Professor Dermot Diamond, Dublin City University
‘Sensor Roadmap: Future Trends on (Marine) Chemical Sensor Development’
COMMON SENSE 40 month meeting
Barcelona, Spain, 26 January 2017
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’

Chemo/Bio-sensing involves selective binding & transduction on the device surface; this also implies the target analyte MUST meet the device surface (location & movement). It provides a signal observable in the macroscopic world (communication).
(Ron Ambrosio & Alex Morrow, IBM TJ Watson)

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
Remote (Continuous) Sensing Challenges: Platform and Deployment Hierarchies

Physical Transducers – low cost, reliable, low power demand, long life-time
Thermistors (temperature), movement, location, power, light level, conductivity, flow, sound/audio, …..

Chemical Sensors – more complicated, need regular calibration, more costly to implement
Electrochemical, Optical, .. For metal ions, pH, organics…

Biosensors – the most challenging, very difficult to work with, die quickly, single shot (disposable) mode dominant use model
Due to the delicate nature of biomaterials enzymes, antibodies….

Gas/Air Sensing – easiest to realise
Reliable sensors available, relatively low cost
Integrate into platforms, develop IT infrastructure, GIS tools, Cloud Computing

On-land Water/ Monitoring
More accessible locations
Target concentrations tend to be higher
Infrastructure available

Marine Water
Challenging conditions
Remote locations & Limited infrastructure
Concentrations tend to be lower and tighter in range
Change in Electrode Function over Time

See Electrochimica Acta 73 (2012) 93–97

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

Continuous contact with river water

Conventional PVC-membrane based ISEs
• 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

- sensor
- sample
- molecular interactions
- signal
- outside world

LOAC Analyser

- sample, standards
- reagents
- source
- detector
- reaction manifold
- waste
- s
- BL blank
- BL sample
Biofouling of sensor surfaces is a major challenge for remote chemical sensing – both for the environment and for implantable sensors.
• Ca. 4,000 (3918) floats: temperature and salinity

• Bio/Chem: Nitrate (64), DO (280), Bio-optics (115), pH (25)

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?

<table>
<thead>
<tr>
<th>EVENT</th>
<th>DATE</th>
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<tbody>
<tr>
<td>Launch (San Francisco)</td>
<td>September 2013</td>
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<tr>
<td>PHASE 1: Innovation Phase</td>
<td></td>
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<tr>
<td>Registration opens</td>
<td>January 1, 2014</td>
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<td>Early-bird Registration deadline</td>
<td>March 2014</td>
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<tr>
<td>OA Solutions Fair and Kick-Off Event</td>
<td>March 2014</td>
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### OVERVIEW

**The Challenge: Improve Our Understanding of Ocean Acidification**

The Wendy Schmidt Ocean Health XPRIZE is a $2 million global competition that challenges teams of engineers, scientists and innovators from all over the world to create pH sensor technology that will affordably, accurately and efficiently measure ocean chemistry from its shallowest waters... to its deepest depths.

There are two prize purses available (teams may compete for, and win, both purses):

- A $1,000,000 Accuracy award – Performance focused ($750,000 First Place, $250,000 Second Place):
  - To the teams that navigate the entire competition to produce the most accurate, stable and precise pH sensors under a variety of tests.

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
SAMI-pH - Ocean pH Sensor

- Measures pH$_T$ (total hydrogen scale) in the marine pH range of 7-9
- Uses a highly accurate colorimetric reagent method
- System does not suffer from the drift that plagues most electrode based pH probes
- Designed to provide researchers with valuable *in-situ* time series data at depths up to 600 meters
- 234-day deployment capability (hourly measurements, 25°C)
- Extra battery package allows the SAMI-pH to run for more than a year
- Can support up to 3 external instruments (e.g., PAR, dissolved oxygen, chlorophyll fluorometer, CTD)
- Supports Seabird underwater inductive modems or external loggers via RS-232

**HEAL OUR OCEANS**
The Wendy Schmidt Ocean Health XPRIZE promises to improve our understanding of how CO$_2$ and other greenhouse gases are influencing ocean health, and how we can better protect marine life.
And for nutrients....
From 29 to 6 participants...

Winners will be announced March 2nd 2017 in Hawaii
Heavy Metals Sensing System
Current State of the Art

- Units are big – basically lab units repackaged into boxes
- Expensive - >€20K per unit + recurrent costs is not unusual
Achieving Scale-up

1. **Evolutionary** development, cost driven down, reliable, improved scalability

2. **Revolutionary** breakthroughs in materials science; hidden complexity, biomimetic platforms, all fluid handling integrated on chip, indefinitely self-sustaining

Cost/Complexity ->

<table>
<thead>
<tr>
<th>Current platforms</th>
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<tr>
<td>€ &gt; 20,000</td>
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<td>€ &gt; 2,000</td>
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<td>€ &lt; 200</td>
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<td>€ &lt; 20</td>
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<tr>
<td>€ &lt; 2</td>
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Massively scaled deployments of the future

Scalability ->
Cost Comparison Analysis (€)

The €20 analyser

Gen1

Gen2

Future

Cost categories:
- Fluidics
- Electronics
- Housing
Extend Period of Use via Arrays of Sensors....?

• If each sensor has an in-use lifetime of 1 week....

• And these sensors are very reproducible....

• And they are very stable in storage (up to several years)....

Then 50 sensors when used sequentially could provide an aggregated in-use lifetime of around 1 year

But now we need multiple valves integrated into a fluidic platform to select each sensor in turn
Microfluidics – Evolution…

Engineering Inspired → BiolInspired
But not everything is integrated.....
Bioinspired Fluidics
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 Actuators

Merocyanine Spiropyran

UV

VIS, Δ

ABS

Off (spiropyran)
On (merocyanine)

NM

400 450 500 550 600 650

0 0.5 1 1.5 2 2.5 3
Poly($N$-isopropylacrylamide)

- pNIPAAm exhibits inverse solubility upon heating
- This is referred to as the LCST (Lower Critical Solution Temperature)
- Typically this temperature lies between 30-35°C, but the exact temperature is a function of the (macro)molecular microstructure
- Upon reaching the LCST the polymer undergoes a dramatic volume change, as the hydrated polymer chains collapse to a globular structure, expelling the bound water in the process

![Diagram of pNIPAAm](image)

- Hydrophilic
- Hydrophobic
- Hydrated Polymer Chains
- Loss of bound water -> polymer collapse
Photo-actuator polymers as microvalves in microfluidic systems

System Components

- Container A
- Container B
- Power Supply
- Microfluidic chip w/ valve
- Fluigent Sensor
- Laptop & Software
Optimisation of valve dimensions

1.7 mm mask

First example of actuating polymer gels as reusable valves for flow control on minute time scales (> 50 repeat actuations)

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

- Fluidic handling completely integrated into the microfluidic chip
  - Valves actuated remotely using light (LEDs)
  - Detection is via LED colorimetric measurements
  - Photo-controlled uptake and release
‘Daisy’ – Micro/Nano Scaled Porous Structure
Merging of Materials, Devices and Data

Data and Information; IOT

Devices and Platforms

MATERIALS
Physics Chemistry Biology Engineering (photonics, electronics, fluidics, 4D materials)
Sensing our Environment: From Innovative Materials to Autonomous Sensors & Earth Observation

Technologies for monitoring the quality of natural waters and drinking water, and compliance of wastewater with regulatory standards, are set to change dramatically in terms of price and performance. The impact of 'big environmental data' will be truly revolutionary for businesses and for citizens.

Water quality issues do not respect national borders – pollution arising from one state can affect neighboring states, and the effects of climate change arise from human activity on a global scale. The scale of the opportunity for new technologies and associated services and businesses is therefore global – solutions developed for one scenario will be adaptable for many related applications and locations. Services will be 'cloud' based, capable of accessing and analyzing data from multiple sources and locations, and providing environmental information that can be highly localized or global in range.

Realising the potential of these technologies requires input that is truly multidisciplinary in nature, and encompassing a wide variety of stakeholders. This symposium will bring together experts in water analysis and monitoring, innovative instrumentation, satellite remote sensing of water status, and water treatment to discuss current and future trends and developments in technologies related to water. Participants will be drawn from University, industry and agency backgrounds, from Europe and North America. Key topics will include the rapidly evolving nature of water quality sensing devices, the integration of information from multiple sources (in-situ sensors, satellite remote sensing, and drone based multispectral imaging), and the increasing use of mobile phones by citizens to perform sophisticated environmental analytical measurements and share data (citizen science and ‘crowd’ sensing). The symposium is supported by NAPES (a European Multipartner project focused on developing next generation water quality sensing technologies – www.napes.eu), The National Centre for Sensor Research (www.ncsr.ie) and the DCU Water Institute.

Confirmed Speakers:
Prof. Dermot Diamond DCU, Prof. Jed Harrison University of Alberta; Prof. Graham Mills, University of Portsmouth; Mr. Coleman Concanon, EPA Ireland; Breda Moore, TE Laboratories; Mr. Liam Curran, Enterprise Ireland; Dr. Bas van der Griff, Deltas

Date: 27th & 28th March 2017
Venue: Croke Park, Jones Road, Dublin 3, Ireland.

Contact: angela.lally@dcu.ie

Cead Mile Failte oraibh uilig!!

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Thanks to…..

• Members of my research group
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• Academic and Industry Research Partners
Thank you for your Attention

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