and valid from one chemical sensor to another one, making it impossible to define a "universal" model for chlorine detection;



- no clear response to pH was obtained;
- chemical and temperature sensors were found to be highly noisy in circulating water, even at a low flow rate of 0.1 m/s, avoiding any detection in these conditions.

Also, several other issues were raised in April 2021:

- weakness of the sensors was discovered: accelerated ageing (*ie* fast increase of the resistance) occurred when the sensors were left inactivated in water and when they were removed from water and re-immersed after some time;
- an identical response of blocks of sensors regardless of the ink used to fabricate the sensors was discovered as described hereafter:

The two kinds of chemical sensors were always printed the same way on the chips: 10 pristine CNTs sensors and 10 CNTs/FF-UR14 sensors were fabricated on the left and right side of the chips, respectively. However, in April 2021, a third material comprising CNTs and another molecule (named CF-OX14) was deposited on the same chip with pristine CNTS and CNTs/FF-UR14. The response of sensors of this chip was probed towards a widely used herbicide in Europe, glyphosate. It came out that the response of the chemical sensors mostly depended on their position on the chip. This is shown on Figure 34. The 10 sensors on the left side of the chip (5 pristine CNTs and 5 CNTs/CF-OX14) were responding identically, while all 10 sensors on the right side of the chip (5 CNTs/FF-UR14 and 5 CNTs/CF-OX14 sensors) also showed a very similar response together. Also, and very surprisingly, comparison of the response of the 5 CNTs/CF-OX14 sensors positioned on the left side was found different than that of the CNTs/CF-OX14 sensors at the right side while it should be the same.



Figure 34. Top, left: chip with chemical sensors fabricated with 3 active materials and their respective position; bottom left: response to the addition of glyphosate of a pristine CNTs sensor positioned on the left side of the chip; top right: response to the addition of glyphosate of two CNTs/FF-UR14 and CNTs/CF-OX14 sensors positioned on the right side of the chip; bottom right: response to the addition of glyphosate of a CNTs/CF-OX14 sensor positioned on the left side.

This response that appeared to be the same by blocks of 10 sensors was further confirmed with another chip, as shown on Figure 35. A chip comprising 20 single sensors fabricated with the same active material was immersed into a beaker of pure water and left activated. The resistance of each sensor was measured over time. It is clear from Figure 35 that sensors are responding by blocks of 10.



Also, this experiment raised another issue: as no chemical was added and no temperature change occurred during this experiment, it is surprising that variations of resistance were observed. This last observation was tentatively attributed to electronics at first glance.



Figure 35 Measurement of the resistance of 20 chemical sensors fabricated with the same active material on the same chip.

An additional experiment confirmed the uncertainty of the response of the chemical sensors. After immersing a chip in a beaker of pure water, the resistances of the single sensors were measured, then the chip was taken out of water, and re-immersed into the same beaker. A variation of 0.3% of the resistance was observed upon immersing the chip for the second time in the same beaker (**A** in Figure 36), then, it reached a value close to the initial one. Then the chip was immersed in a second beaker containing water of the same quality. A brutal decrease of 1 k $\Omega$ , corresponding to 2.8% of the initial resistance value, was observed (**B** in Figure 36) before the mean resistance reached a value approximately 0.1 k $\Omega$  lower than the initial one. The chip was finally immersed into a third beaker (**C** in Figure 36) also containing pure water. An immediate decrease of about 0.1 k $\Omega$  occurred, then an increase in resistance was observed, and the value of the measured resistance was about 0.1 k $\Omega$  higher than that measured in the previous beaker after stabilization.



Figure 36 Measurement of the resistance of a chemical sensor in pure water. In A, the sensor in taken out of water and reimmersed in beaker 1, in B, the sensor is immersed in a second beaker containing pure water; in C, the sensor is immersed in a third beaker containing pure water.

These experiments showed the uncertainty of the response of the chemical sensors and, more specifically, that the response appears not to depend on the composition of the matrix. They also question the interpretation of previous electrical characterizations of the sensors: were the changes in resistance obtained after each addition of NaOCI due to the added chemicals, or were they due to the "instability" of the sensors? The question is even more of importance as the variation of the resistance reported in Figure 35 while there is no addition of chemicals is in the same order of magnitude that that previously, which was interpreted as a response to "chlorine" for sensors of similar initial resistances.



It was then concluded that, at that point, the response of the single sensors was highly random and not representative to the presence of the species present in water.

Consequently, in May 2021, we stopped all investigations reported above as it did not make sense to keep on working with devices to which we were not sure what they were responded to. After presenting these data to the coordination of the project, we proposed to the FIWARE4WATER consortium a remediation plan to go back to more fundamental studies to try to get some understanding of the behaviour described above and to possibly elaborate a pH sensor. We also stopped using the chips for which the electronic issue was raised.

### I.6. The remediation plan

# i. Identification of the possible sources of misfunction

This plan stem from the different issues raised above and was elaborated in June 2021. As issues on both the hardware and software and electronics sides were raised, it was decided to mainly focus on the study of the formation and the characterization of the active material of the chemical sensors. This appeared as the top priority as the active material is the element that was supposed to make sensors selective. It would not have been wise to further investigate data analysis or electronics with devices for which a random response shown to be partially due to the active material was obtained (see results of Figure 36). In a second step, and in case the formation of the sensing material was shown to be controlled, further investigations on the use of the **E** molecule to possibly elaborate a pH sensor was proposed.

More precisely, and as shown above (Figure 8, Figure 9, Figure 22 - Figure 26), there were too many uncertainties in the response of the sensors (ie variation of resistance) to continue to confidently move forward to a multi-parameter sensor that could be inserted into networks. Was it due to the presence of chemicals or "electronics", or both, or even to another phenomenon? In particular, the response of pristine CNT and CNT/FFUR14 sensors to pH was not clear. The similar response observed for these two kinds of sensors reported on Figure 8 - Figure 9 could arise from an "electronic issue" described with the results obtained on Figure 34 - Figure 36, but it could also be due to other reasons, such as a bad/non-efficient functionalization of the CNTs by FFUR-14 or the absence of sensitivity of FFUR-14 to the targeted species. Also, the sensitivity to pH, if any, was not fully understood. Pristine multi-walled CNTs (MWCNTs) have been described to be sensitive to pH as they can give electrons to H<sup>+</sup> from their valence orbital. (Abdullah Abdulhameed 2021) Note that single-walled CNTs (SWCNTs) are also known to be sensitive to pH thanks to a change in their electronic structure due to a refill or a depletion of their valence band when interacting with  $OH^{-}$  or  $H^{+}$ . (Yang, et al. 2009) Further, MWCNTs are made of several CNTs of increasing diameters. In case that the conductive one is the most internal one (ie the tube with the smallest diameter), it appears difficult to have the information of the recognition event occurring at the outer tube properly transferred to the internal conductive nanotube, and, thus, to detect any change in the resistance of the sensor. This is schematized on Figure 37.





Figure 37. Schematic representation of the detection of a chemical species by a functionalized MWCNT whose conductive nanotube is the one with the smallest diameter.

Also, both sensors fabricated with pristine MWCNTs and MWCNTs/FFUR-14 show a variation of resistance when a solution of sodium hypochlorite is added. In case that the response of pristine CNT sensors to the addition of a solution of sodium hypochlorite was a chemical one, then pristine CNT sensors would respond to both pH and the sodium hypochlorite solution, without possible differentiation. Pristine CNTs look thus definitely not interesting to be used as sensing material for the design of selective sensors. It was primarily anticipated to decorrelate the response of pristine CNT sensors to other analytes and then extract the response to the targeted analyte. However, this process looked too uncertain and not reliable as it suggests that the precise composition of water is known which is exactly what must be determined. In other words, sensors should be tested against any chemical possibly found in water for calibration, which is difficult to imagine.

# ii. Response to pH and sodium hypochlorite

The FFUR-14 compound was thus tested against pH change. As shown on Figure 38, a similar experiment than that described on Figure 14 for **E**, revealed that, within experimental error, the emission spectrum of FFUR-14 is not significantly influenced by addition of an acidic HCl solution at a pH of 1. The acid/molecule ratio was even higher than one order of magnitude in the case of FFUR-14.





Similarly, the response of the FFUR-14 compound to a solution of sodium hypochlorite was probed by emission spectroscopy. Figure 39 shows that even in presence of a large excess (> 1000) of NaOCl, no noticeable change was observed. This is an indication that FFUR-14 does not significantly interact with any of the species present in solution.





Figure 39. Emission spectrum of FFUR-14 before (black) and after (red) addition of a large excess (> 1000) of NaOCI.

### iii. Understanding the response of the chemical sensors

As shown on Figure 8, a CNT/FFUR-14 sensor looks to respond to pH changes. At that point, two solutions could be considered: either this response is due to the electronics, and is not a chemical one, or it is due to CNTs that are not covered by the FFUR-14 molecules. In the latter case, the functionalization of the CNTs with the FFUR-14 compound would not be optimized and complete. We thus undertook the characterization of the functionalization of the CNTs. Figure 40 shows an image of a 300\*130 nm2 area of the CNTs/FFUR-14 material obtained by Tip-enhanced Raman spectroscopy (TERS). (Antonino Foti 2022) Basically, this technique combines the high specificity and sensitivity of plasmon-enhanced Raman spectroscopy with the high spatial resolution of scanning probe microscopy. The image shows two CNTs (identified by the dashed red profiles), labelled CNT-A and CNT-B, respectively. Some FFUR-14 compound can be found on top of the CNTs (zones 1, 4, 5, and 6), while some FFUR-14 is not in direct contact of the CNTs, and there are also some parts of the CNTs surface which are not covered (zones 2 and 3). This image cannot be taken as representative of the whole active material surface, but it shows that the functionalization is not complete, in terms of surface coverage, and could explain why CNT/FFUR-14 sensors are responding similarly than pristine CNT sensors. Some non-functionalized CNTs of the CNTs/FFUR-14 sensor can be in direct contact to the solution, as it is the case for pristine CNTs sensors, thus explaining the similar response observed for the two kinds of devices.



Figure 40. TERS Image of 2 CNTs (delimited by the dashed red lines) showing the partial coverage of the CNT surface by FFUR-14.

On the other hand, an aqueous sodium hypochlorite solution is usually a mixture of several chemicals, including sodium, hypochlorite, and chloride ions, and hypochlorous acid. Precise analysis of a "chlorine" solution thus looks quite complicated.



We thus finally probe the response of FFUR-14 to chloride. The result is reported on Figure 41 and, again, no change in the emission intensity was observed, which kind of confirmed the non-response of FFUR-14 to the solution of sodium hypochlorite reported above.



Figure 41. Emission spectrum of FFUR-14 before (black) and after (red) addition of a large excess (> 1000) of NaCl.

From what is presented above, we decided to focus on the process used to functionalize CNTs by the molecules in order to elaborate in the end a sensor with a sensitivity that would effectively be due to the functionalization of the CNTs by the molecule. Also, and based on the preliminary experiments reported on Figure 14, we chose to investigate the possibility to use molecule **E** for the design of a CNT/**E** sensor that could be sensitive to pH. These studies were expected to both determine a reliable process to functionalize CNTs and to prove the utility of the functionalization of the CNTs by **E** on the sensors' response. In other words, we aimed at determining how to optimize and characterize the functionalization of CNTs with **E** and to prove selectivity of the chemical sensors to pH thanks to this molecule (and not to pristine CNTs). Further, pristine CNTs are known to electronically undergo interactions with many species. This, again, shows that using pristine CNTs should be avoided in view of elaborating selective sensors. This also emphasizes the importance to functionalize CNTs with molecules in order to perform selective sensing.

# iv. Investigations on the formation and characterization of the active material of the sensors: in search of a new process to functionalize CNTs

Prior to develop selective sensors, an important part of this work is to understand and control the functionalization process of the CNTs by the molecule on one hand, and to characterize it, on another hand. As revealed by Figure 40, the process used to functionalize CNTs is far from optimal. It basically consists in preparing a dispersion of pristine CNTs in a solvent and add to it a solution of FFUR-14. The dispersion of pristine MWCNTs was primarily prepared in 1,2-dichlorobenzene as solvent by ultrasonication, then centrifugation was applied to eliminate non-dispersed MWCNTs. The supernatant was kept as ink to be printed for fabricating the pristine CNTs sensors. A solution of FFUR-14 in 1,2-dichlorobenzene was to be added to the suspension of pristine CNTs to obtain a CNTs/FFUR-14 ink. However, 1,2-dichlorobenzene is an aromatic solvent that can stack on the walls of CNTs, then avoiding the functionalization by the FFUR-14 (or any other) compound. Also, this solvent has been described to form sonopolymers when ultrasonicated. These polymers are byproducts that result from a sonochemical degradation of 1,2-dichlorobenzene which wrap around CNTs in an irreversible manner, then hindering the functionalization by other molecules. An internal experiment showed that pure 1,2-dichlorobenzene previously used was degrading under sonication. In fact, as shown on Figure



42, sonicating 1,2-dichlorobenzene for 30 min yielded a brown solution that testifies that degradation occurred.



Figure 42. Pictures of 1,2-dichlorobenzene (left beaker) and 1,2-dichlorobenzene after 30 min of sonication (right beaker).

At that point, it appeared as evidence that the process used until then to disperse CNTs was degrading the solvent in addition to affording a non-optimal functionalization of the CNTs. This called into question the design of selective sensors.

We thus switched to the use of another solvent. *N*-methyl-2-pyrrolidone (NMP) was chosen as it is known to easily disperse CNTs and form relatively stable suspensions. Also, in the conditions needed to prepare dispersion of CNTs, it did not show any observable degradation.

SWCNTs were then dispersed in NMP by the conventional sonication process. The Transmission Electronic Microscopy (TEM) image of the deposit obtained from this suspension is shown on Figure 43, left. It is clear that the external walls of CNTs are not contaminated by any amorphous matter that could come from solvent degradation. This image shows that clean CNTs can be deposited from a suspension.

This result is very encouraging for further functionalizing CNTs by organic molecules. CNTs were thus mixed with a solution of **E** in order to decorate them with the organic molecules. After solvent evaporation, the same area than the one shown on Figure 43, left, was probed by TEM analysis. It is shown on Figure 43, right. One can clearly see that some amorphous matter was deposited onto the walls of the CNTs. The blue arrows have been added to focus on a specific place. They point a single CNT that appears to have no any material around it on the left image, but is covered by some amorphous matter on the right image after contact with **E**.





Figure 43. Left: TEM image of CNTs deposited from NMP; right: TEM image of the same CNTs after being in contact with a solution of E. The blue arrows point the same place of the sample.

This result can be viewed as a snapshot of the coverage of the CNTs by the organic molecule, and analysis of the whole CNTs surface shows that it is well covered, revealing that efficient functionalization of CNTs by **E** seems to have successfully been performed.

### Design of resistive devices

As described in the first part of the project, electronic issues were raised with the chips previously used. We then designed simple single resistors in view of depositing the CNTs properly functionalized onto them. These devices were made of two metallic electrodes with pads (Figure 44). The active material is supposed to be deposited above and between the electrodes, while the pads will be used to create electrical contact with the measurement system and get access to the value of the resistance of the as-designed devices.



Figure 44. Design of a single resistor.

Unfortunately, because of lack of time, it was not possible to investigate the response of such a sensor.

### About the release of nanomaterials

Eurofins and Carso are the two French organisms that can make validation tests for legally allowing the insertion of sensors into networks. In view of the insertion of the Nanosensor into the network of the city of Cannes, and before the different issues on the sensor were raised, they had been contacted at the end of 2020. It was confirmed that both chemical sensors (and so nanomaterials) and electrodes were not to be considered for the tests (text law # 571 of 11/25/2002). Only the materials in contact with water that should be checked are the globtop, the PCB, the glue used to stick the PCB onto the PVC tubing, and the PVC itself.

As described at the beginning of the project, the polymer membrane is expected to protect the material from release into water. Stabilization of the resistance for a period of at least 2 months was obtained in lab conditions after deposition of this membrane, while the sensor used to die within (at best) a few days before. However, if aging due to release of the active material was to be observed in flowing water, the two solutions proposed above for lowering the noise of the response of the sensor could be used.

# I.7. Recommendations in the future development of sensors

As presented, the issues raised lead to the conclusion that the response of the sensors was relatively random and not understood. In fact, it appeared that the variation of the resistance obtained when adding a water solution could either be due to the chemicals dissolved into it or to another effect, which was not the consequence of a "chemical interaction" between the sensing material and the solution. The misfunction of the sensor was further amplified by the fact that the electronic chip also showed some irregular responses. At that point, we concluded that issues were both on the hardware and software and electronics sides.



In face of this heap of problems, it appeared a top priority to go back to the fundamentals of the sensors, that is the way the active material is working, and, even before that, to proceed to a real characterization of it. It was senseless to go further in the development and deployment of a device whose response was not reliable and understood.

Investigations that were carried out during the remediation plan brought some explanations for the misfunction of the sensor. It was shown that the sensitive material was not that expected and that the part of it that was supposed to interact with species in the solution was not.

Thus, to try to tackle these issues, organic molecules that are shown to be sensitive to the targeted species and different from the ones used before the remediation plan should be used.

Then, the formation of the active material (CNT+ organic molecule) should be controlled, and it should be fully characterized to have a chance to understand the way the sensor works. This is a mandatory step before further development.

The high noise observed in circulating water is not explained. One can propose to add to the sensor device a system to break the flow before the water is in contact with the sensing part. Another possibility would be to use a derivation, and then the sensor will not be directly inserted into the network and will not be in contact with circulating water. This last option was agreed upon as a possible one by Suez Smart Systems.

Concerning the issues due to the chip (especially the response of the sensors due to their position on the chip and not due to the ink), they neither have been investigated during the course of Fiware4water, so their causes are not identified. Therefore, it is difficult to propose any change, except that it looks necessary to design a new chip.

# I.8. Nanosensor Conclusions

During the remediation plan, investigations to understand some of the misfunctions of the sensors raised during the first part of the project have been undertaken. Focus has been made on the formation and characterization of the active material which is a high priority key point for the design of selective sensors. This has led to the following conclusions:

- the solvent previously used was degrading with the process used to disperse CNTs and was probably responsive to an inefficient functionalization of the CNTs by the organic molecules.
- FFUR-14, the molecule used for sensing pH and "chlorine", was found to be not sensitive to either of them by emission spectroscopy.
- designing sensors with pristine CNTs appear to be not useful, as they could respond to a wide variety of chemicals.

Improvements that have been made and solutions found:

- a molecule (E) which was experimentally shown to be sensitive to acidic pH and designed to potentially functionalize CNTs was synthesized and studied instead of FFUR-14 to elaborate a material possibly sensitive to pH.
- a new process for the effective functionalization of CNTs by **E** was proposed, and the coverage of the surface of CNTs by **E** as evidenced by electronic microscopy.



# II. NANOsensor and French Demo Case

# II.1. Site description

The Cannes basin, the French Demo Case (DC2) for the project, is located in the south of France, on the shores of the Mediterranean Sea (see Figure 45); it is therefore a region subject to high temperatures during the summer period. On the other hand, it is a tourist region whose population increases three-fold during the Cannes Festival or during the summer holiday period. The combination of high heat and high population density requires fine-tuned and optimised management of water resources and facilities. The operators of the French Demo Case have been confronted with these situations for several years.



Figure 45: Geographical location of the French Demo Case (DC2) – Cannes basin located in the south of France, on the shores of the Mediterranean Sea

# II.2. General context

The French Demo Case (DC2) is the drinking water supply system of SICASIL (Syndicat Mixte des Communes Alimentées par les Canaux de la Siagne et du Loup, in English, *Mixed Water Union of Municipalities Supplied by the Siagne and Loup Canals*). SICASIL has delegated the operation of its facilities to SUEZ under a Public Service Delegation contract.

Table 2 specifies the four business issues (BI01 to BI04) driving the French Demo Case.

Table 2: Four business issues for the French Demo Case

Reference	French business issues
BI01	Forecast water resources availability
BI02	Forecast water demand
BI03	Detect water leaks
BI04	Detect abnormal water quality events



The NANOsensor multiparameter probe (previously called PROTEUS), designed and developed by CNRS, was expected to be upgraded and evaluated within the F4W project. Table 3 shows the macro-planning and associated actions.

Table 3: NANOsensor: macro-planning and associated actions

Period	Associated actions
June 2019 – May 2020	Finalise the design and development of the probe by CNRS and EGM
June 2020 – May 2021	Test a prototype of the NANOsensor on the TZW test bench according to a previously defined hydraulic and quality experimentation protocol
June 2021 – May 2022	Test one or more prototypes of the NANOsensor, at full scale, on the distribution network of the French Demo Case (DC2 – Cannes basin)

3S and TZW have jointly carried out actions on the NANOsensor in the framework of the second period (June 2020 to May 2021) mentioned in Table 3. The objective was to define and validate a protocol for the tests to be conducted for the NANOsensor on the TZW test bench.

3S called on the experts at CIRSEE (International Centre for Research on Water and Environment), which is the most important research centre of the SUEZ Group and the third party of 3S for the F4W project.

# II.3. Actions performed by CIRSEE for the NANOsensor

Two main actions were performed by CIRSEE:

- 1. Definition of quality parameters for continuous water quality monitoring
- 2. Validation of the protocol to evaluate the NANOsensor on the TZW test bench

Both actions are detailed below.

#### Definition of quality parameters for continuous water quality monitoring

A questionnaire was first published by CNRS to define the parameters that should ideally be measured by the NANOsensor. Using this questionnaire, SUEZ operators of the French Demo Case and CIRSEE defined the best parameters needed to monitor the water quality at the production plant outlet and in the distribution network (see Table 4).

Temperature
Conductivity
Free chlorine
Turbidity
TOC (Total Organic Carbon)
Bacterial content
THM (Trihalomethanes)
Metals
Compounds from PE (polyethylene) pipes

Table 4: Parameters selected by the SUEZ operators and CIRSEE for monitoring water quality

These criteria are linked to the operating conditions of the resources and the SICASIL treatment plants.



Subsequently, an exchange between CIRSEE and SICASIL led to the modification of the list in Table 4 to identify parameters of greatest operational interest for monitoring water quality in order to determine natural water degradation or intrusion into the network (see Table 5). These criteria can be used in most drinking water distribution networks.

Criteria	Parameter
Physical	Temperature
	Conductivity
	Flow
	Pressure
Chemical	Free chlorine
	рН
	Turbidity
	Organic matter (UV254 or TOC)
Microbiological	Bacterial content

Table 5: Parameters selected by the SUEZ operators and CIRSEE for monitoring water quality

Finally, four quality parameters were selected for the NANOsensor in the F4W project (see Table 6). The validation of these parameters was done in collaboration with CIRSEE, SUEZ operators of the French Demo Case and CNRS for the feasibility of the prototypes.

Parameter	Measurement range
Free chlorine	[0; 1 mg/L]
Temperature	[0; 30°C]
рН	[6.5; 9]
Conductivity	[200; 2000 μS/cm]

#### Validation of the protocol to evaluate the NANOsensor on the TZW test bench

CIRSEE studied the test protocols proposed by TZW and possible corrections were discussed and amended according to the parameters retained for the NANOsensor and according to the metrological needs on the drinking water distribution network (measurement range, sensitivity, detection threshold, reliability). This task was stopped in April 2021 with the abandonment of the NANOsensor tests on the TZW test bench.

# III. Alternative to NANOsensor for the French Demo Case

### III.1.Installation of four nano::stations multiparameters probes

At the beginning of the project, 3S decided to install four multiparameter probes (nano::stations manufactured by s::can) other than the NANOsensor for two reasons:

- 1. Monitor the water quality in part of the French Demo Case distribution network as soon as possible
- 2. Collecting water quality measurements as soon as possible in order to build up the most exhaustive data history possible for the development, by 3S and TZW, of scientific models dedicated to the business problem BI04 "Detect abnormal water quality events".



These two reasons were also intended to secure the implementation of the French Demo Case in case of problems with the NANOsensor. On the other hand, the installation of the NANOsensor, in the third year of the project (see Table 3), on the distribution network of the French Demo Case would have allowed, in the best of cases, to have only one year of measurements, or even less in case of delay, which would have questioned the exhaustiveness of the measurements history thus constituted. In the end, this decision paid off, given the technical problems encountered with the NANOsensor, described in deliverable D3.5.

The installation of the four nano::stations in the distribution network of the French Demo Case and is detailed in deliverable D4.3.

Figure 46 shows the instrumentation of the French Demo Case planned at the beginning of the F4W project: at least one NANOsensor prototype and four nano::stations installed in the drinking water distribution network. The NANOsensor was to be connected directly to the F4W platform while the four nano::stations were connected in a classical way: Sensor / RTU / SCADA TOPKAPI / AQUADVANCED<sup>®</sup> Water Networks "Distribution" (a software product, published by 3S, dedicated to the management of drinking water distribution.



Figure 46: Instrumentation of the French Demo Case planned at the beginning of the F4W project: at least one prototype of the NANOsensor and 4 nano::stations

# III.2. Connection of a nano::station to the F4W platform

During the project it was discussed to connect one of the four nano::stations directly to the F4W platform, replacing the NANOsensor (see Figure 46). This was discussed and approved by the SUEZ operators.



This modification of the communication chain was not implemented in the end for the following two reasons:

- The modification of the communication chain would have required a stop of the acquisition of the measurements of this nano::station during several days, even several weeks. It was considered more important not to interrupt the acquisition of measurements in order to build up the most exhaustive measurement history possible for the construction of scientific models, developed by 3S and TZW, dedicated to the French business issue BI04 "Detect abnormal water quality events".
- 2. SUEZ currently operates the SICASIL drinking water supply system under a public service delegation contract that expires at the end of 2022. At the beginning of 2022, a new call for tenders was launched by SICASIL for a new public service delegation contract. The action to modify the communication chain, which was not foreseen in the current operation contract, was abandoned to rule out any idea of SUEZ trying to influence its public client SICASIL, in the context of the new call for tenders.

# IV. EURECAT printed sensor

Functional Printing & Embedded Sensors department at Eurecat entered Horizon 2020 Fiware4Water European Project in late 2021 (final agreement amendment signed in December 2021) to contribute with the demonstration of a novel solid-state multiparametric electrochemical sensor for smart water applications. The demonstrator consists in a free chlorine electrochemical sensor and temperature sensor platform with its wireless compact autonomous electronic control unit (ECU) and software for data acquisition in a remote pc. The validation scenario proposed was relevant conditions in a pilot of drinking water distribution network in TZW installations. The key technological advantage of Eurecat's multiparametric sensor is its reliability at low cost enabled by fabrication through printing technologies.

The temperature sensor was based on a resistive measurement, where the resistance of a conductive path is monitored with the change in the temperature. Increasing the temperature of the system, decreases the conductivity of the track, increasing the global resistance.

The electrochemical free chlorine sensor was based on an amperometric measurement, that correlates the change in the electrical current produced by the chemical reactions of the chlorine species with the free chlorine concentration. The HOCl and OCl<sup>-</sup> compounds are the ones that are controlled through the amperometric measurements and would be the molecules that we refer as free chlorine. The need for miniaturization of such sensors has led to the concept of solid-state amperometric sensor. In this type of sensor construction electrolytes are transformed into solid contact transducers with the ability to convert ionic current into an electric current. The applicability of solid-state amperometric sensors is very extensive due to their simplicity, ease of operation and low cost. Compared to other analytical techniques, amperometric sensors have several advantages, such as a direct determination, the possibility of being a portable system by not requiring complex instrumentation or specific environmental conditions, and the measurement does not alter the solution studied. Figure 47 shows an example of the miniaturization of an amperometric sensor.





Figure 47. Schematic representation of the 3-electrode amperometric measurement (left) and it's conversion into a miniaturized printed solid-state printed amperometric sensor (right).

The amperometric sensor typically consists of a three-electrode structure, where one is the working electrode (WE), the other is the reference electrode (RE) and a final counter electrode (CE), and the current is measured in a chronoamperometry method, where a very specific potential is applied between the WE and the RE and the current generated from the electrochemical reduction of the free chlorine species is measured between the WE and the CE. Applying a known potential reduces drift problems to zero and results in greater accuracy and control of the measured species.

This project is based on the construction of the electrochemical solid-state sensor using scalable printing techniques, being screen and inkjet printing the most compatibles. Screen printing is a printing technique that allows you to cover large areas at a very low cost and is the most widely used technique in printed electronics. This is based on the deposition of inks that adhere to the substrate through a mask that defines the design. The mask is placed at a certain distance from the substrate, and by pressure and displacement the mask contacts the substrate by depositing the ink. From the other side, inkjet printing does not need any type of mask, allowing more versatility in the design. This is a non-contact printing process, thus avoiding the risk of sample or substrate contamination. In addition, it allows control of the thickness of the deposited layer, as well as the amount of ink used, which allows obtaining areas in accordance with the requirements needed.

To develop the automated and scalable fabrication process technology based on printed sensors, a series of processes necessary for its fabrication and characterization have been carried out in a sequential manner.

### IV.1. Fabrication Route

The design of the printed electrodes was designed to be done by means of scalable automatized industrial techniques following printed electronics principles. As mentioned, this type of printed sensor was based on an amperometric 3-electrode system, for the free chlorine sensor, and a resistive track for the temperature sensor. The construction of the multiparametric printed sensor is based on 3 main parts: the electrode design according to requirements, the printed electrodes and their individualization. The general fabrication process is schematically depicted in Figure 48. First, the sensing area of the free chlorine sensor.





Figure 48. Sequential fabrication process diagram for the multiparametric printed sensor.

This sequential fabrication strategy benefits of a straightforward scalability, taking advantage of two well established industries. On the one hand, the graphic industry is capable of printing with a variety of techniques and a very high throughput. Printed electronics is rapidly advancing thanks to decades of experience with conventional inks, only requiring adjusting the processes to the new functional (conductive) inks. On the other hand, many automatized drop methodologies are also found in the pharmaceutical or conventional electronics industries, both with a record of decades of experience and well-established processes.

Prior to fabrication the design of the sensor is a key part. The printed sensor was designed following a geometry to obtain two sensors with the dimensions required for the measurement in a distribution network, taking care the materials and the substrate.

The dimensions of the sensors were designed to obtain a measurement inside a 4 cm diameter pipe. For this, it is necessary that the length of the sensor was larger than 8 cm, due to the distance from the access channel to the pipe. In Figure 49, the dimensions of the multiparametric printed sensor can be observed.



Figure 49. Specifications of the design of the sensor, where a) is the width of the connectors, b) the length to the sensing area, c) length of the sensing area, d) total length of the sensor and e) width of the sensing area.

Once the dimensions of the sensors were defined together with all the required dimensional specifications, the printing procedure is carried out. In this case, the used techniques were inkjet and screen printing, both very extended techniques in graphic industry.

The substrate chosen for this project was a 2 mm poly (methyl methacrylate) (PMMA), given Eurecat's extensive experience in printing on a wide variety of materials. This provides good adhesion with the used inks, as well as being robust, thus avoiding flow problems in the pipe. To avoid misalignment of the different layers to be printed due to shrinkage of the substrate it was pre-treated for 2 h at 130 °C.



For the construction of the amperometric WE, different materials were evaluated, being gold the one selected for its application, owing to its high chemical stability and good performance against the free chlorine measurement. For the construction of the conductive tracks, silver was selected as the material due to its high electrical conductivity and good adhesion to polymeric substrates. For the RE, the use of a layer of silver/silver chloride (Ag/AgCl) is also very common. The use of Ag/AgCl as RE provides an improvement in the level of precision and decreases the response time of the sensor. In addition, this reference performs better in long-term continuous measurements given the stability of the Ag/AgCl potential. For the CE, and for the definition of the contact pads, graphite was the main used, given its protection against scratches and oxidation of the silver by environmental oxygen. A final dielectric material was used to isolate the silver conductive tracks and to define the sensing area. After the printing procedure the sensors were individualized by cutting with the laser printer, leaving 3 support points for fastening.



Figure 50. a) Images of Eurecat's multiparametric printed sensors as prepared and b) detailed view of the sensors delivered as die-cut samples.

As can be seen in Figure 50, after printing, robust printed sensors were obtained with a good alignment of the dielectric on the silver or carbon layers (see the open "hole" of the dielectric that forms the area of the amperometric electrode). Furthermore, in Figure 51 images of the final multiparametric printed sensor can be observed.





*Figure 51. Images of the final sensor after the printing and cutting procedures.* 

**Forty-eight (48) printed sensors were delivered to TZW for their tests at their installations.** The printed sensors being prepared by automated printed techniques enabled large volume manufacturing with high reproducibility and cost-effectiveness.

### IV.2. Characterization

To determine the functionality and performance of manufactured printed sensors, it is necessary to be able to evaluate them according to different characteristics and considering factors that will be discussed in this section.

Starting with the temperature sensor, the characteristics in terms of linearity, sensitivity, hysteresis and the reaction to temperature changes were analyzed using a climatic chamber (CCI Solatron, see Figure 52a), taking into account the resistance changes of the sensor, measured using a commercial multimeter (Agilent 34410A, see Figure 52b) and a software that collected the data (Keysight BenchVue, see Figure 52c).



Figure 52. Lab equipment used to characterize the graphene sensors. a) CCI Solatron Climatic Chamber b) Agilent 34410A multimeter c) KeySight BenchVue software.

For each variable characterised, different specific test were performed. Firstly, to assess the sensitivity of the sensor, the experiment done consisted of a progressive increase in temperature during time from 10 °C to 40 °C. It is important to take into account that the selected range of temperature was defined according to the maximum temperature that the sensor could withstand in this stage of the project. Figure 53 show that the printed sensor presents an excellent linearity in the range of temperatures tested with a sensitivity of 74.3  $\pm$  0,6 mΩ/°C. In addition, the low standard deviation value clearly shows a good reproducibility between sensors.





*Figure 53. Sensitivity results for the printed temperature sensor.* 

Once the tests were performed, the sensitivity was defined as the resistance changes of the sensor for each degree increased. The repeatability of the sensor was studied with a cyclic test (2 cycles), starting from low temperatures until reaching higher ones and then going back to the starting point. With this test the hysteresis of the sensor could be analysed. As can be observed in Figure 54 the heating cycle has the same sensitivity as the cooling cycle, enhancing the good performance of the printed sensor.



Figure 54. Temperature validation cyclic protocol.

After validating the reproducibility and the sensitivity of the printed sensor in one heating-cooling cycle, the performance of the sensor for more cycles was tested. The summary main results of the experimental procedure can be observed in Figure 55. As seen, the sensitivity of the sensor remains constant after more than 5 cycles of heating-cooling procedure with a value of  $73.9 \pm 0.9 \text{ m}\Omega/^{\circ}$ C. In summary, and as main results, here we demonstrate the development of a printed temperature sensor that shows a good linear temperature dependence, minimal hysteresis, and low baseline drift in the temperature range of interest (10-40 °C).





Figure 55. Temperature validation for multiple cycles protocol.

Following with the free chlorine sensor, the characterization was done in laboratory conditions with a commercial potentiostat (Autolab PGS-TAT204). As previously explained, the electrochemical technique that was used for the free chlorine measurement was the chronoamperometry, where a known potential was applied while recording the generated current.

When a compound with one (or two) chlorine molecule is added to the water, it dissociates, generating free chlorine, together with other oxidizing compounds such as hypochlorous acid, which, in any case, ends up dissociating to hypochlorite ion (OCI-) and a proton ( $H^+$ ) according to equilibrium reaction 1

$$HOCl \leftrightarrow OCl^- + H^+$$
 (1)

By applying a known potential on the surface of the working electrode, the species of HOCl and OCl<sup>-</sup> are reduced by reduction reactions 2 and 3, being these:

$$HOCl + 2e^- \to Cl^- + OH^- \tag{2}$$

$$OCl^{-} + H_2O + 2e^{-} \rightarrow Cl^{-} + 2OH^{-}$$
 (3)

This reaction consumes the electrons generated from the oxidation reaction of the reference electrode through oxidation reaction 4, generating a current that is measured between the electrodes:

$$Cl^- + Ag \to AgCl + e^-$$
 (4)

Therefore, the correlation of the free chlorine concentration with the measured current is that described in Equation 5:

$$I = nFA \sqrt{\frac{D}{\pi t}} C_{HOCl}$$
(5)



Where n is the number of electrons needed to reduce or oxidize a molecule, F is Faraday's constant, A is the planar area of the electrode, D is the diffusion coefficient of the species, and t is time.

So, for the measurement it is necessary to exactly know the potential value to be applied for the reduction of the free chlorine, therefore a linear sweep voltammetry was performed between 1.0 V and -0.2 V in a 1 ppm free chlorine solution to appreciate the spot where the specie change their oxidation state. As seen in Figure 56, the region between 0.1 V and 0.3 V is the part of the electrochemical process where the free chlorine is reduced in the electrode, owing to the flat profile of the curve. Within this region, any potential could be used, however, as lowest the applied voltage, less deterioration the printed electrode will suffer, being the 0.1 V the one selected for this application and the one that we are going to work from now on.



Figure 56. Linear sweep voltammetry of the printed sensor from 1.0 V to -0.2 V in 1 ppm free chlorine solution.

Once the working potential was selected, the validation of the free chlorine printed sensor was performed. For each measurement, the free chlorine concentration was validated with a colorimetric measurement using the well known DPD method. To obtain the calibration curve, the sensor was dipped in a 0 ppm tap water solution and the chronoamperometric measurement was performed for 60 s to stabilize the measure. After that time, the final current value was correlated with the free chlorine concentration. Calibration curve was performed between 0-1 ppm of free chlorine according with the application to achieve the most accurate sensitivity, increasing the concentration at each step. As observed in Figure 57 the calibration curve shows a clear linearity in the desired concentration range with a sensitivity of 0.37  $\mu$ A/ppm.



*Figure 57. Characterization of the amperometric measurement at different free chlorine concentrations.* 



The same calibration procedure was done with different sensors to obtain their reproducibility. As observed in Figure 58, the printed sensors present very similar sensitivity with a value of  $0.370 \pm 0.004$   $\mu$ A/ppm. This very small deviation value elucidates the excellent reproducibility of the printed sensors and the measurement technique regarding its sensitivity, however, for each sensor a calibration is needed, owing to the displacement in the current region.



*Figure 58. Characterization of the amperometric measurement at different free chlorine concentrations to obtain reproducibility before and after normalization.* 

It is well known that pH and temperature are the main parameters that influence in free chlorine concentration, and this relationship can be observed in equations 6, 7 and 8. In equation 6 we can observe the equilibrium reaction between the free chlorine species. In this equilibrium the hypochlorous acid (HOCI) dissociates in the hypochlorite ion (OCI<sup>-</sup>) and a proton (H<sup>+</sup>), therefore this reaction it is clearly dependant of the pH in the media and their dissociation constant as observed in equation 7. At the same time, this dissociation constant is temperature dependant as demonstrated in equation 8. Therefore, the amperometric measurement of free chlorine has to be studied between different ranges of pH and temperature to characterize their performance and selectivity.

$$HOCl \leftrightarrow OCl^- + H^+$$
 (6)

$$C_{Free\ Cl} = C_{HOCl} \left[ 1 + 10^{(pH - pK_a)} \right]$$
(7)

$$pK_a = \frac{3000}{T_{meas} + 273} - 10.0686 + 0.0253(T_{meas} + 273)$$
(8)

To perform the study of the interferents, solutions with the same concentration of 0.5 ppm of free chlorine at different pH values (pH from 5.00 to 9.00) and different temperatures (from 10 to 25  $^{\circ}$ C) were measured with the amperometric method applying the 0.1 V. In Figure 33 the current response of the printed sensors can be observed. Regarding the pH (Figure 59a), there are no significative change in the current value, therefore, this is an indicator that the amperometric sensor is capable to read both species of free chlorine that are present in both acid and basic media (HOCI and OCI<sup>-</sup>).

Then, the study of the temperature interference was done. In that case, and as can be observed in Figure 59b, no influence was observed between 15-25 °C, obtaining very similar values of free chlorine. However, a small deviation can be observed in temperatures lower than 10 °C.





*Figure 59. Free chlorine amperometric measurements with a) different pH regions and b) different temperatures.* 

After the interference study was done, the stability of the printed sensor was evaluated to monitor their lifetime. For this study the printed sensor was calibrated in the range between 0-1 ppm of free chlorine. After calibration batch continuous measurements of were performed every 5 min and the free chlorine value was correlated with a referential DPD colorimetric measurement. In Figure 60 the % of the free chlorine measurement error is plotted in comparison with the real value obtained with the DPD method. As elucidated the first two days of measurement the obtained value has an error < 5%, demonstrating the reliability of the sensor after its calibration. After the third day, the error increases up to 10%, increasing even more reaching up to 15% in day 5. From this point, the sensor response becomes a bit unpredictable, obtaining values with both positive and negative errors until the error increases up to 20% in the second week of continuous measurement.





Figure 60. % Error of the amperometric free chlorine measurement regarding the DPD reference method after 2 weeks of measurement.

- IV.3. Electronic control unit
  - i. Compact autonomous electronic control unit device (ECU) for use at the point of need (PoN)

The overall point of need device of Fiware4Water is composed by 3 elements:

1. The multiparametric printed sensor that has been already explained that can be seen in Figure 61.



Figure 61. Image of the multiparametric printed sensor.

2. A conventional electronic control unit with a slot to fit the wires of sensor and make a measurement giving a real time result that is show on screen in plot format. It is an autonomous device that measure in a loop that takes one measure each 30 minutes. The illustration of the electronics is shown in Figure 62.





Figure 62. a) Image of the electronic control unit and b) image of the electronics with the 3D printed case and a main schematic of the connections.

3. A desktop application (Figure 63) developed by FPED Eurecat team that is used to configure the main state machine of the measure. Then when all parameters are introduced, the application upload the configuration to device to prepare to start measure.



*Figure 63. Screenshot of the desktop application, where the configuration.* 

### ii. ECU hardware description

The purpose of the first stage was to develop a simple device capable of obtaining fast results and presenting them on a monitor screen. This autonomous device, together with the printed sensors, was designed to test the measurement capabilities through laboratory and real tests.

Even though the first iteration of the electronic control unit was designed to meet the objectives set for the first stage, a microcontroller with USB connection and external memory to make big measures during a long time.



To give more possibilities to the design of the case, the electronics hardware was divided into 6 parts that were schematically illustrated in Figure 64Figure 64. Schematic illustration to show the different parts of the electronic reader.:

- Main circuit (a): including the main microcontroller with up to 1MB of RAM, an external SD card memory up to 8GB to store configurations and data, BLE connection to future implementation, an internal Flash memory of 64MB to future implementation and a RGB Led to use to indicate transmission and power state.
- USB galvanic insolation (b,c): System to isolate and reduce noise that PC could transmit in USB wire when connects device to the computer to supply power and communication data.
- Power management (d): Part of the motherboard that adapts power from external supply to manage currents and voltages necessary for each component of the electronical device.
- IC of Temperature measurements (e): System to read temperature channel with an autocalibration hardware.
- IC of electrochemical measurements (f): System to read electrochemical measurements. In this case, is used for Amperometric measurement applying -100mV on the printed electrode to read the result current on the WE channel.
- External connector (g): It will be used in the future to connect an external expansion PCB.



*Figure 64. Schematic illustration to show the different parts of the electronic reader.* 

### iii. State Machine

The device allows to import a custom state machine to perform measurements applying different parameters that the user can modify as current range, sample time, select timeout before next step and which name the user wants to export the data to the SDCard memory. In Figure 65 will be displayed a schematic illustration that explain how firmware works, how does calibration with the calibration state machine file, that could execute for each point to obtain free chlorine, and how works to make the real measures applying parameters founded during calibration routines.





*Figure 65 State machine of main struct of firmware device.* 

### iv. Electronic reading description

The proposed system is composed of the blocks present in Figure 66. The main circuit involves the microcontroller, the sensing electronics, the external memory and the USB power connector.

The analog core of the system, the sensing electronics and the control circuit, is the responsible for providing the cell with the constant voltage required for amperometric measurements and for processing the output current of the sensor. The sensing element of the system is a three-electrode electrochemical cell; whose operation is based on redox reactions. The cell's electrodes are working electrode (WE), reference electrode (RE) and counter electrode (CE). The potentiostat block ensures a constant V<sub>CELL</sub> voltage between WE and RE. The resulting current I<sub>CELL</sub> is amplified using a transimpedance amplifier. Because I<sub>cell</sub> is read out from the CE, no current should be contributed by the RE. More in detail, for measuring the concentration of chlorine, a constant voltage V<sub>CELL</sub> = V<sub>WE</sub> – V<sub>RE</sub> is applied on the cell. The polarity of V<sub>CELL</sub> determines the type of electrochemical reaction that takes place (oxidation, if V<sub>CELL</sub> > 0, reduction, if V<sub>CELL</sub> < 0). The user is allowed to set the value of the desired V<sub>CELL</sub> voltage. To select the corresponding voltage where free chlorine is reduced onto the WE, we



made a linear sweep voltammetry as shown in Figure 56, resulting 0.1 V the selected voltage. As a result of the chlorine reduction reaction which takes place on the WE when applying 0.1 V, a low-value current  $I_{CELL}$  is generated between WE and CE. A transimpedance amplifier converts this small current into a voltage ( $V_{OUT}$ ). This output voltage increases with the concentration of chlorine. The microcontroller acquires this voltage via an A/D converter and based on its value calculates the cell current. The system is conceived for high linearity over a wide range of input signals. Furthermore, it is designed for a high accuracy, with special regard to noise immunity and stability. The implementation of the power supply using galvanic isolation increases noise robustness and stability.



Figure 66. Blocks diagram of main functions of Eurecat ECU.

Specifications	
Electrodes	Printed sensor (CE: C; WE: Au; RE: Ag/AgCl)
Technique	Chronoamperometry
Channel	1
Potential range	±1 V
Potential step	±1 mV
Sampling interval	200 ms
Sampling Count	-
Current resolution	50 nA
Size	84mm x 52mm x 24mm
Weight	60g
Power Supply	5V 500 mA
Comsuption	250 mW
Communication	USB 2.0

#### Table 7. Specification parameters of the Electronic Control Unit.

### IV.4. Printed Sensor Integration

Another key step to perform the measurement of the printed sensor is the connection with the ECU and the integration with the distribution network line. To perform this integration a 3D printed adaptor was designed with a slider connector. With this slider the sensor pads contact with the connector and then is connected with the ECU via cables. Furthermore, the sensor was protected in the bottom part



to avoid water leakages that can damage the connection. In Figure 67 the images of the 3D printed adaptor and the connection performed can be observed. As seen the sensor perfectly fits in the designed piece obtaining good connection and being able to achieve the measurement.



*Figure 67. Images of the adapter to perform the connection of the ECU with the printed sensor.* 

### IV.5. Measurement with ECU and app

After the development of the printed sensor and the connector to obtain measurement with the electronic we perform the continuous measurement of free chlorine. The different steps are described to perform the measurement will be explained in the following sections.

The ECU is able to connect the with the printed sensor via USB selecting the different devices connected to the computer. When the connection is performed, a blue led will appear in the electronics. In Figure 68 the screenshot of the electronic connection of the ECU and the ECU connected is shown.



*Figure 68. Screenshot of the app connection with the electronics and the ECU connected with the computer.*


As previously explained, to perform the measurement of free chlorine, it is necessary to obtain a calibration of the sensor. For this calibration, we must start a new measurement in the app screen and upload the calibration configuration as observed in Figure 69a and Figure 69b. After uploading the configuration, a new window will appear with the charged configuration where the measurement can be started. Then, the sensor was dipped in two solutions of 0.2 and 1 ppm, and the obtained current values were used to perform the calibration.



Figure 69. Screenshot of the a) app new measurement and b) configuration with c) the screenshot of the windows that appear after charging the configuration prior to start the measurement.

Once the calibration was performed, the concentration and current values have to be updated in the app as seen in Figure 70a and the calibration was updated in the measurement. From this point the app will generate the free chlorine value in ppm directly form the obtained current value as can be observed in Figure 70b.



Figure 70. a) Screenshot of the app with the uploaded configuration and b) screenshot of the window with the live measurement.



In conclusion to lab development and preliminary validation at EURECAT, the free chlorine and temperature multiparametric sensor was successfully developed as a PoN autonomous compact system with wireless communication for the F4W application. The PoN system is composed by the multiparametric sensor (as a fungible that can be replaced easily), the ECU and the software application for remote control of the sensor and showed correct and reliable free chlorine measurement in the conditions proposed. Lifetime of fungible sensor was evaluated to design the experiments in the pilot line at TZW. For the purpose forty-eight printed sensors were delivered as fungibles of the PoN to TZW for their relevant environment validation. Furthermore, the performance of the sensor was increased by applying intelligent processes of the raw data gathered by the sensors. These processes involve smoothing, filtering, outlier removal, and other compensation methods. A further explanation is written in deliverable D4.3.



## **Conclusion and Perspectives**

During the first part of the project (June 2019 - May 2021), investigations to understand the ageing of the sensors were conducted. Also, signal analysis and the synthesis of new molecules for multidetection purposes were undertaken. This work led to the first set of conclusions:

- an improvement in the lifetime of the sensors up to 2 months was shown by mainly changing the gloptop and protecting the active material with a membrane to avoid/minimize any release into the water;
- increasing the value of the current used to activate the chemical sensors by a factor of 5 allowed a decrease in the noise by one order of magnitude;
- 5 molecules were designed in order to anticipate multiple detections. Sensitivity to fluoride (molecule A), aluminum (molecules B and D), glyphosate and aminomethylphosphonic acid (molecule C), zinc (molecule D), and pH (molecule E) was obtained with these.
- variation of the resistance of the chemical sensors was observed upon the addition of a sodium hypochlorite solution for both pristine and MWCNTs/FFUR-14 sensors.

However, during the first semester of 2021, several issues about the Nanosensor were raised. The electronic chips that were initially chosen for the project have failed to give a reliable response. The response of the sensors has been partially attributed to electronic issues as some variation in the resistance was sometime observed without any addition of chemicals. A worrying point is that this variation was of the same order of magnitude than that interpreted as a chemical response. A similar observation was made when the sensors were taken out of a solution and immersed into the same solution. Further, a similar response of pristine CNTs and CNTs/FFUR-14 sensors was observed, and the variation of resistance of the chemical sensors was found to be dependent on their position on the chip. As a direct consequence, not enough data of correct quality was obtained to define any calibration model.

In consequence, in May 2021, all investigations on the initial devices were stopped as it appeared reasonable to not keep on working with devices for which we were not sure what they were responded to. After presenting these data to the coordination of the project, a remediation plan was proposed to the Fiware4water consortium. It suggested to go back to more fundamental studies in order to get some understanding on the failure of the sensors and to possibly elaborate a pH sensor.

Investigations carried out during the remediation plan have revealed that an inefficient functionalization of the CNTs used to occur as a non-neglectable part of the surface of CNTs was not covered by the molecule used, labelled FFUR-14. In addition, this compound was not sensitive neither to an acidic solution nor to a sodium hypochlorite solution, as far as emission spectroscopy is concerned.

However, after the identification of some issues, the remediation plan ended up encouraging results, especially, since efficient functionalization of CNTs was obtained thanks to a proper process. This was to be solved otherwise no selective sensor could be envisaged. Unfortunately, because of lack of time, it was not possible to fabricate a resistive sensor with CNTs properly functionalized.

In future work, as the functionalization process of CNTs by the organic molecules is now shown to be efficient, one can elaborate chemical resistive sensors with the molecules that have been synthesized and shown to be sensitive to some chemicals. Then, in order to develop a multi-parameter sensor, it will be mandatory to design a robust and reliable electronic chip that will support the sensing elements of a multi-parameter sensor and that will accommodate several single chemical sensors.



The problems with the Nanosensor produced a cascading effect of serious risks, making it impossible to solve some of the planned subtasks, such as deploying it to the French demo case or creating the software to improve raw data. Therefore, the project decided to focus the subtasks on a newly added printed sensor and the existing nano::stations.

The printed sensor was introduced in late 2021, with the idea of replacing the Nanosensor with a novel solid-state multiparametric electrochemical sensor with a fabrication route of printed electronic principles. The successful development would then enable the correct extraction of raw data that could be further processed afterwards by intelligent algorithms and software.

Finally, to integrate sensor data with the FIWARE4WATER architecture, a specific MQTT bridge was developed during the project which collected the data from the Nanosensor and send it to a Stellio context broker of the architecture. The development is directly related to the Nanosensor, since the data is extracted from the hardware called EdgeSpot. The problems with the Nanosensor affects a wrong extraction of raw data, but the frequency and format are not. Therefore, the software component was developed without being affected, and can be replicated or reused for future sensor integrations.



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