

'Materials Science and the Sensors Revolution' Re-Inventing Chemical Sensing for Widely Distributed Environmental Sensing

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presented at the workshop

'Microfluidics and Microsensor Technology for Oceanographic and Environmental Science Applications'

National Oceanography Centre
University of Southampton Waterfront Campus April 10th 2013



Keynote Article: August 2004, Analytical Chemistry (A



Dermot Diamond **Dublin City University**

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.

gital communications networks are at the heart of modern society. The digitization of communications, the development of the Internet, and the availability of relative ly inexpensive but powerful mobile computing technologies have established a global communications network capable of linking billions of people, places, and objects. Email carrimmant ly 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

Dermot Diamond, Anal. Chem., 76 (2004) 278A-286A (Ron Ambrosio & Alex Morrow, IBM TJ Watson)

Flooding Cork November 2009 – in the news Trish Examiner





Calls for warning system as website predicts floods

By Fiachra Ó Cionnaith

WEDNESDAY, NOVEMBER 25, 2009

CALLS have been repeated for a complete roll-out of a nationwide flood alert system after an independent website appeared to indicate that the flooding crisis in Cork city could be easily predicted.

Reacting to almost a fortnight of heavy rain and flooding in large parts of the south and west, Fine Gael environment spokesman Phil Hogan said it was essential that a "badly needed" national system was implemented to warn people in danger of a flood crisis.

However, he claimed despite plans being in place for such a step to be taken, there was little impetuous from Government to ensure the vital defence is implemented.

"The widespread devastation caused by the flooding has highlighted the immediate need for an action plan so this never happens again," said the opposition spokesperson.

"This is vital for preparing for future events. It may not always be possible to stop the waters but people need to know what is coming to prevent as much damage as possible.

"Britain operates an advanced monitoring system for flooding and communicate directly to potentially affected people through a variety of mediums such as telephone messaging, media alerts to action and through other methods such as loud-hailer and siren systems. This could be provided for Ireland."

His comments came after the independent website corkfloodwatch.com appeared to detail the exact levels floodwaters were due to rise to over the past week across Cork city and county.

The figures would have helped to give those in potentially affected areas a clearer indication of whether they were likely to face further flooding, allowing them time to prepare effectively.

According to the site — which is run by the National Centre for Sensor Research, the Tyndall National Institute, IDS Monitoring, and the South Western River Basin District — by yesterday evening flood water levels in Cork city had fallen below a metre from a high of more than five metres over the weekend.

Responsibility has yet to be decided; Legal proceedings not yet happened



Podge and Rodge and Environmental Monitoring

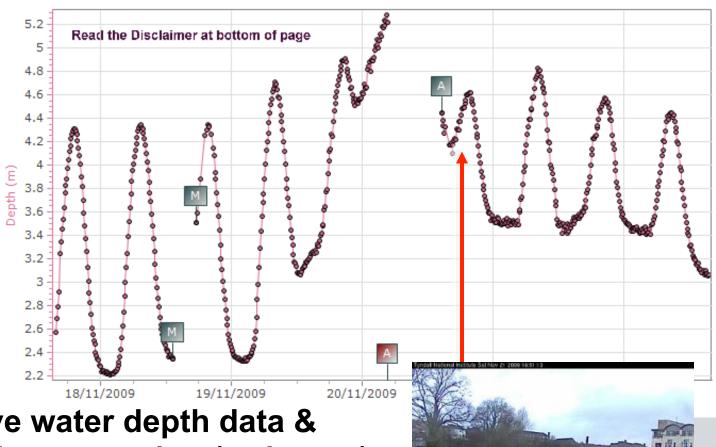






Autonomous River Depth Measurements €250million flood damage





Live water depth data & video streaming (web-cam). Providing data in real time for monitoring and analysis



Grand Challenge for Analytical Chemistry

- distributed environmental sensing
 - "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





So lets do in-situ chemical sensing....

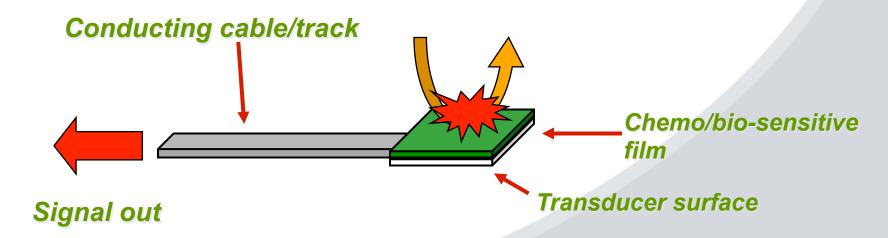
Just stick a chemical sensor into the sample and off you go....





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'

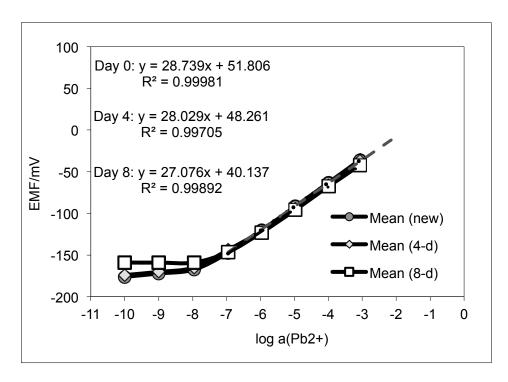


Chemo/Bio-sensing involves selective **BINDING** & **TRANSDUCTION** on the device surface; this also implies the target analyte MUST meet the device surface (**LOCATION** & **MOVEMENT**). It provides a signal observable in the macroscopic world (**COMMUNICATION**)

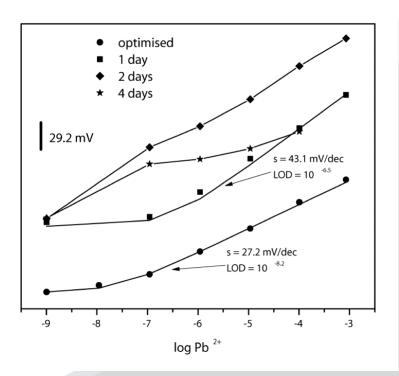


Change in Electrode Function over Time





stored in 10⁻⁹M Pb²⁺, pH=4

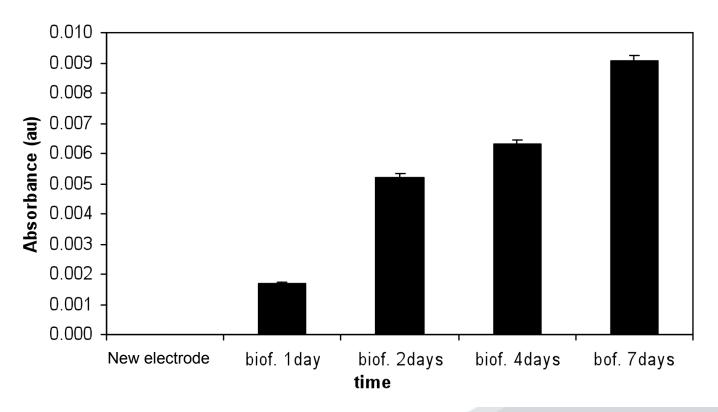


Continuous contact with river water



Biofilm Formation on Sensors



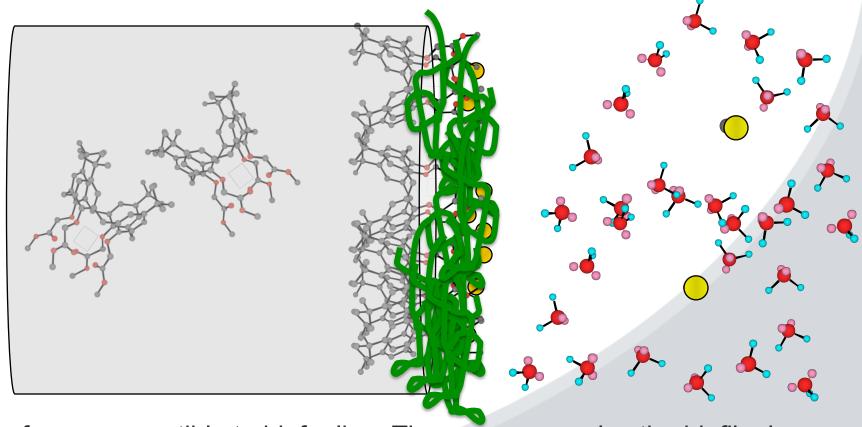


- Electrodes exposed to local river water (Tolka)
- 'Slime test' shows biofilm formation happens almost immediately and grows rapidly



Fundamental Problem: Sensor surface will change with time!





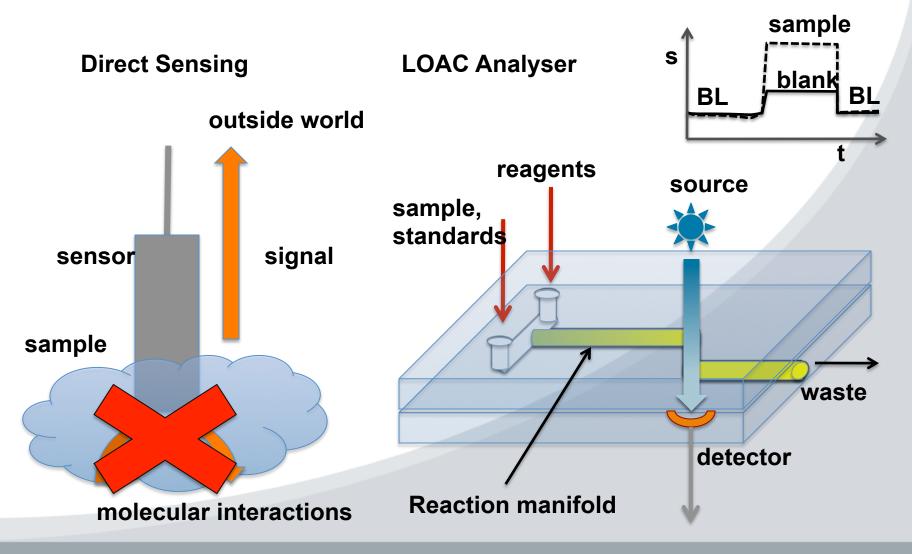
Surfaces susceptible to biofouling: The sensor samples the biofilm layer, not the bulk solution!

=> drift, loss of sensitivity/LOD/Selectivity => regular calibration (liquid handling) => high cost of ownership



Direct Sensing vs. Reagent Based LOAC/ufluidics





MicroTAS/Lab on a Chip/Microfluidics CL



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, <u>rather than on the solution</u> <u>of problems</u>

Editorial 'Solving Problems', George Whitesides, Lab Chip 10 (2010) 2317-2318



Phosphate: The Yellow Method



- yellow vanaomolybdophosphoric 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)



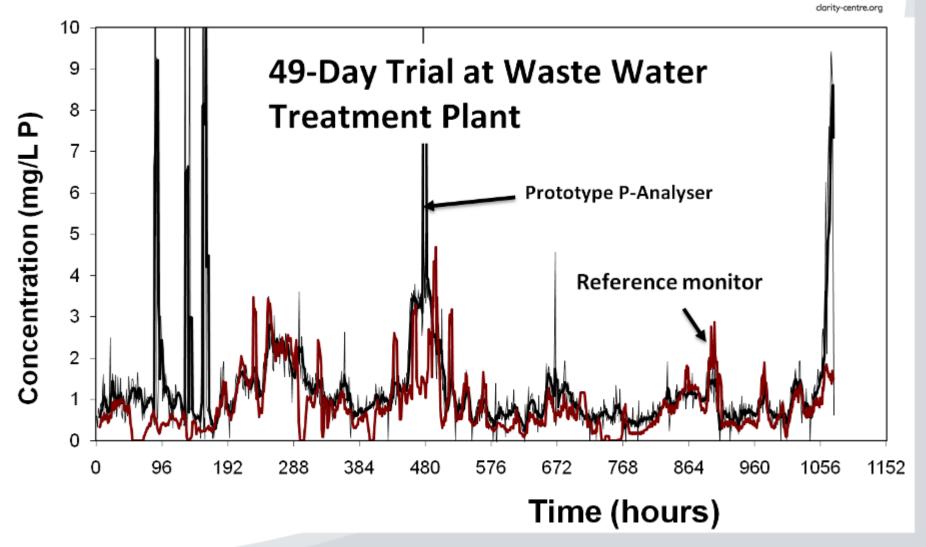
2nd Generation Analyser: Design CLARITY





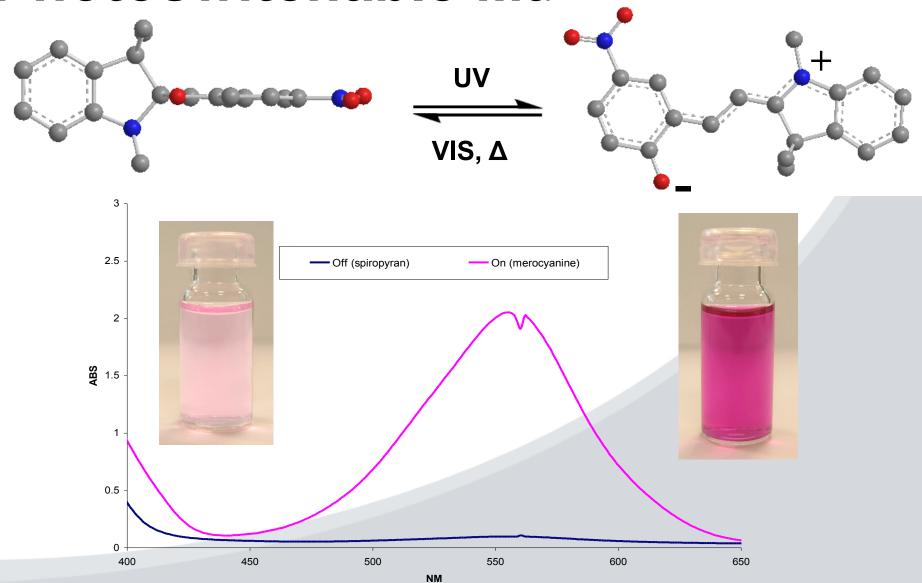


Autonomous Chemical Analyser,



Photoswitchable Materials

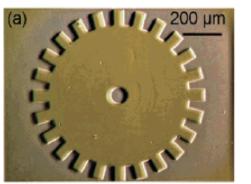


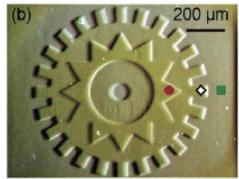




Polymer based photoactuators based on pNIPAAm







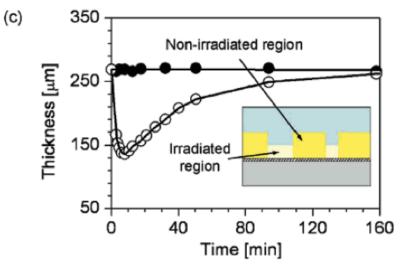


Figure 3. (a, b) Images of the pSPNIPAAm hydrogel layer just after the micropatterned light irradiation. Duration of irradiation was $(\bullet, \text{red}) \ 0$, $(\diamond) \ 1$, and $(\blacksquare, \text{green}) \ 3$ s. (c) Height change of the hydrogel layer in (\bullet) non-irradiated and (\bigcirc) irradiated region as a function of time after 3 s blue light irradiation.

poly(N-isopropylacrylamide) (PNIPAAm) Formulation as by Sumaru et al¹ 1) Chem. Mater., 19 (11), 2730 -2732, 2007.

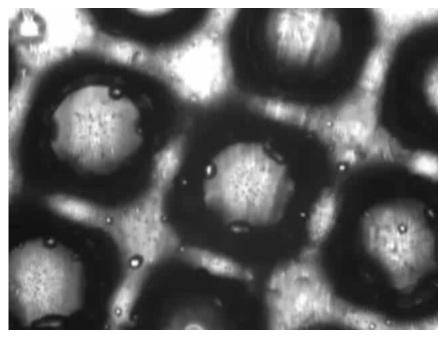
Limitations

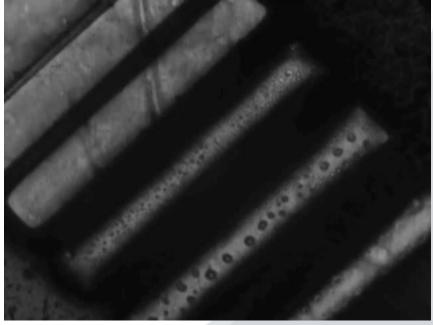
- (1) Gel must be acidified to swell
- (2) Recovery to swollen form is slow



Build Dynamic pNIPAAm Structures within Microchannels







Ntf2 pillars speed x3

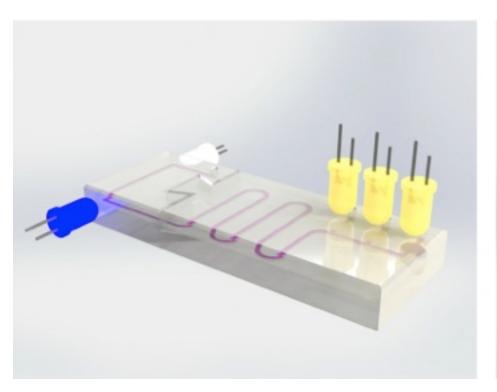
DCA lines speed x4

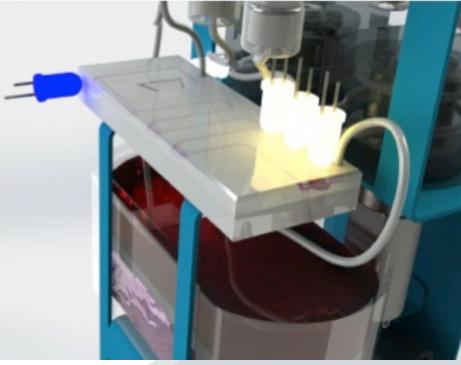
With Dr Peer Fischer, Fraunhofer-Institut für Physikalische Messtechnik (IPM), Freiburg



Photo-Fluidics & Detection







- Fluidic handling completely integrated into the microfluidic chip
- Valves actuated remotely using light (LEDs)
- Detection is via LED colorimetric measurements



Conclusions



- Demand will rise rapidly for autonomous platforms capable of remote monitoring of important environmental quality parameter
- Cost basis for these platforms must be driven down substantially; while maintaining or improving performance
- Tremendous scope to link exciting fundamental materials science with solving practical needs
- Deployments will open access to new data sources for environmental scientists
- New issues related to 'big data' will emerge who owns the data?

