How Fundamental Materials Science will Generate Revolutionary Breakthroughs in Environmental Monitoring Technologies

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Sensors100 ‘Sensors in the Environment Conference’
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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
‘Grand Challenge for Analytical Chemistry’

• “A ‘Grand Challenge’ posed for analytical chemistry is to develop a capability for sampling and monitoring air, water and soil much more extensively and frequently than is now possible”

• “Such goals will require improvements in sampling methodology and in techniques for remote measurements, as well as approaches that greatly lower per-sample and per-measurement costs”

Royce Murray, Editorial, Analytical Chemistry, February 2010
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.

Dermot Diamond
Dublin City University (Ireland)

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...
Internet-enable every sensor measurement!

Major Business Opportunities in this Space

- Stakeholder (individual)
- Stakeholder (Gov. Agency)
- Stakeholder (Industry Partners)
- Stakeholder (Public Service)

Internet Scale Data Mining and Control

Integration Hub

Internet scale control

Environment Food Health

Internet-enable every sensor measurement!
Apple hiring medical device staff, shares break $600 mark

Apple, iWatch & Health Monitoring

May 7th 2014

‘Over the past year, Apple has snapped up at least half a dozen prominent experts in biomedicine, according to LinkedIn profile changes.

Much of the hiring is in sensor technology, an area Chief Executive Tim Cook singled out last year as primed "to explode."

Industry insiders say the moves telegraph a vision of monitoring everything from blood-sugar levels to nutrition, beyond the fitness-oriented devices now on the market.’

"This is a very specific play in the bio-sensing space," said Malay Gandhi, chief strategy officer at Rock Health, a San Francisco venture capital firm that has backed prominent wearable-tech startups, such as Augmedix and Spire.

‘Healthkit’ personal health information platform developed in collaboration with Mayo Clinic
Google Contact Lens

United States Patent Application  20140107445
Kind Code  A1   Liu; Zenghe     April 17, 2014
Microelectrodes  In  An  Ophthalmic  Electrochemical  Sensor

Abstract
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
congestion of the analyte in a fluid to which the eye-mountable device is exposed.

• Use model is 24 hours max, then replace;
• likely to leverage Google Glass infrastructure;
• Novartis now working with Google.


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
• 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
After decades of intensive research, our capacity to deliver successful long-term deployments of chemo/bio-sensors in remote locations is still very limited.
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

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

Dr. David Band, St Thomas’s Hospital London

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


Ligand (and variations of) used in many clinical analysers for blood Na⁺ profiling.
Lowering the LOD of ISEs (1999)


Lowering the Detection Limit of Solvent Polymeric Ion-Selective Electrodes. 1. Modeling the Influence of Steady-State Ion Fluxes

Tomasz Sokalski,* † ‡ § Titus Zwickl,† Eric Bakker,* † ‡ and Ernö Pretsch* †

Department of Organic Chemistry, Swiss Federal Institute of Technology (ETH), Universitatsstrasse 16, CH-8092 Zürich, Switzerland, and Department of Chemistry, Auburn University, Auburn, Alabama 36849
ISEs: Low Limit of Detection

- See series of papers by Pretsch, Bakker and Sokalski

Lower limits of detection should be possible if the primary ion concentration in the internal filling soln is kept low.

Ion transfer across membrane OCCURS IN BOTH DIRECTIONS!

At low sample concentrations, outer boundary region rapidly becomes saturated due to ion transport from internal filling solution.

Filling Soln

\[ \text{ML}^+ \]

\[ M^+ + L \]

\[ M^+ \]

\[ V \]
Figure 2. Measurement procedure of potentiometric trace level determinations of Pb^{2+} by calibrating with a series of lead ion solutions at higher concentration. Shown are the emf responses as a function of the sample activity for each of the separate measurements. The slopes for each of the five-point calibrations are, from top to bottom, 28.5, 28.4, 28.6, 28.6, 28.5, and 28.9 mV/decade.

Figure 6. Potentiometric determination of Pb^{2+} in unspiked Zurich tap water at different pH values (see also Figure 5). Horizontal dotted lines: measurement of free lead in the native sample (lower value) and of total lead after buffering the pH to 4.0 (higher value). Vertical arrow: lead concentration obtained with ICPMS.

Mass production of SCISEs and SCREs
(Alek Radu and Salzitsa Anastasova)

- Using Screen Printer DEK 248 silver paste was printed on plastic sheets.
- Next, carbon was printed twice, with 15 minutes of curing in oven at 200°C between successive prints.
- After finishing carbon, the insulating layer was printed and UV-cured.
- Conducting polymer Poly (3-octylthiophene) (10⁻² M in Chloroform) was dropcast (initially) or grown electrochemically (later) on printed platforms.
- The CP is covered with a PVC membrane cocktail containing active components for ISEs and reference electrodes (Fluka)
Improving sensor reproducibility

Manual fabrication, conventional design

SP fabrication, **manual deposition of CP layer (POT) and sensing layer**

After zero point correction, slopes are virtually identical: single point calibration for each sensor
EC-deposition of CP Layer -> highly Reproducible Sensors

SP fabrication, **electrochemical deposition of CP (PEDOT)**, manual deposition of sensing layer;
Applied to analysis of river water samples

<table>
<thead>
<tr>
<th>electrode number</th>
<th>Baseline, mV Day0</th>
<th>Slope, mV Day0</th>
<th>LOD Day0</th>
<th>Eo/mV Day0</th>
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<tr>
<td>1</td>
<td>-176.11</td>
<td>28.75</td>
<td>-8.00</td>
<td>53.87</td>
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<tr>
<td>Mean</td>
<td>-176.18</td>
<td>28.74</td>
<td>-7.96</td>
<td>52.63</td>
</tr>
<tr>
<td>SD</td>
<td>0.12</td>
<td>0.01</td>
<td>0.04</td>
<td>1.38</td>
</tr>
</tbody>
</table>

\[ y = 0.9705x + 0.0947 \]
\[ R^2 = 0.9912 \]

**Screen Printed ISEs**

- V. low cost (cents), mass-produced
- Almost perfect reproducibility -> calibrate 1 per batch!
- V. high sensitivity -> LOD in low PPB for Pb\(^{2+}\); better than ICP-MS!, ..... & V. selective

- Each ISE used once; unknown estimated using 4-point standard additions

Would it be possible to use these electrodes in a remote autonomous instrument?
Change in Electrode Function over Time

See Electrochimica Acta 73 (2012) 93–97

Day 0: \( y = 28.739x + 51.806 \)  
\( R^2 = 0.99981 \)

Day 4: \( y = 28.029x + 48.261 \)  
\( R^2 = 0.99705 \)

Day 8: \( y = 27.076x + 40.137 \)  
\( R^2 = 0.99892 \)

EMF/mV

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

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
Control of membrane interfacial exchange & binding processes

Remote, autonomous chemical sensing is a tricky business!
Direct Sensing vs. Reagent Based LOAC/ufluidics

Direct Sensing
- Outside world
- Sensor
- Sample
- Molecular interactions

LOAC Analyser
- Source
- Reaction manifold
- Reagents
- Sample, standards
- Detector
- Waste
- Blank
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.

Phosphate: The Yellow Method

Mixture (Reagent)

\[(NH_4 VO_3) + (NH_4)_6 Mo_7 O_{24}\cdot 4H_2 O, HCl \text{ conc.}\]

Sample

\[(KH_2 PO_4)\]

\[(NH_4)_3 PO_4\cdot NH_4 VO_3\cdot 16 MoO_3\]

- yellow vanadiumolybdophosphoric acid is formed when ammonium metavanadate and ammonium molybdate (mixture) reacts with phosphate (acidic conditions)

- In conventional (molybdate) method, ascorbic acid is used to generate the well-known deep blue complex (v. fine precipitate)
Microfluidic Chip

- Micromilled PMMA
- 12.5mm Optical Cuvette Length
- 200um wide serpentine mixing channel
Deployment at Osberstown WWTP

- Phosphate monitoring unit deployed
- System is fully immersed in the treatment tank
- Wireless communications unit linked by cable
- Data transmitted to cloud
Biofouling of sensor surfaces is a major challenge for remote chemical sensing – both for the environment and for implantable sensors.
Autonomous Chemical Analyser

49-Day Trial at Waste Water Treatment Plant

Prototype P-Analyser

Reference monitor
Achieving Scale-up

1. Evolutionary development, cost driven down, reliable, improved scalability
   - Current platforms
     - $>$20,000
     - $>$2,000
     - $<$200

2. Revolutionary breakthroughs in materials science; hidden complexity, biomimetic platforms, all fluid handling integrated on chip, indefinitely self-sustaining
   - Massively scaled deployments of the future
     - $<$20
     - $<$2
     - $<$200
Cost Comparison Analyser (€)

The €20 analyser

- Fluidics
- Electronics
- Housing
Use 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
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

UV → VIS, Δ

Merocyanine Spiropyran

Off (spiropyran) → On (merocyanine)

ABS

400 450 500 550 600 650

NM
Non-specific (BSP) and specific (MC) Interactions

BSP

H$_2$O

MC

Charged species
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
Polymer based photoactuators based on pNIPAAm

poly(N-isopropylacrylamide) (PNIPAAm)

Formulation as by Sumaru et al\textsuperscript{1}


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

Trihexyltetradecylphosphonium dicyanoamide [P_{6,6,6,14}]^{+}[dca]^{-}

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
Thanks to.....

Members of my research group

NCSR, DCU

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Thanks for the invitation