‘New Concepts in Chemical Sensing based on Stimuli-Responsive Materials’

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Invited Lecture presented at

Symposium D "Organic Electronics and hybrids: materials and devices”
Brazilian MRS Conference ‘XIII SBPMat’, João Pessoa
September 28-October 2, 2014
Ireland...
Dublin & DCU Location
Insight Centre for Data Analytics

- Biggest single research investment ever by Science Foundation
- Biggest coordinated research programme in the history of the state
- Focus is on ‘big data’ related to health informatics and pHealth
- Materials science will play a central role in the practical realisation of new concepts in chemical sensing and biosensing
Incredible advances in digital communications and computer power have profoundly changed our lives. One chemist shares his vision of the role of analytical science in the next communications revolution.

Digital communications networks are at the heart of modern society. The digitization of communications, the development of the Internet, and the availability of relatively inexpensive but powerful mobile computing technologies have established a global communications network capable of linking billions of people, places, and objects. Email can instantly transmit complex documents to multiple remote locations, and websites provide a platform for instantaneous notification, dissemination, and exchange of information globally. This technology is now pervasive, and those in research and business have multiple interactions with this digital world every day. However, this technology might simply be the foundation for the next wave of development that will provide a seamless interface between the real and digital worlds.

The crucial missing part in this scenario is the gateway through which these worlds will communicate. How can the digital world sense and respond to changes in the real world? Analytical scientists—particularly those working on chemical sensors, biosensors, and compact, autonomous instruments—are...
Grand Challenge

• To develop a scalable model for chemical sensing in remote, hostile locations (e.g., inside the body, in the environment)
  – Completely autonomous devices
  – Must provide reliable, high quality data
  – Capable of long-term (months, years) independent operation

• We can do this already –can’t we?
  – No! There are no examples of long-term implantable chem/bio-sensors;
  – in the environment (water), units cost typically €20K++
An eye-mountable device includes an electrochemical sensor embedded in a polymeric material configured for mounting to a surface of an eye. The electrochemical sensor includes a working electrode, a reference electrode, and a reagent that selectively reacts with an analyte to generate a sensor measurement related to a concentration of the analyte in a fluid to which the eye-mountable device is exposed. The working electrode can have at least one dimension less than 25 micrometers. The reference electrode can have an area at least five times greater than an area of the working electrode. A portion of the polymeric material can surround the working electrode and the reference electrode such that an electrical current conveyed between the working electrode and the reference electrode is passed through the at least partially surrounding portion of the transparent polymeric material.
• Ca. 3,600 floats: temperature and salinity
• Only 216 reporting chem/bio parameters (ca. 6%)
• Of these nitrate (38), DO (202), Bio-optics (43), pH (3)

DO is by Clark Cell (Sea Bird Electronics) or Dynamic fluorescence quenching (Aanderaa)

See https://picasaweb.google.com/JCOMMOPS/ArgoMaps?authuser=0&feat=embedwebsite

‘calibration of the DO measurements by the SBE sensor remains an important issue for the future’, Argo report ‘Processing Argo OXYGEN data at the DAC level’, September 6, 2009, V. Thierry, D. Gilbert, T. Kobayashi
pH sensing – wasn’t that solved by Nikolskii in the 1930’s?

Wendy Schmidt Ocean Health XPRIZE

$2,000,000 up for grabs! Task is to provide a way to do reliable measurements of pH in the ocean environment

The winner will almost certainly be a reagent based platform, not a conventional chemical sensor
After decades of intensive research, our capacity to deliver successful long-term deployments of chemo/bio-sensors in remote locations is still very limited.
Any good news?
CH$_4$/CO$_2$ sensing using IR Sensors

- Control Based on MSP430 microcontroller
- Data communication by GSM to cloud database
- Power allowing 10 weeks at 4 samples/day
- Extraction from gas source at 0.6 L/min
- Sampling using IR sensors to measure CH$_4$/CO$_2$ and/or pressure
- Weatherproof casing rated to IP68
Camila at DCU

• Training in the NCSR (left); on site with Fiachra and Dylan (top); Effect of Solar Panel, data from this deployment (Bottom)
To Mairiporã City

anaerobic lagoon operated by SABESP (Ernane, Diego and Ademar)
Monitoring GHG emissions

Collaboration with University of São Paulo, Brazil
– Two systems deployed, substantial commercial interest for more

**Anaerobic lagoon, WWTP, Mairiporã**

**Effluent pond, Pirassununga**

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**Accumulator bag moved**

**Daily fluctuations**

Adaptive Sensors Group, DCU

FTC visit: 19th September 2013
So everything is great! Yes??

No! Chem/Bio-sensors are difficult to keep working in water and (even worse!) blood
What is a Chemo/Bio-Sensor?

‘a device, consisting of a transducer and a chemo/bio-sensitive film/membrane, that generates a signal related to the concentration of particular target analyte in a given sample’

Conventionally, chem/Bio-sensors employ selective BINDING & TRANSDUCTION at the device surface, which is pre-functionalised with binding sites selective for a chosen analyte. Binding events at the surface provide a signal observable in the macroscopic world (COMMUNICATION)
Typical membrane cocktail (%w/w); PVC: 33%, NPOE (plasticiser): 66%; ionophore/exchanger: 1% (ratio at least 2:1 by mole); dissolve in a volatile solvent e.g. THF and cast membrane from this solution.
Blood Analysis; Implantable Sensors

Fig. 3. Comparison of plasma sodium analysis using the array-FIA approach with a SMAC analyser. Good correlation without bias is obtained [5].

1985: Catheter Electrodes for intensive care – function for 24 hrs

Dr. David Band, St Thomas’s Hospital London


Ligand (and variations of) used in many clinical analysers for blood Na⁺ profiling
Change in Electrode Function over Time

See Electrochimica Acta 73 (2012) 93–97

 stored in $10^{-9}$M Pb$^{2+}$, pH=4

Continuous contact with river water

Conventional PVC-membrane based ISEs
Biofilm Formation on Sensors

- Electrodes exposed to local river water (Tolka)
- ‘Slime test’ shows biofilm formation happens almost immediately and grows rapidly
Remote, autonomous chemical sensing is a tricky business!
Direct Sensing vs. Reagent Based LOAC/ufluidics

Direct Sensing

- Outside world
- Sensor
- Signal
- Sample
- Molecular interactions

LOAC Analyser

- Source
- Reagents
- Sample, standards
- Reaction manifold
- Detector
- Waste
- Blank

Graph:
- Sample vs. Time
- BL
Many people, myself included, expected that the ability to manipulate fluid streams, in microchannels, easily, would result in a proliferation of commercial LoC systems, and that we would see applications of these devices proliferating throughout science. In fact, it has not (yet) happened.

Microfluidics, to date, has been largely focused on the development of science and technology, and on scientific papers, rather than on the solution of problems.

How to advance fluid handling in LOC platforms: re-invent valves (and pumps)!

- Conventional valves cannot be easily scaled down - Located off chip: fluidic interconnects required
  - Complex fabrication
  - Increased dead volume
  - Mixing effects

- Based on solenoid action
  - Large power demand
  - Expensive

Solution: soft-polymer (biomimetic) valves fully integrated into the fluidic system
Photoswitchable Materials

\[
\begin{align*}
\text{Off (spiropyran)} & \quad \leftrightarrow \quad \text{On (merocyanine)} \\
\end{align*}
\]

BREAKING NEWS: For more background and discussions, see the wonderful poster by Larisa Florea: ‘Photo-Responsive Polymers based on Spiropyran as Sensors and Actuators’, L.Florea, A.Dunne, H.Straub, S.McArdle and D.Diamond; on display at a secret location in the poster hall....
Polymer based photoactuators based on pNIPAAm

**Figure 3.** (a, b) Images of the pSPNIPAAm hydrogel layer just after the micropatterned light irradiation. Duration of irradiation was (●, red) 0, (◇) 1, and (■, green) 3 s. (c) Height change of the hydrogel layer in (●) non-irradiated and (◇) irradiated region as a function of time after 3 s blue light irradiation.
Photo-actuator polymers as microvalves in microfluidic systems

Can we go from this:
To Photo-Fluidics & Detection

- Fluidic handling completely integrated into the microfluidic chip
- Valve structures created post chip fabrication by in-situ photopolymerisation
- Valves actuated remotely using light (LEDs)
- Detection is via LED colorimetric/fluorescence measurements

Fluidic Chip is completely sealed – no need for interconnects to detection/flow components
Conclusions

• Our strategy is to create an integrated environment based on cutting edge technologies that allow us to control the placement and 3-D form of emerging multifunctional materials in highly precise locations

• Strongly linked with fundamental materials chemistry and materials biology research

• Integrated with suites of characterisation equipment; e.g. SEM, imaging microscopies, spectroscopies

• Progress requires an international research effort
  – Academic partnerships and exchanges
  – Industry must be involved
  – Multinational and indigenous SMEs/spin-outs
Thanks to.....

Thanks for the invitation.