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Water and air quality monitoring with multi-parameter chemical sensors

Managing non-idealities from lab to field

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Abstract—Among the thousands of chemical sensors proposed each year, very little of these ever reach sufficient maturity to be field-tested. Indeed, as the testing conditions progressively complexify compared to lab conditions, more and more non-idealities appear that require increasingly sophisticated validation tools. This paper discusses the challenges of real life deployment for chemical sensors with two examples, a carbon nanotubes chemistor array and a PEI-functionalized microwave resonator.

Keywords—carbon nanotube; chemistor array; microwave resonator; polyethyleneimine; calibration; Sense-City; water quality; air quality; environmental monitoring

I. INTRODUCTION

Air and water quality has become a major public health issue [1]. An increasing number of cities are therefore interested in deploying technologies that will allow them to better monitor air and water pollution, and then limit it as much as possible. While traditionally, the concentrations of a reduced number of selected pollutants are measured in near real-time by a small number of high-accuracy monitoring stations located at strategic points in the cities, there is a growing need for compact, low cost, low power solutions that can be deployed discreetly in large numbers in urban area [2]. This has driven extensive research into advantageous transductions modes and sensing materials. Despite frequently demonstrating strong benefits compared to regular technologies, most new approaches are known to suffer from high noise, strong sensitivity to environmental perturbations (temperature, humidity, chemical interferences) and rapid ageing. While these may be compensated for in lab settings, these issues turn out to be critical for real life use of new technologies. The present paper discusses two examples of innovative sensing technologies, a carbon nanotube (CNT) chemistor array and a PEI-based microwave resonators, and the lesson-learned by bringing these technologies closer to real life deployment.

II. CARBON NANOTUBE CHEMISTOR ARRAY FOR PH AND CHLORINE MONITORING IN DRINKING WATER

A. End-to-end sensor node integration

Carbon nanotubes water quality sensors have been heavily studied [3] but most studies focused on single

parameter testing in lab setting. Toward multiparameter measurement in real conditions, a compact multiparameter sensor node based on pristine (p-CNT) and functionalized (f-CNT) carbon nanotubes for temperature, conductivity, pH and chlorine monitoring was proposed (see Fig. 1) [4].

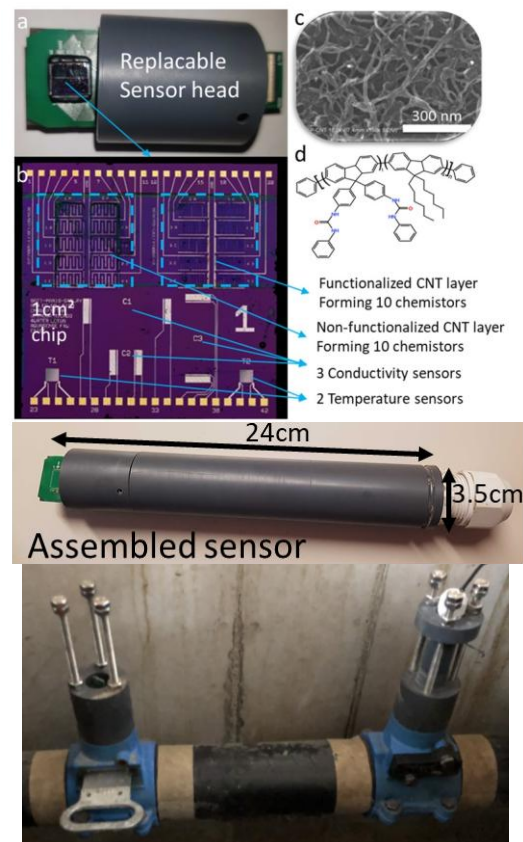


Fig. 1: Principle of the integrated CNT chemistor array: a 1cm² silicon chip is integrated into a replaceable sensor head which can be mounted into a sensor node. The latter is designed for in-pipe installation. The chip includes 2 temperature sensors, 3 conductivity sensors and 20 CNT chemistors on interdigitated electrodes, 10 with pristine CNT (p-CNT) and 10 with FF-UR functionalized CNT (f-CNT).

B. Lab testing in deionized water

Lab testing in deionized water consists in varying a single target parameter by chemical addition, either in

deionized water (with freely varying pH) or in buffered deionized water (usually phosphate buffer) to set the pH (at the cost of adding various possibly interfering chemicals). Monitoring of temperature and pH is highly recommended.

While our CNT devices have different resistances out of fabrication (generally ranging from 1 k Ω to 100 k Ω), we showed that, in deionized water, they have strongly reproducible relative sensitivity (i.e. sensitivity divided by baseline). Regarding chlorine at pH 7, relative sensitivity is -1.4%/mg/L \pm 70% for pristine CNT, -3. %/mg/L \pm 11 % for f-CNT. Regarding pH, relative sensitivity is 1.6%/pH unit \pm 20% for p-CNT, 1.8%/pH unit \pm 10% for f-CNT.

Functionalization with FF-UR provides differentiated response to chlorine, which may be explained by the sensitivity of FF-UR to ClO $^-$ ions in water which is suggested by ab-initio modelling with implicit solvent [5]. Modelling however indicates likely ionic interferent, notably Mg $^{2+}$. The latter was confirmed in deionized water: no response to 100 ppm of Mg $^{2+}$ could be observed for a p-CNT device while 3% relative variation was observed for a f-CNT device.

C. Lab testing in drink water

Strongly expecting interferent effects, the core of the sensor characterizations then focused on drinking water to assess realist performances. Drinking water was sampled directly from the tap and stabilized overnight; its initial pH was then controlled by HCl or NaOH addition, then bleach was added to control the chlorine level (which also increased the pH). In drinking water, it was observed on 3 different sensor nodes that the CNT devices, both functionalized or not, are very good HClO sensors (-26%/mg/L relative variation of resistance up to 1 mg/L of HClO), irrespective of pH between 6 and 8.5, with very high device to device (<14%) and sensor to sensor (11%) reproducibility. This is state of the art result in the CNT literature.

D. Uncertainty-resilient calibration

Unfortunately, this extremely positive result also had very negative impacts: in drinking water, unlike in deionized water, we could observe no clear differentiation from the polymer functionalization and no capability to detect pH in the presence of chlorine. Digging deeper, we realized that the widely increased sensitivity to HClO in tap water meant that the expected response to 1 pH unit variation was of the same range of magnitude as the error in response due to the uncertainty in HClO measurement (approx. 0.05 mg/L).

We thus proposed a Bayesian formalism to integrate input and output uncertainties into the calibration model [6]: sensor inputs and outputs are considered random variables; instead of predicting a single value for chlorine and pH, based on the sensor outputs and on the calibration relationship, one derives a distribution of predicted values (Fig. 2). In addition to properly incorporating input and output uncertainties, this approach allows more complex calibration relationships, particularly enabling that calibration relationship be formulated as Gaussian process. Such formulation is much more generic than generalized

polynomial regression and still requires much less input data than the more frequently used neural network approaches.

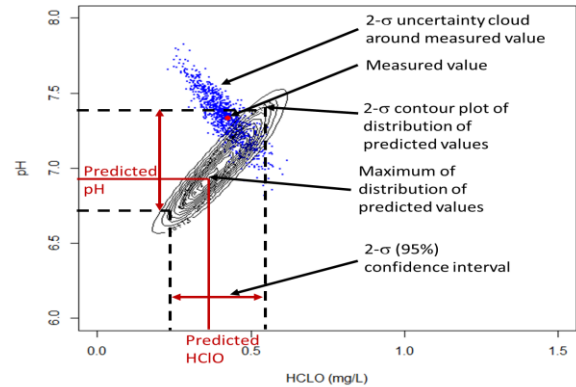


Fig. 2: Principle of Bayesian calibration

The advantages of this methodology were obvious on our datasets: in a leave-one-out test (predict one point knowing all the other points), the mean absolute error (MAE) on pH went down from 1.4 with standard linear regression down to 0.24 (for a measurement uncertainties on pH at 0.15) with Gaussian process. The MAE on HClO decreased from 0.056 mg/L down to 0.039 mg/L. For 100 random splits of the data in 80% train, 20% test data, the MAE on HClO and pH were respectively found to be 0.044 mg/L and 0.32.

While these results confirmed the possibility to use the sensors for pH and chlorine sensing in real water, they also answered the question regarding p-CNT/f-CNT differentiation: using generalized polynomial regression, the differentiation effect between p-CNT and f-CNT could be retrieved, with relative differences in calibration coefficients ranging from 10% to 150% over 3 different sensors nodes.

III. FROM LAB SETTING TO FIELD DEPLOYMENTS

A. The sense-city platform

The actual transferability of the methods and results described above in real environment is a major question for future applications. Beyond this one example, similar questions arise for any lab system targeting applications in non-controlled environments, particularly urban settings. The Sense-City facility (<https://sense-city.ifsttar.fr/>) at University Gustave Eiffel was precisely designed and built to provide a validation environment for urban technologies [7]: it comprises 2 urban scenarios (Fig. 3) of 400 m 2 each (including utilities and underground networks) which may be placed within a mobile climatic chamber enabling control of temperature, hygrometry, sun and gas exposure, and rain. The entire space is monitored by an array of analyzers and sensors providing reference measurements for calibration.

B. Water quality monitoring

Regarding water quality, Sense-City includes a 40m-long water loop in which sensors can be tested (Fig. 1) up to about 8 bar and 1 m/s. The loop is outfitted with temperature, pressure, flow, conductivity and chlorine

sensors. As of now, 8 assembled CNT sensors were tested there, from one or two days to one year, to study ageing behavior with and without flow and to demonstrate transferability of lab algorithms to these conditions. Analysis of these datasets are still ongoing, but in a preliminary manner, results show a strong increase of noise level in field conditions (from 0.1% in lab to 1% in field) which requires heavy signal processing and increases expected detection limits. On the other hand, one sensor was tested 15 days under flow, then was left for one year in static drink water (no flow), then still demonstrated response to chlorine with and without flow after this long period.

C. Air quality monitoring

Regarding air quality, Sense-City includes notably the following analyzers model from Envea: AC32e for NO and NO₂, O342e for O₃ and CO12e for CO and CO₂; and a Vaisala WXT536 weather station. The next section illustrates use of this facility for air quality sensor development.



Fig. 3: The Sense-City facility. Foreground: urban scenario with 3 buildings and a drivable road. Background: mobile climate chamber.

IV. PEI-BASED MICROWAVE RESONATOR FOR HUMIDITY MONITORING

A. System description

A microwave sensing platform was proposed (Fig 4): it consists of a dual microstrip line interdigitated resonator printed on a flexible Kapton substrate. One resonator was associated with 1,2-epoxybutane polyethyleneimine as sensitive material forming the sensitive channel, while the other resonator was left without coating as reference [8]. The bare resonator was designed to operate at 3.6 GHz and to have a maximum field density between the interdigitated lines. The two resonators are connected to a 4-port Vector Network Analyzer (VNA), itself connected to a RaspberryPi to enable continuous data acquisition. The sensing features are extracted from the raw scattering parameters S_{ij} spectra: magnitude and/or phase of reflexion (S_{11}) and transmission (S_{21}), difference in resonance frequency between the signal and reference channels.

B. Humidity sensor in lab and field conditions

First the system was characterized in temperature and hygrometry in laboratory environmental chambers, showing a strong, non-linear sensitivity to humidity from 0 to 90% relative humidity (RH) (Fig. 5) and an linear sensitivity to temperature from 20 to 35°C (-0.67MHz/°C).

Then, the sensor was deployed outdoor for 7 days in Sense-City platform. Its response was calibrated for 5 days (based on Gaussian process as described in section II.D) against RH, temperature, NO, NO₂, O₃, CO and CO₂. Then the calibration was tested on the 2 remaining days. The sensitivity to RH was found to be very close to lab results: -5.4MHz/% above 70% RH, -1.7%MHz/% between 50% and 70%RH. Moreover, the sensor was able predict RH from 50% to 90% RH with MAE of 4% and correlation coefficient of 0.91. Finally, including the other environmental parameters in the calibration and prediction was shown to degrade the result, which means that the sensor does not suffer significant interferences in real conditions, which is an exceptional result.

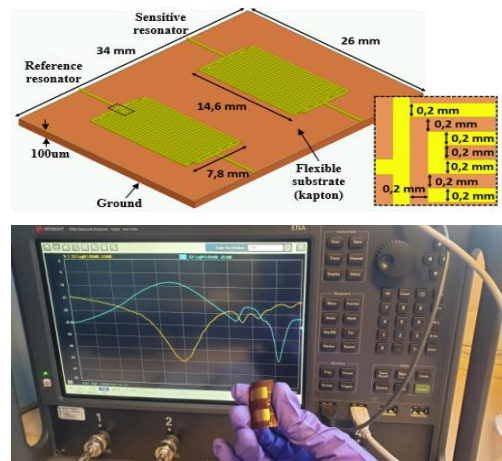


Fig. 4: Top - Resonator design. Bottom – VNA-measured S11 and S12

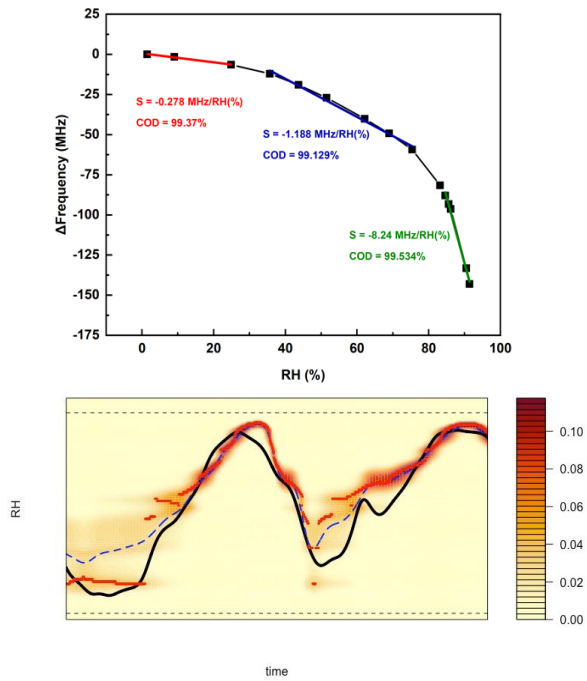


Fig. 5: Top – RH calibration curve in lab settings. Bottom – RH prediction in Sense-City: black line – true RH value; red line – predicted value; blurred area: 95% confidence interval around prediction; blue dotted line: mean of probability distribution.

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