Strategies for Realising Long-Term Autonomous Chemical Sensing Devices

Deirdre Cogan, Fiachra Collins, Kate Meagher, John Cleary, Thomas Phelan and Dermot Diamond
CLARITY Centre for Sensor Web Technologies,
National Centre for Sensor Research,
Dublin City University, Dublin 9, Ireland
dermot.diamond@dcu.ie

***Abstract*—Despite decades of intensive research and massive investments in research and development, the unit cost of long-term monitoring of the molecular world of chemistry and biology is still far too high to be practical. This paper reviews the challenges that are preventing the emergence of low cost, reliable chemical sensors and biosensors capable of functioning in a long-term autonomous manner. Strategies for advancing the capabilities of autonomous chemical sensors are discussed, with particular emphasis on direct spectroscopy and reagent based microfluidics for environmental monitoring of nutrients and greenhouse gases.**

Keywords-chemical sensing; biosensing; autonomous sensors; environmental monitoring; nitrate, greenhouse gases, sensor networks

I. INTRODUCTION

In recent years, interest in sensor networks has risen rapidly, driven mainly by the almost ubiquitous availability of wireless communications networks, the increasing power and capabilities of mobile phone platforms, and the need to exploit new sources of data (and hence revenue) beyond conventional phone calls. Phones now can be used to access, generate and exchange audio, video and photo files, and they now have an increasing array of sensors incorporated as standard (e.g., accelerometers, gyroscopes etc.). The increasing interest in new data sources is exemplified by vision statements and strategic movement of very large computing, ICT, network, mobile phone companies into sensor networks. Examples include the Nokia 'Morf' concept, IBM/INTEL activity in Smart Cities, and the HP 'Cense' vision [1].

However, despite the enormous activity both into sensor networks and into the development of improved chemical sensors over the past decade, there has virtually no penetration of chemical sensing platforms into widely distributed sensor network deployments, although the key barriers have been repeatedly highlighted [2,3]. The simple message is that current technologies for autonomous chemical sensing are still not fit for purpose, and do not meet the cost/performance requirements for inclusion in environmental deployments [4].

A striking illustration of the failure to integrate chemical sensing capabilities into widely deployed sensor networks is given by data provided by the Argo project [5], (Fig. 1).

Of the almost 3,600 sensing floats currently active, less than 200 have any chemical sensing capability, and of these, none employ reagent based analysers, and only two are reporting pH measurements. The 'Bio-Optics' sensors (18 locations) are using direct optical colorimetry to infer algal populations from local colour, while the nitrate measurements (27 locations) are all based on direct UV absorbance.

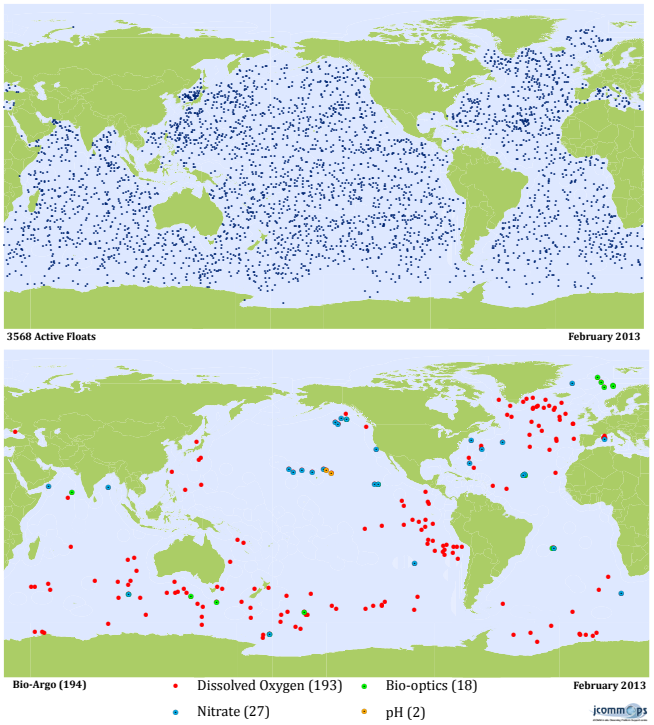

Figure 1: Data from the Agro project website showing the striking difference density of sensor floats reporting temperature and salinity (top, 3568 active) and chem/bio parameters (bottom, 194 active) [5].

II. STRATEGIES FOR ACHIEVING SCALABLE LONG-TERM AUTONOMOUS CHEMICAL SENSING

The clear message from these numbers is that chemical sensors and biosensors do not meet the specifications for these deployments, due to price/performance and reliability issues. In a way, this is understandable, given the rather fragile nature of electrode surfaces modified for chemical sensing purposes, and the extremely hostile nature of the marine environment. The situation on land with

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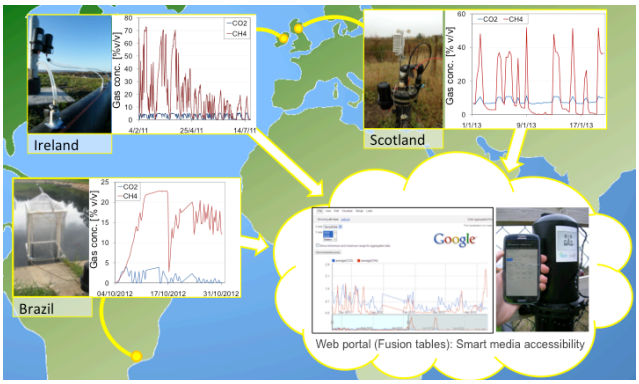

Figure 3: Sample data and photos of deployments of sensing platforms in Ireland, Scotland and Brazil. Data from these deployments is accessed through Cloud-based interfaces like 'Google Fusion Tables'.

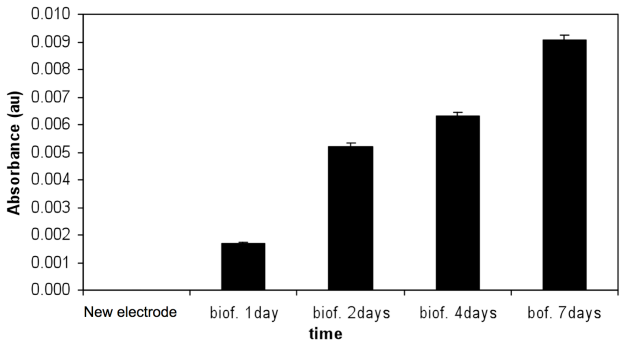

Figure 2: Growth of Biofilm on ion-selective electrode surfaces can be detected within one day of exposure to river water (error bar is standard deviation for n=3 replicates). See [6] for details.

deployments in lakes, rivers, waste water, ground water, is scarcely better. Even though the sensors tend to be much more accessible, scalable deployments demand that the devices must be low cost, and capable of functioning reliably in a totally autonomous manner for long periods of time (several months at least). Unfortunately, our experience is that simple chemical sensors like ion-selective electrodes quickly develop biofilms (Figure 2), and can drastically lose calibration within a few days when directly exposed to river water [6].

Therefore, electrochemical sensors need to be enclosed within a less hostile fluidic environment, and regularly recalibrated to extend the timescale over which they remain functional. This is an essential requirement if chemical sensors are to become part of a scalable sensor network model. However, this also means that the sensor must become part of a more complex fluidic system that can acquire samples, add reagents, perform calibrations with standards, perform cleaning cycles and so on. These functions in turn require control of fluid movement, using pumps and valves, storage of reagents and standards and analytical waste. This pushes the unit cost up to unscalable levels, in the range €15,000-€20,000 or more, with the bulk of the component cost arising from fluid handling [7]. Direct spectroscopic measurements are therefore an attractive option, as direct measurements can be made in the sample, and there is no responsive sensing surface to protect. However, the quality of the analytical information available through direct spectroscopy in the UV-Vis region is limited, mainly due to inability to detect most analytes of interest and lack of specificity for those that do absorb, like nitrate (ca. 190-230 nm) [8].

Direct IR spectroscopy can also be employed, and a number of environmentally important gases can be directly detected with good selectivity and sensitivity using this approach. We have developed very reliable autonomous sensor platforms for monitoring greenhouse gases like CH_4 and CO_2 [9], and deployments of these sensors are currently active in Ireland, Scotland and Brazil. The rugged construction of these autonomous platforms enables long-term in-situ monitoring of gas levels to be performed. The system is remotely deployable with GSM communications and integrated CH_4 and CO_2 infrared gas sensors. A remote server (currently running in our laboratories) receives transmissions from the deployed systems. From here, the data are parsed into the database whereupon it is uploaded onto the online portal (Google Fusion Tables [10]). Figure 3 shows these deployments and presents some sample data in each case in the Google Fusion Tables web interface [11]. So far, >40,000 measurements have been gathered from 6 deployments over a period of >1,000 days.

The web-based monitoring via an online portal enables gas activity to be characterised in a real-time and fully autonomous process. This is particularly important to waste sector activities such as landfilling and anaerobic wastewater treatment plants, where greenhouse gas emissions are required to be controlled and reduced. The autonomous nature of the monitoring platforms, and their high degree of reliability, allow longer term deployments, which is the key

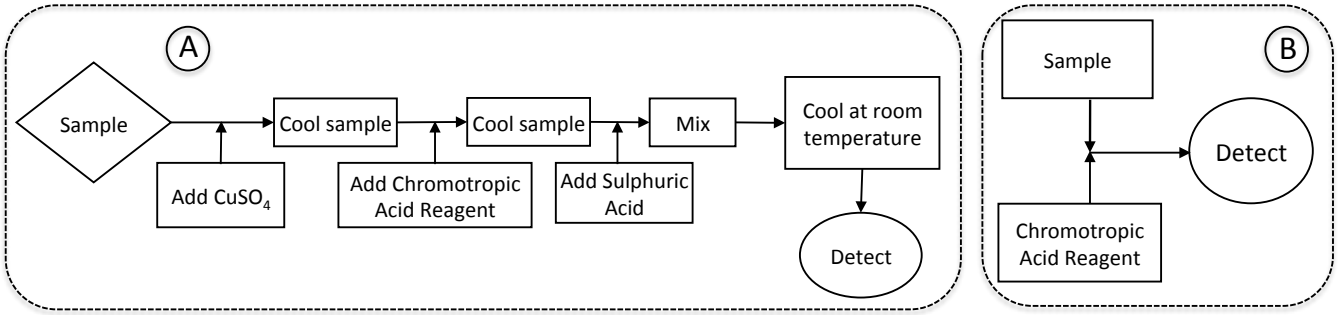

Figure 4: (A) The conventional chromotropic acid method for direct determination of NO_3^-, showing the various stages involved in generating the coloured complex; (B) The simplified chromotropic acid method.

to scalability. Furthermore, the time series data emerging from these deployments permit the identification of numerous events, which otherwise would have been missed using the existing infrequent manual sampling routines, which in turn can provide new insights to natural processes in the environment, and to more effective management of wastewater treatment plants and landfill sites [12,13].

III. REAGENT BASED MICROFLUIDICS

While this success with long-term gas sensing is generating significant interest, we are keen to produce platforms with similar capabilities for monitoring important analytes in water, such as nutrients like phosphate and nitrate. The most successful approach in our experience is to use reliable reagent based analytical methods coupled with optical detection, usually colorimetric based on LEDs and photo-detectors integrated with a microfluidic platform. Provided the reagents employed are stable, and can be mixed reproducibly with the sample under controlled conditions, the colour generated should also be reproducible, and the data therefore reliable, for as long as the reagent lasts. Using microfluidics (which typically involves relatively small sample/reagent volumes), it is relatively easy to perform several thousand assays using as little as 100 mL of reagent.

Previously we reported considerable success with a low cost platform for monitoring phosphate using the well-known 'yellow method' [9]. A key outcome from this work has been the realisation that the best approach is to make the required fluidics design as simple as possible, as this reduces costs and improves overall reliability. For phosphate, the fluidic design could not have been simpler – a 'T' design with one channel for sample and standards, and the other for reagent. For nitrate, the Griess method has been extensively investigated and applied with some success [14-16]. However, the need to use a reduction step (usually through a Cd-reduction column) and the indirect nature of the measurement (involves estimating NO_3^- through subtraction of NO_2^- from total NO_2^- and NO_3^-), makes for a more complex method than is ideal [17].

In terms of direct reagent based methods for nitrate detection, perhaps the best known is based on chromotropic acid [18], in which a yellow colour (λ_{max} ca. 430 nm) is formed when nitrate is mixed with the chromotropic acid reagent in the presence of concentrated sulphuric acid [19]. The various stages in the conventional laboratory version of the method are shown in figure 4 (A) [20]. Obviously, implementing this method in an autonomous fluidic system would be problematic, and, at least in this form, would have little chance of success because of the multiple stages involved, and the very aggressive nature of the concentrated sulphuric acid (>90% v/v). However, we have managed to modify this to a much simpler single reagent addition [21] followed by measurement of the colour using a low cost PEDD photodetector (figure 4 (B)) [22]. Figure 5 shows calibration curves generated using nitrate standards using the simplified method with a UV-Vis spectrophotometer and a prototype fluidic platform comprising two peristaltic pumps (reagent, sample), a mixing junction and integrated PEDD detector. The correlation coefficient in both cases was excellent.

The simplified method was also applied to a sample taken from the Broadmeadow estuary Co. Dublin (found

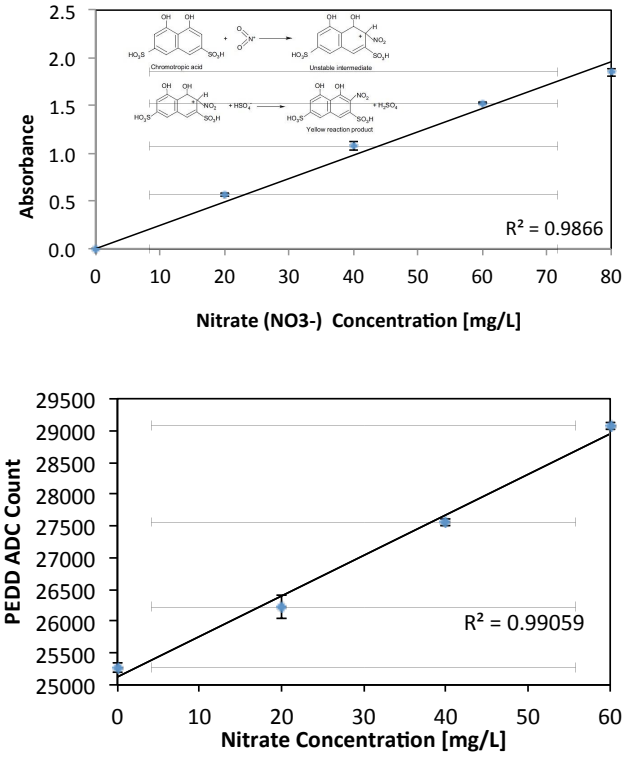

Figure 5: (top) Calibration plot for nitrate standards with a UV-Vis spectrophotometer to validate the simplified chromotropic acid method (scheme for the reaction given in the inset); (bottom) calibration plot generated with a prototype fluidic platform for nitrate detection using the simplified method.

10.18 mg/L) and compared to that of a HACH colorimeter (DR890, HACH LANGE Ireland) (found 10.70 mg/L). Based on these promising initial results, and the fact that the sulphuric acid concentration can be reduced to ca. 50% v/v if a heating stage is integrated into the method, the modified method is now much more amenable for integration into a fluidic platform.

IV. CONCLUSIONS

Direct sensing of key environmental chemical and biological parameters via platforms that require only occasional servicing (months, or years), and are available at a price point that facilitates scaled up deployments remains very challenging. Evidence of penetration of chemical sensors and biosensors into large-scale environmental sensor network deployments is scant due to high cost of ownership and the need for regular maintenance. The most reliable devices currently available operate in 'non-physical contact' mode with the sample. Spectroscopic sensors can be successfully used in long-term deployments to study particular gases, and

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measurements of the optical characteristics (scattering, fluorescence, absorbance) can be related to colour, turbidity, algal blooms, nitrate absorbance, while non-contact conductivity provides information on water salinity.

These devices are relatively robust and can be low cost, but tend to provide rather non-specific information about the general condition of the sample. Introducing very selective chemical and biological sensing approaches is much more difficult, for the reasons outlined above. Reagent-based microfluidics appears to be a good option in some cases, provided a suitable colorimetric or fluorescence method is available, and the reagents are stable under the conditions of deployment. Direct exposure of electrochemical sensors is not a good option for long-term water monitoring. Incorporation of these sensors into a microfluidic chip that can perform the required sampling and sample processing, and which exposes the sensors only occasionally to the sample is a reasonable strategy. However, for microfluidics to become adopted more widely for these applications, much lower cost fluid handling strategies that incorporate innovative pumping and valving functions need to be developed.

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