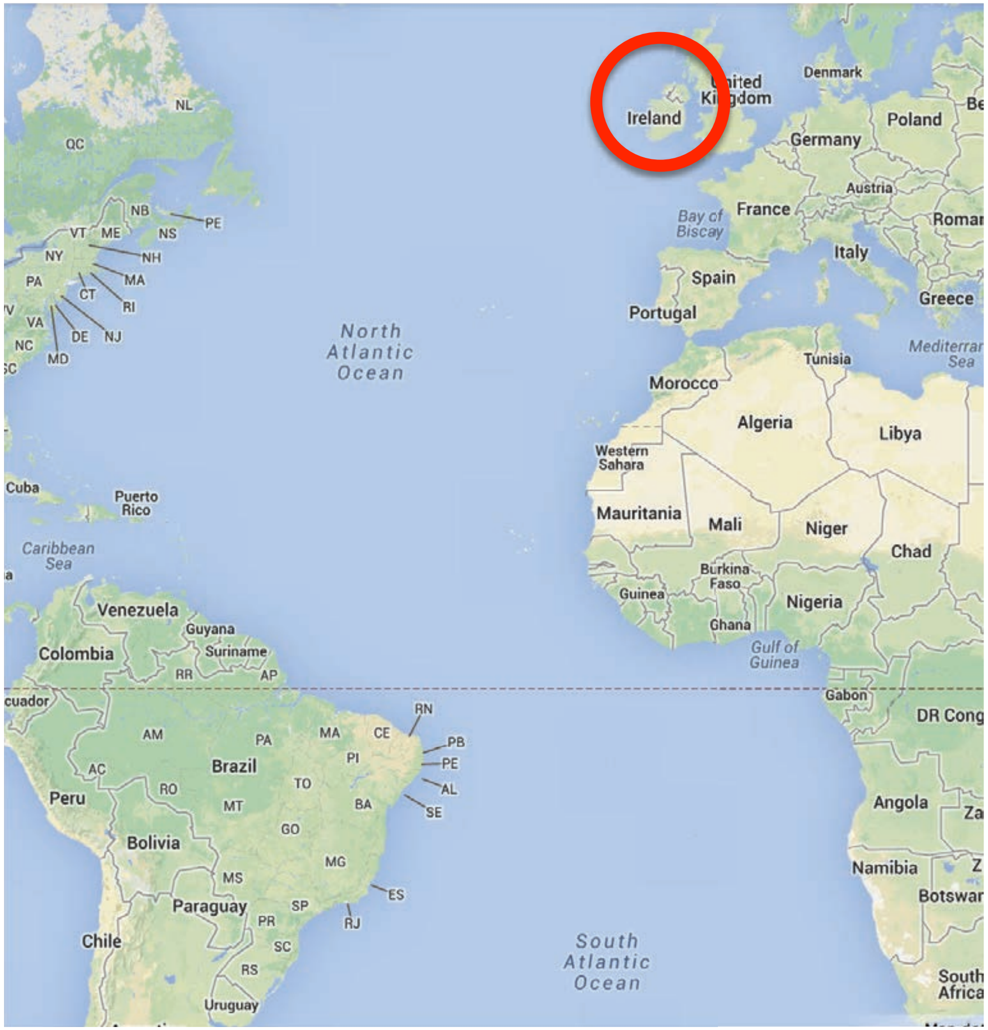
''‘New Concepts in Chemical Sensing based on Stimuli-Responsive Materials’ ’

Prof. Dermot Diamond
Director National Centre for Sensor Research
Funded Investigator, INSIGHT Centre for Data Analytics
Dublin City University

Invited Lecture presented at

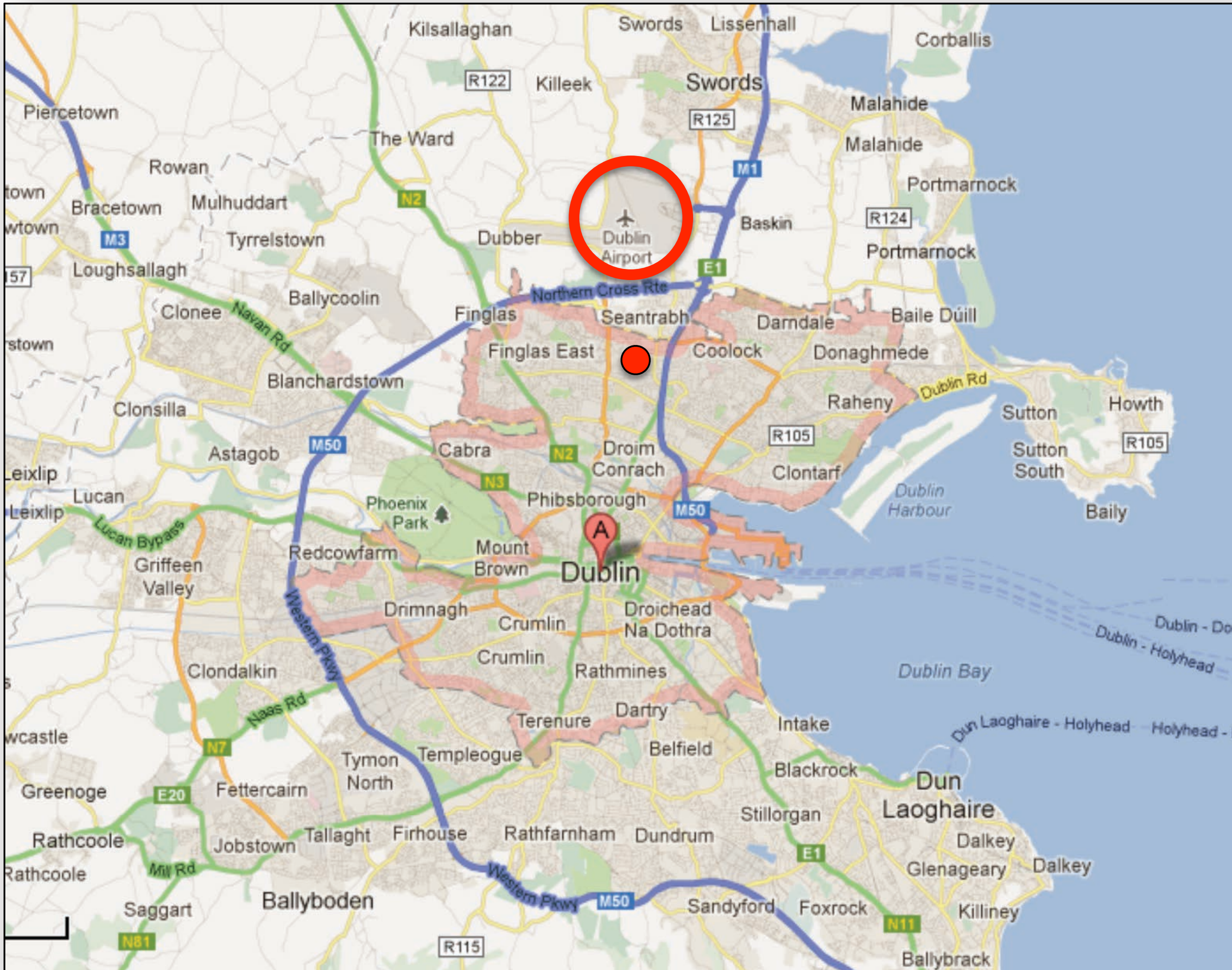
Symposium D "Organic Electronics and hybrids: materials and devices”
Brazilian MRS Conference ‘XIII SBPMat’, João Pessoa
September 28-October 2, 2014

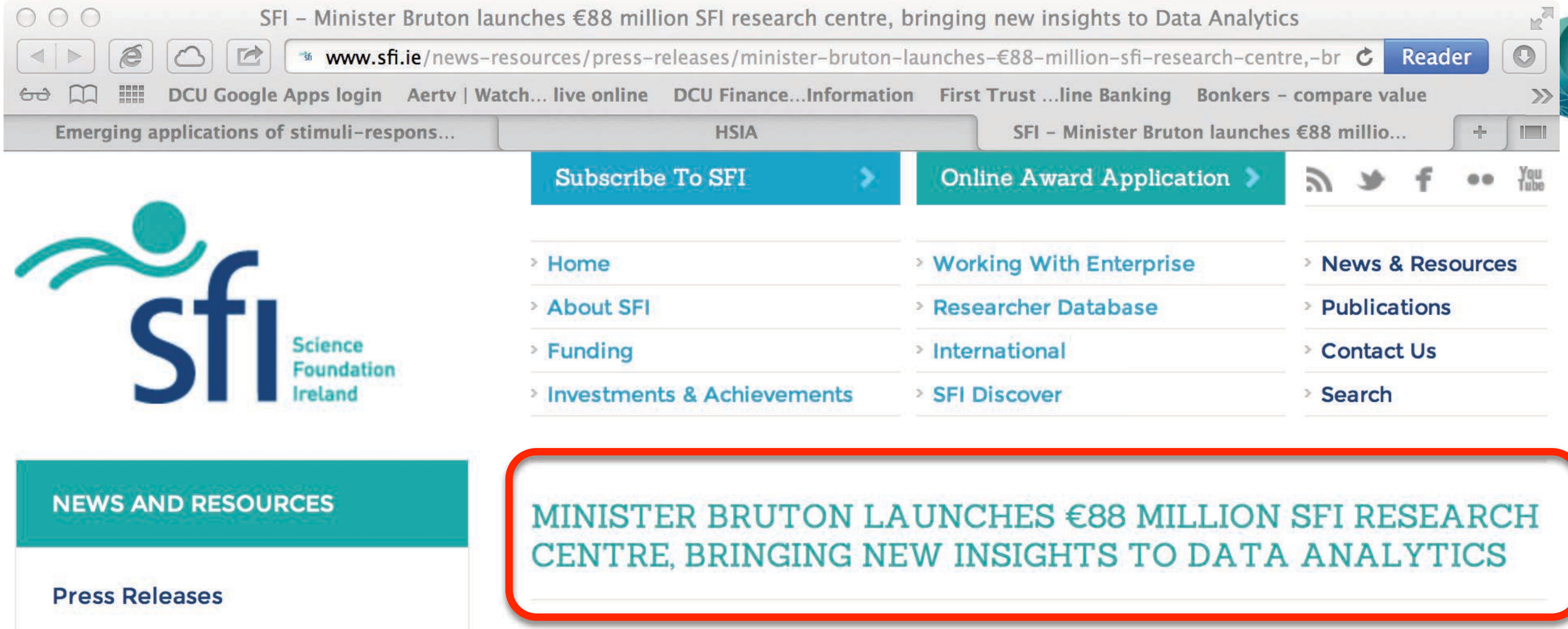
Ireland....



sfi DCU UCC OÉ Gaillimh NUI Galway UCD Dublin

Dublin & DCU Location



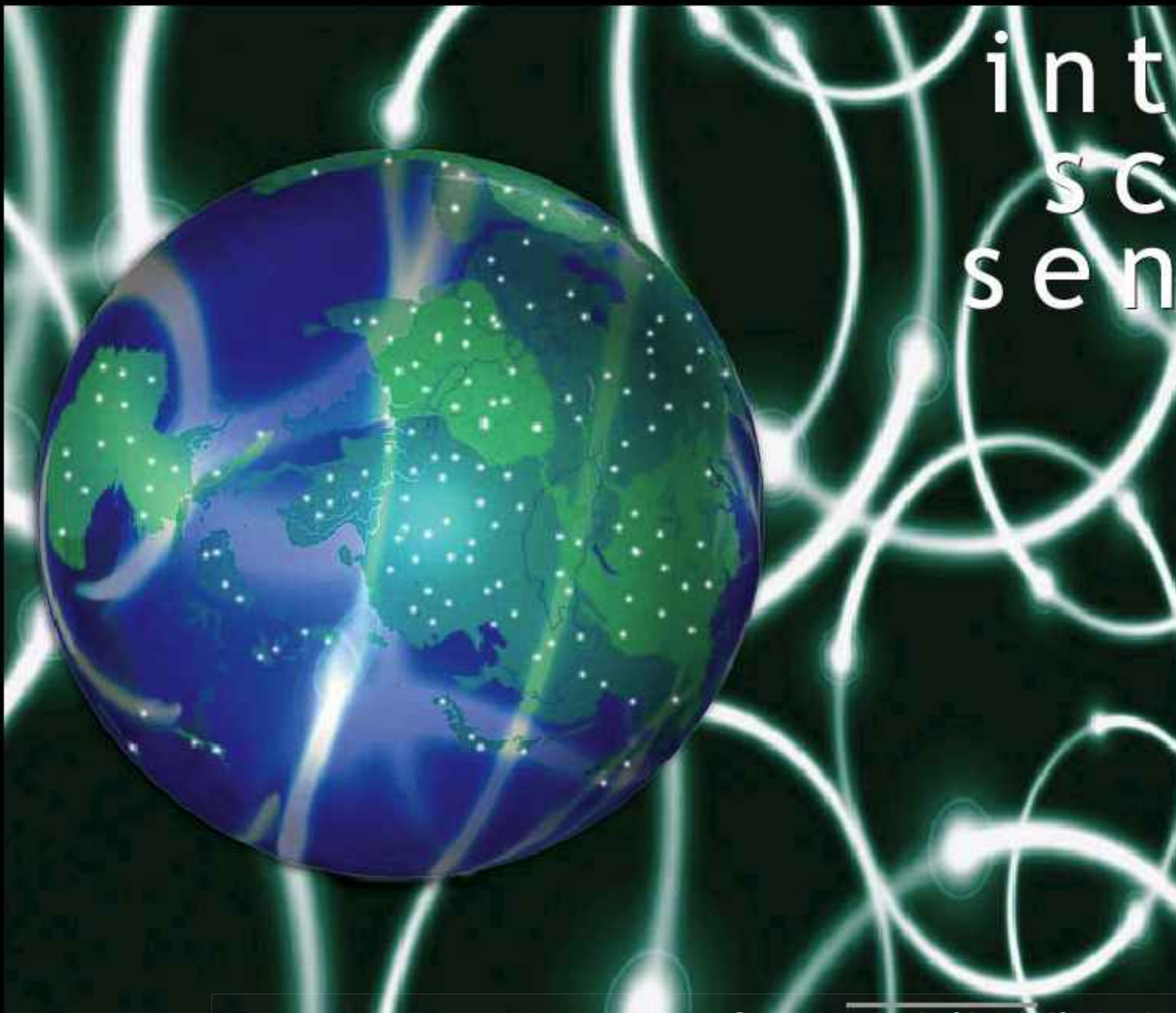


Insight Centre for Data Analytics

- 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

SFI DCU UCC OÉ Gaillimh NUI Galway UCD Dublin

Keynote Article: August 2004, Analytical Chemistry (A



internet scale sensing

Dermot Diamond
Dublin City University
(Ireland)

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

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

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++

Google Contact Lens

United States Patent Application ***20140107445***

Kind Code A1 Liu; Zenghe April 17, 2014

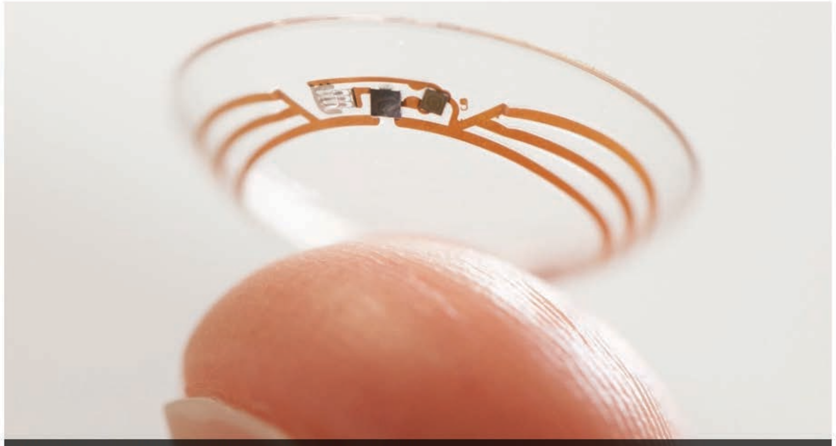
Microelectrodes In An Ophthalmic Electrochemical Sensor

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 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.

Google Smart Contact Lenses Move Closer to Reality

8.6k SHARES | Share on Facebook | Share on Twitter | + WHAT'S THIS?



Google's Smart Contact Lens is like your contact lens, except it's a whole lot smarter.

IMAGE: GOOGLE

LANCE ULANOFF

1 DAY AGO

Google's plan to bring smart contact lenses to diabetes sufferers inched closer to reality as the company secured two patents last week for the cutting edge, biometric sensor technology.

Known [illegible] as "Ophthalmic Electrochemical Sensors," these contact lenses will feature flexible electronics that include sensors and an antenna. The sensors are designed to read chemicals in the tear fluid of the wearer's eye and alert her, possibly through a little embedded LED light, when her blood sugar falls to dangerous levels.

SEE ALSO: Incognito Wearables You'd Never Guess Were Gadgets

According to the patent:

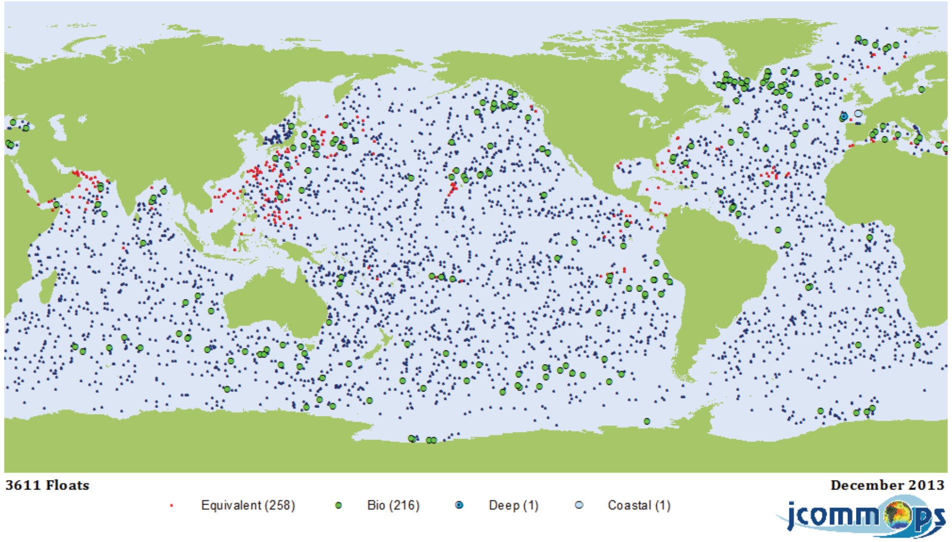
> "Human tear fluid contains a variety of inorganic electrolytes (e.g., Ca.sup.2+, Mg.sup.2+, Cl.sup.-), organic solutes (e.g., glucose, lactate, etc.), proteins, and lipids. A contact lens with one or more sensors that can measure one or more of these components provides a convenient, non-invasive platform to diagnose or monitor health related problems. An example is a glucose sensing contact lens that can potentially be used for diabetic patients to monitor and control their blood glucose level.

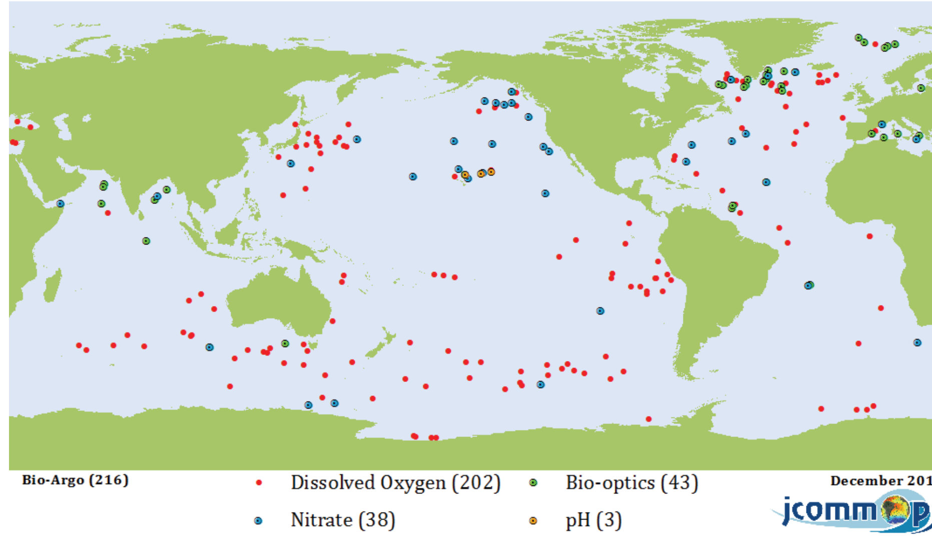
Google's project is one of a number of in-eye wearable sensor technologies currently under

Use model is 24 hours max; then replace and discard

http://www.gmanetwork.com/news/story/360331/scitech/technology/google-s-smart-contact-lenses-may-arrive-sooner-than-you-think

Argo Project (accessed March 9 2014)





- **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)**

@€60K ea!

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?

EVENT	DATE
Launch (San Francisco)	September 2013
PHASE 1: Innovation Phase	
Registration opens	January 1, 2014
Early-bird Registration deadline	March 2014
OA Solutions Fair and Kick-Off Event	March 2014

Overview

Competition Guidelines

Competition Schedule

Registration Process

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

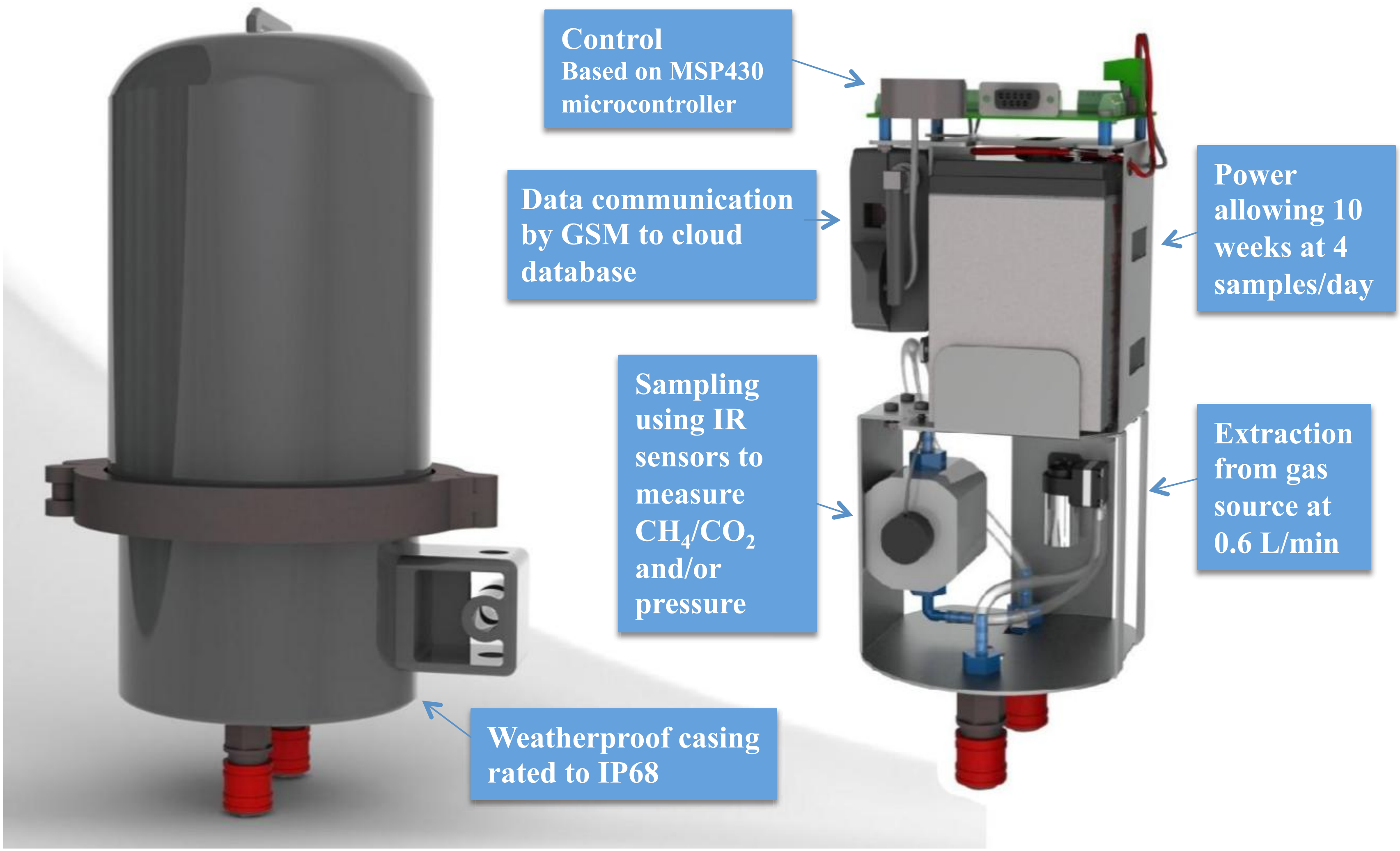
$2,000,000 up for grabs!
Task is to provide a way to do reliable measurements of pH in the ocean environment

The winner will almost certainly be a reagent based platform, not a conventional chemical sensor

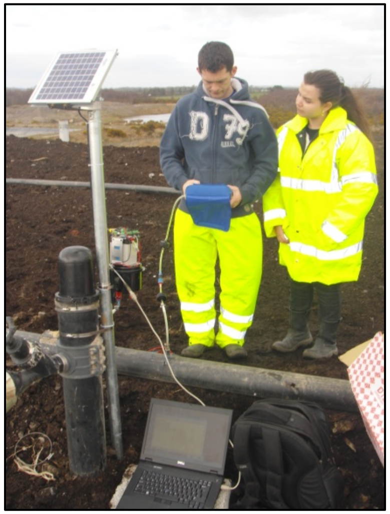
After decades of intensive research, our capacity to deliver successful long-term deployments of chemo/bio-sensors in remote locations is still very limited

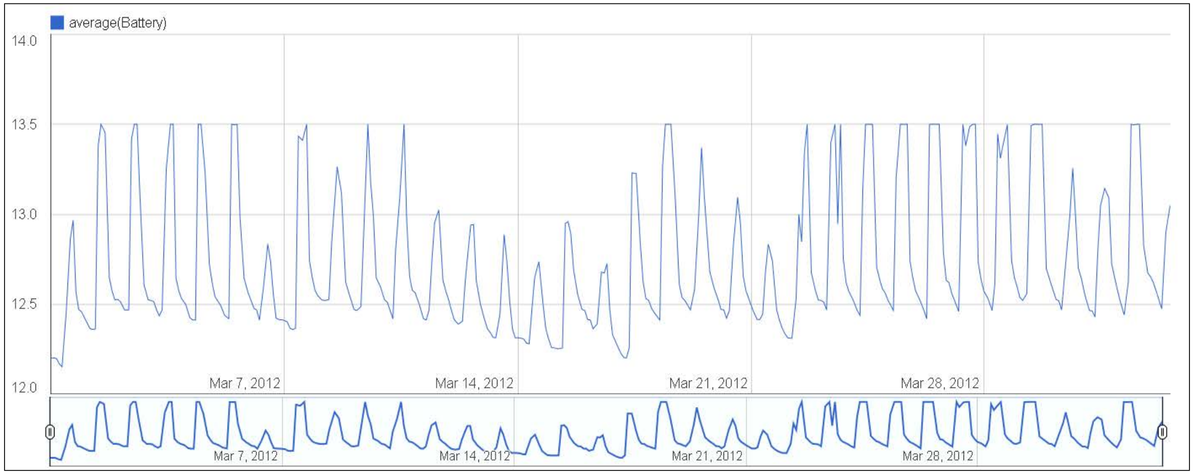
Any good news?

CH_4/CO_2 sensing using IR Sensors

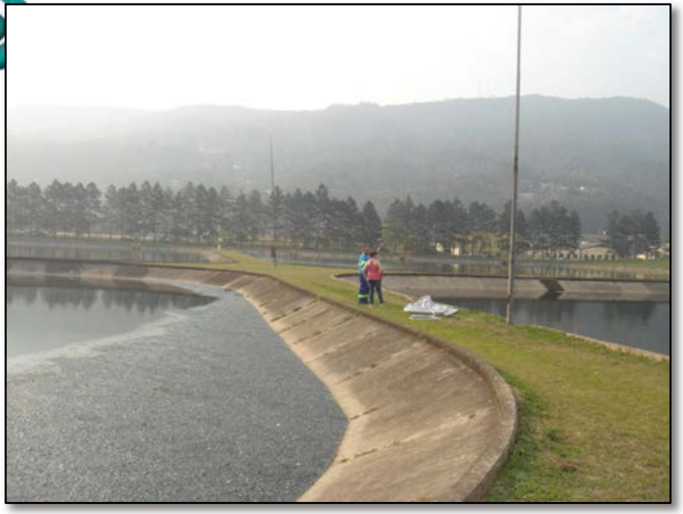


Camila at DCU





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



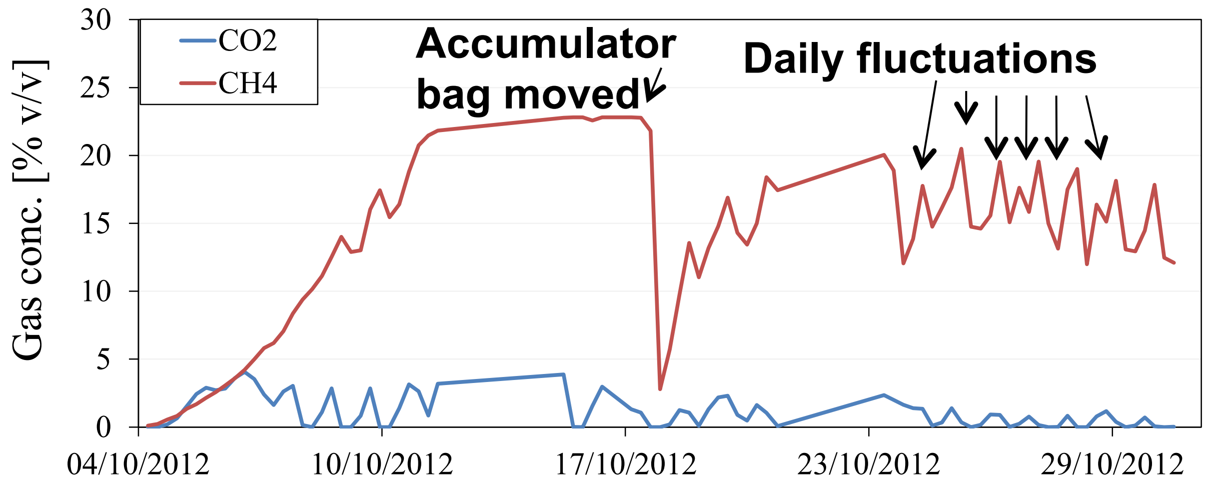

To Mairiporã City

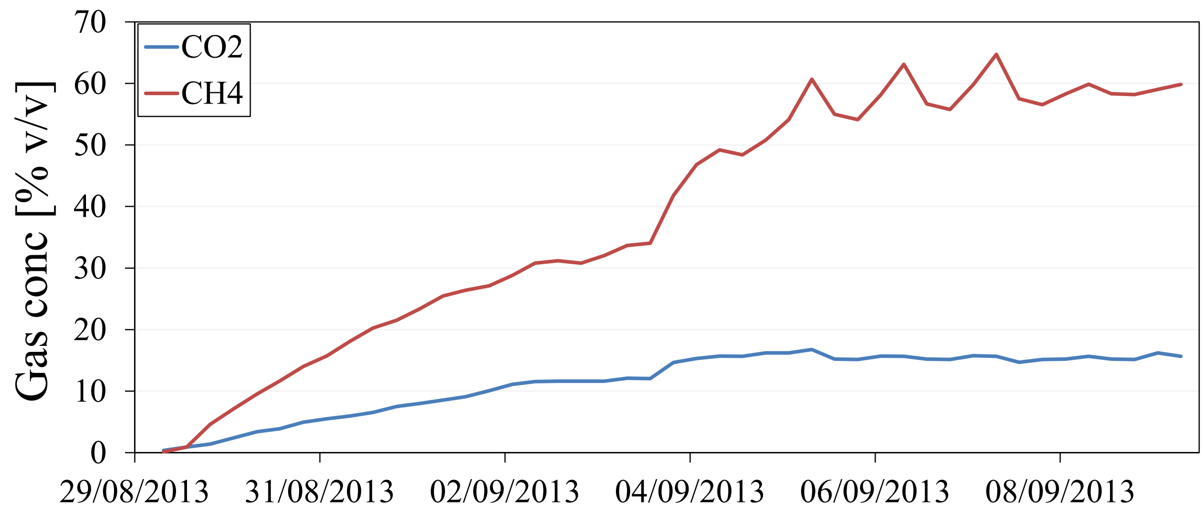
anaerobic lagoon operated by SABESP (Ernane, Diego and Ademar)

Monitoring GHG emissions

Collaboration with University of São Paulo, Brazil

– Two systems deployed, substantial commercial interest for more



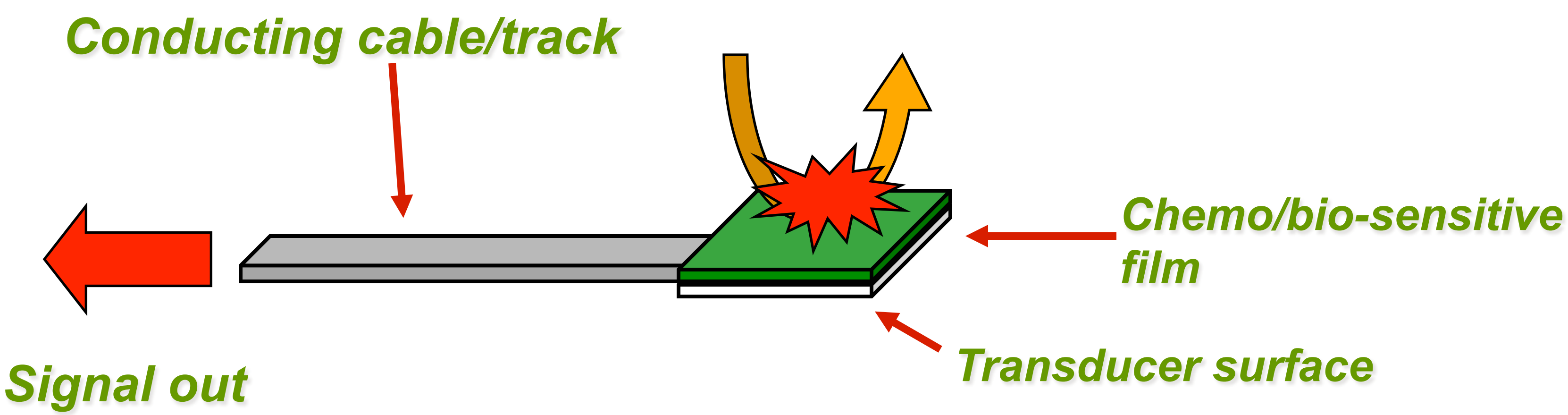


So everything is great! Yes??

No! Chem/Bio-sensors are difficult to keep working in water and (even worse!) blood

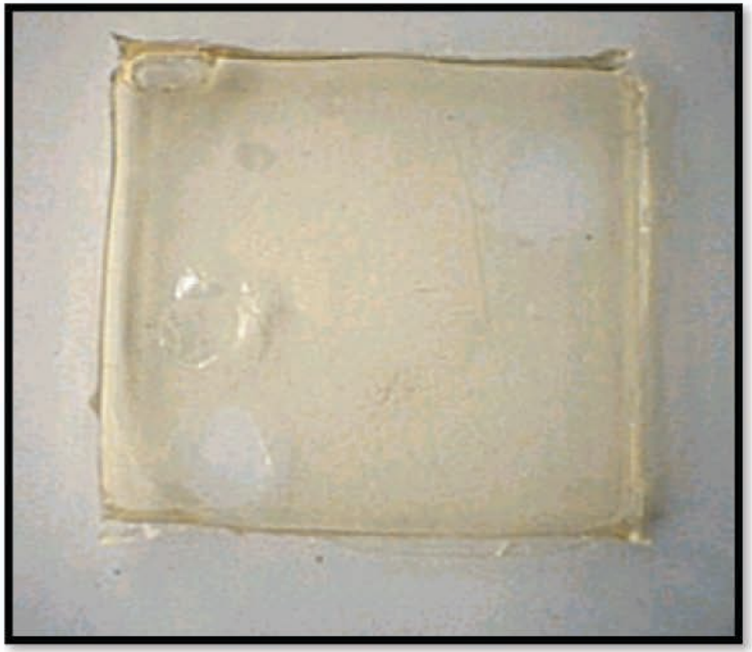
What is a Chemo/Bio-Sensor?

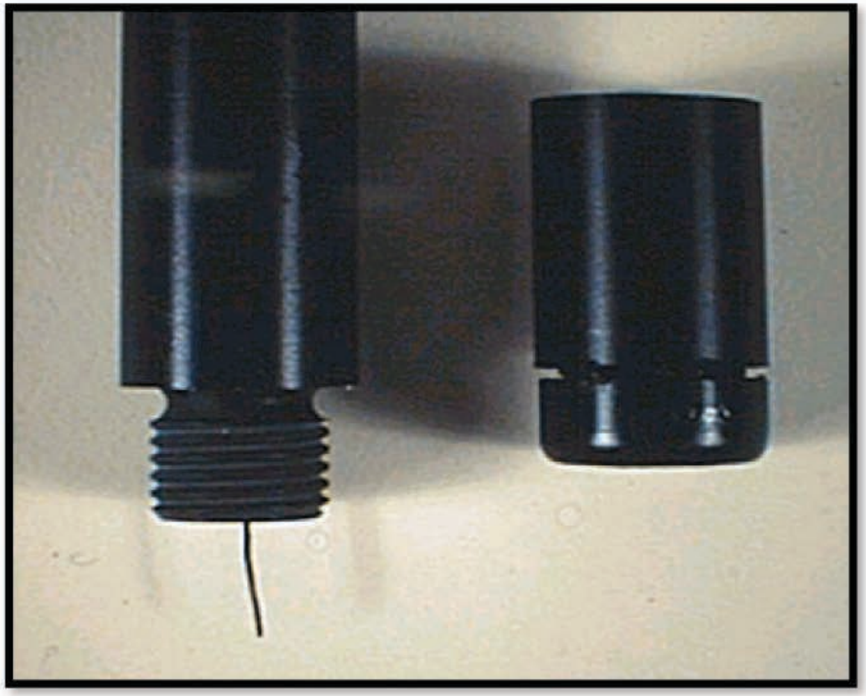
‘a device, consisting of a transducer and a chemo/bio-sensitive film/membrane, that generates a signal related to the concentration of particular target analyte in a given sample’



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**)

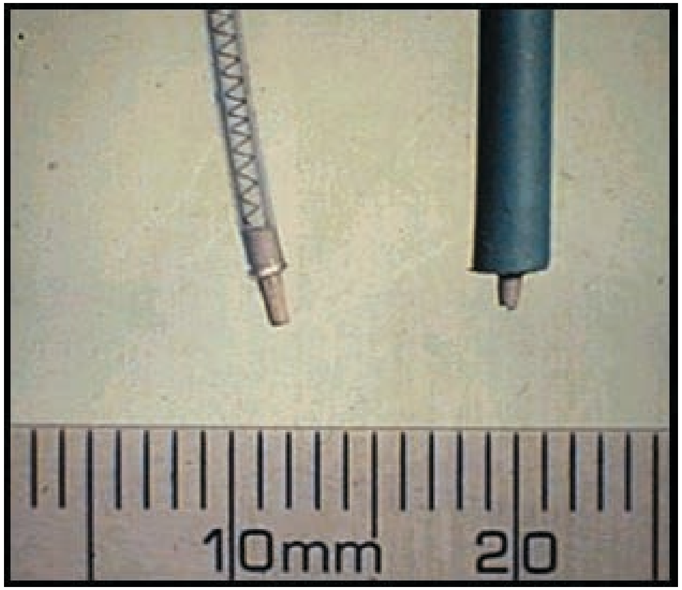
PVC - Membrane ISEs





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; Implantible Sensors



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

Dr. David Band, St Thomas's Hospital London

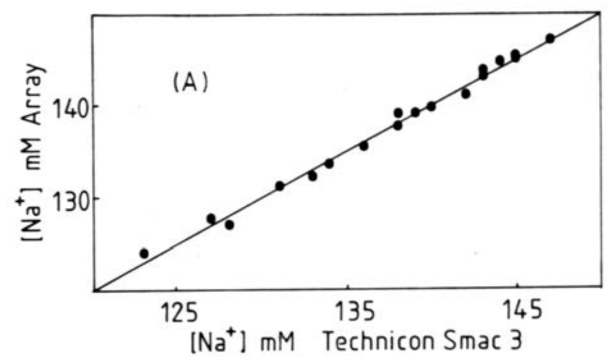
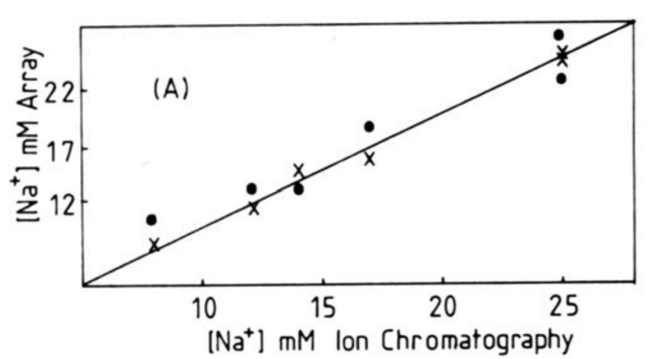


Fig. 3. Comparison of plasma sodium analysis using the array-FIA approach with a SMAC analyser. Good correlation without bias is obtained [5].

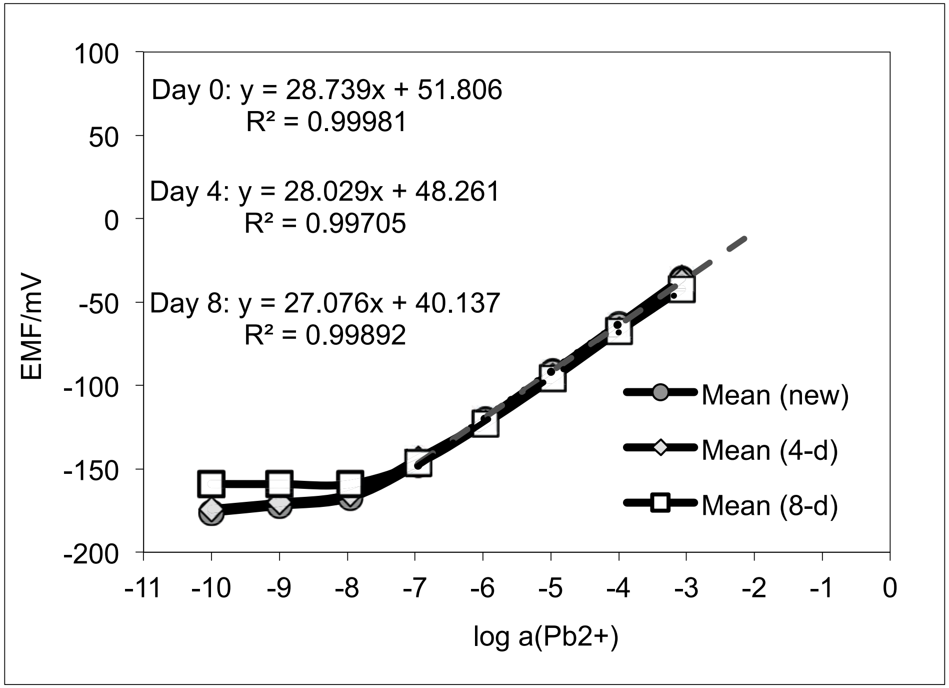


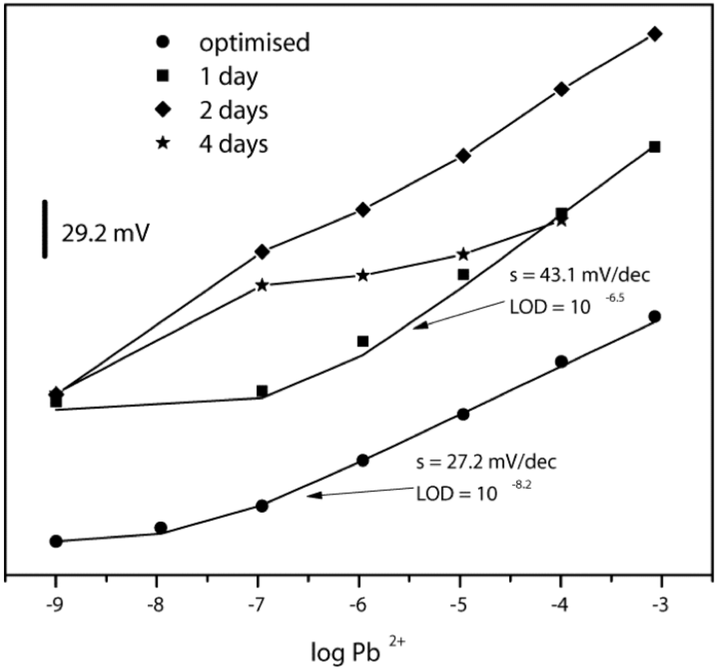
Anal. Chem., *64 (1992) 1721-1728.*

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



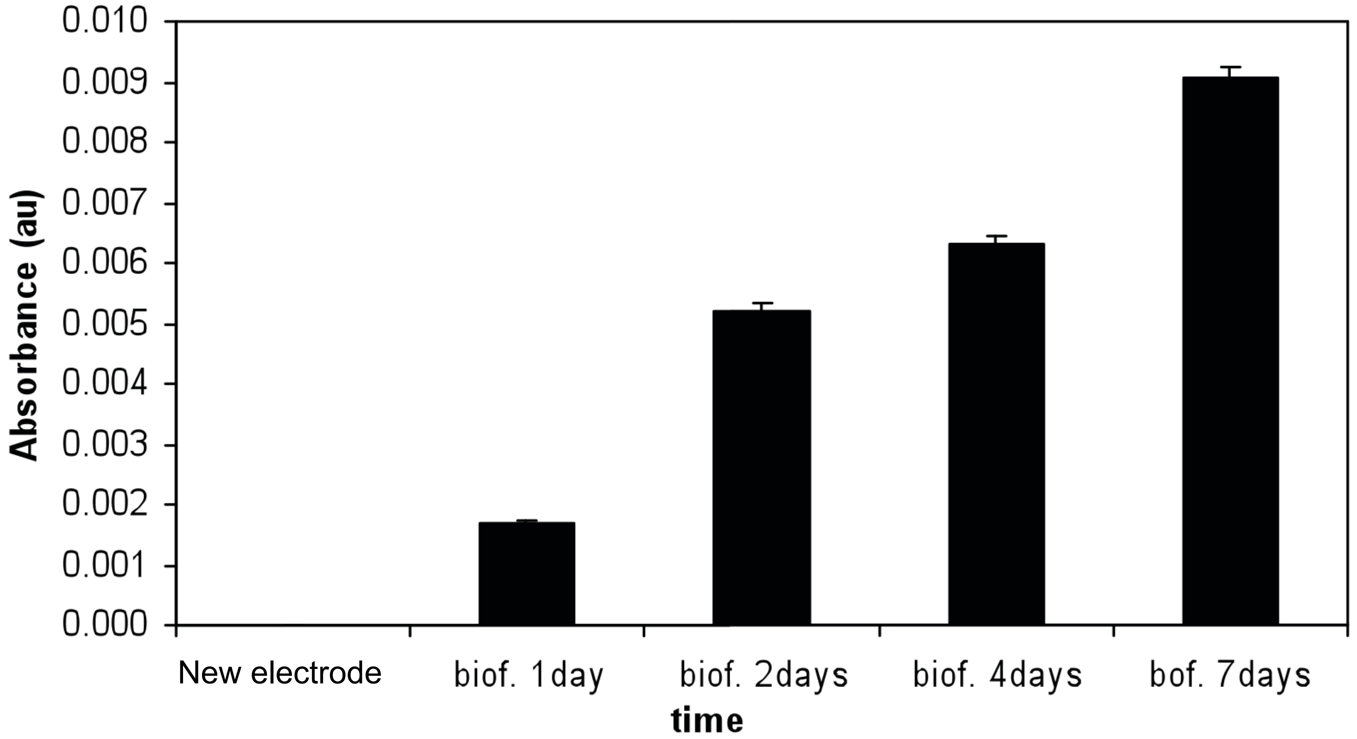


stored in 10^{-9}M Pb^{2+}, pH=4

Continuous contact with river water

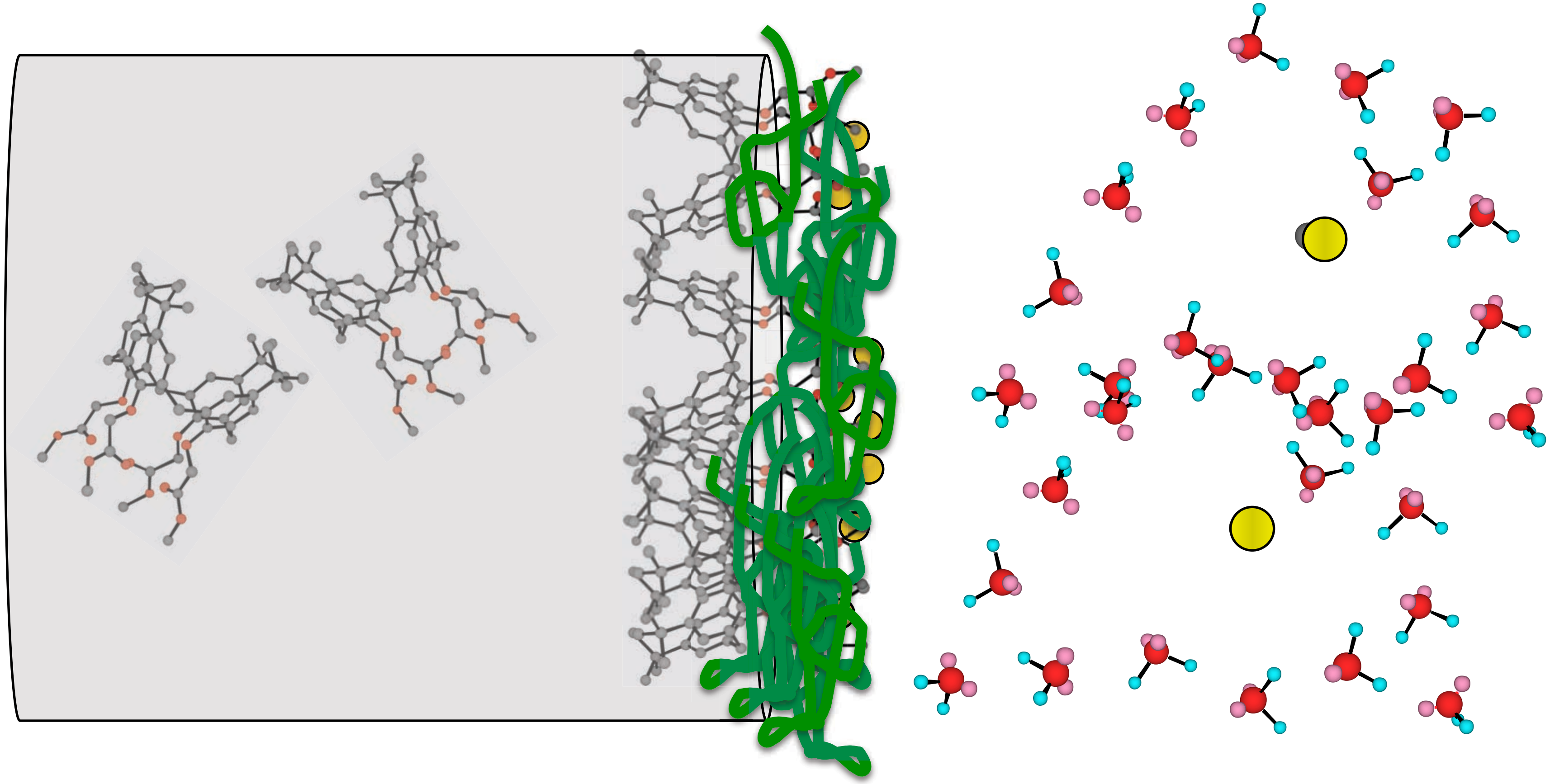
Conventional PVC-membrane based ISEs

Biofilm Formation on Sensors



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

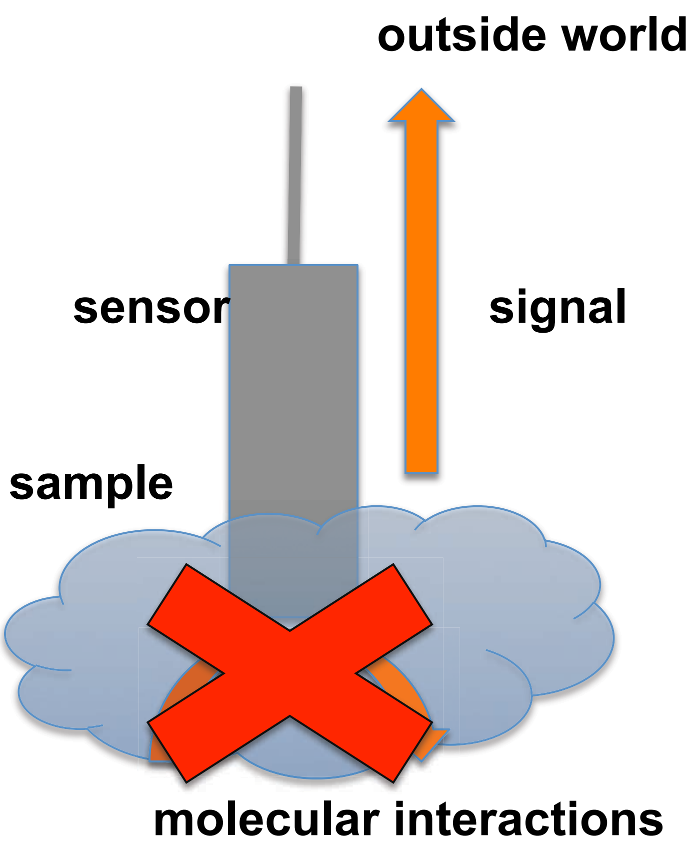
Control of membrane interfacial exchange & binding processes



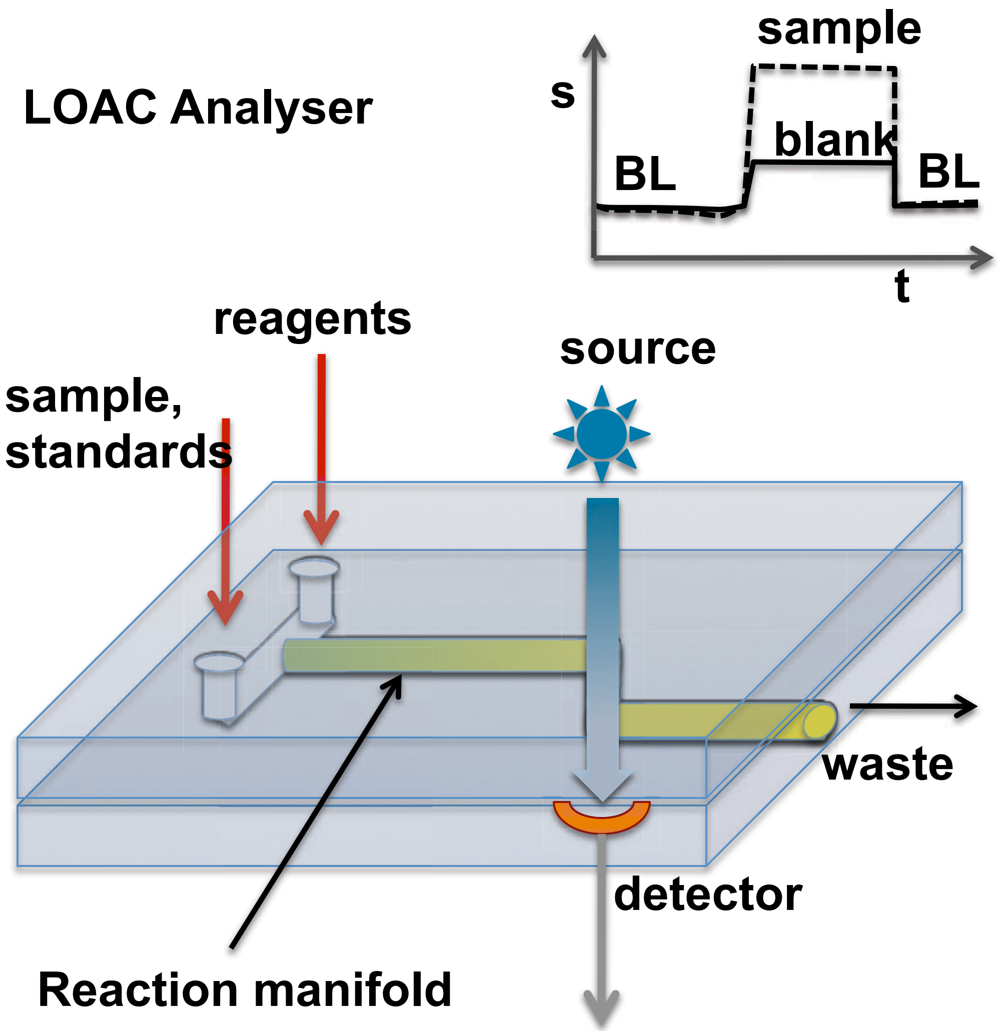
Remote, autonomous chemical sensing is a tricky business!

Direct Sensing vs. Reagent Based LOAC/ufluidics

Direct Sensing



LOAC Analyser



MicroTAS/Lab on a Chip/Microfluidics

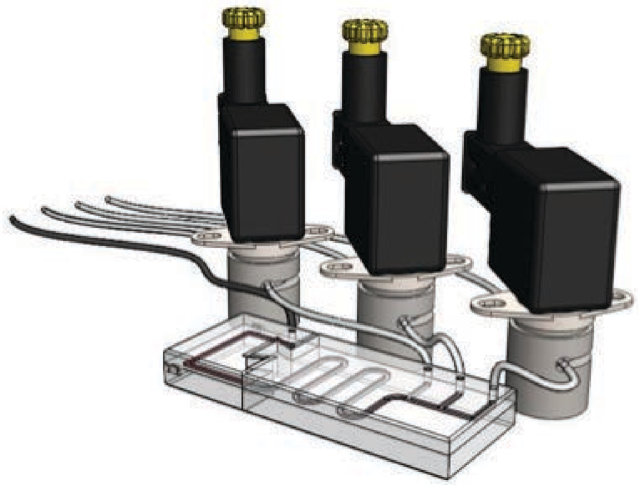
Many people, myself included, expected that the ability to manipulate fluid streams, in microchannels, easily, would result in a proliferation of commercial LoC systems, and that we would see applications of these devices proliferating throughout science. In fact, it has not (yet) happened.

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

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

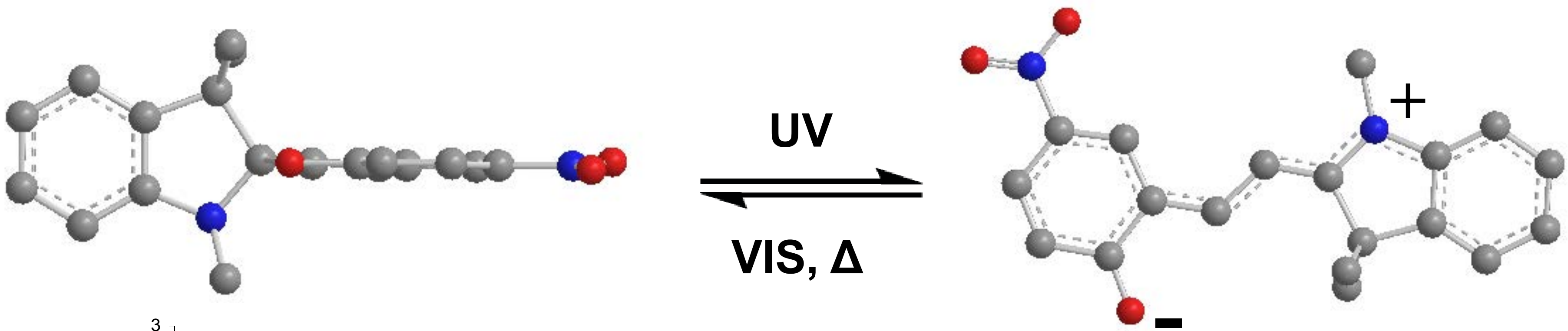
How to advance fluid handling in LOC platforms: re-invent valves (and pumps)!

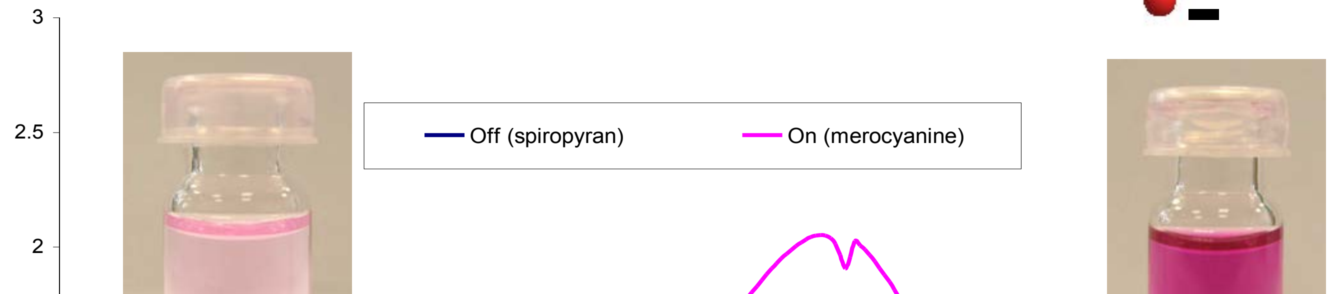
- **Conventional valves cannot be easily scaled down - Located off chip: fluidic interconnects required**
  - Complex fabrication
  - Increased dead volume
  - Mixing effects
- **Based on solenoid action**
  - Large power demand
  - Expensive



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

Photoswitchable Materials





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

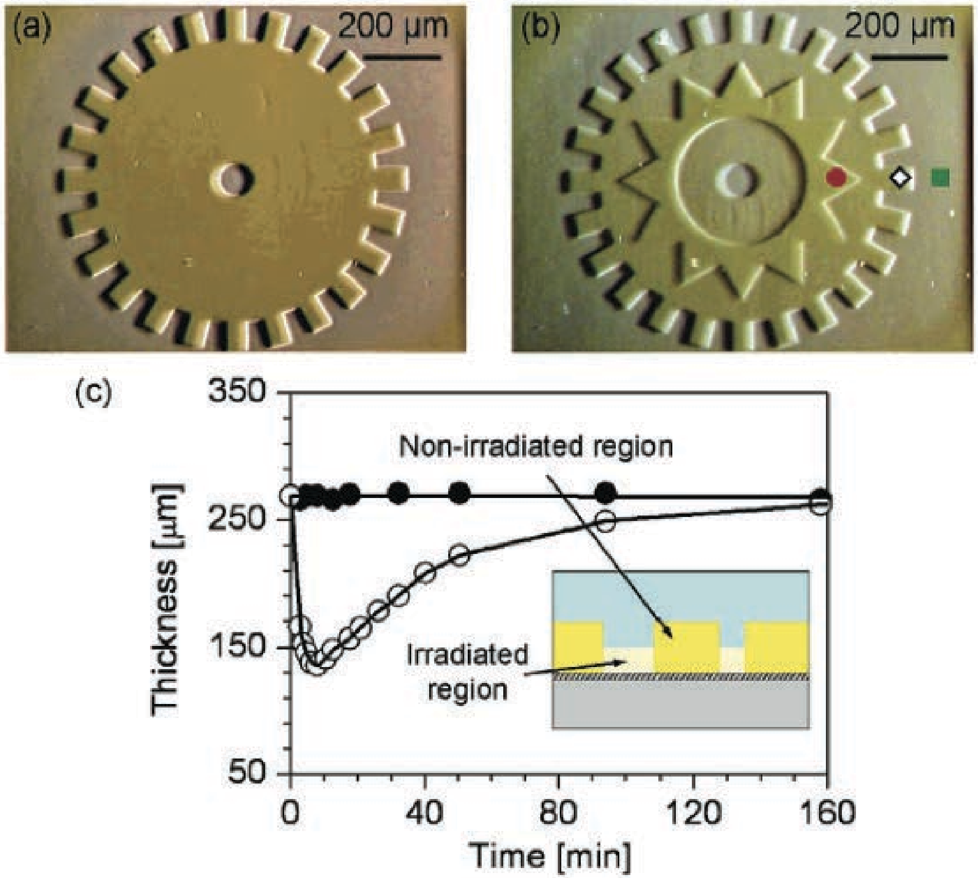
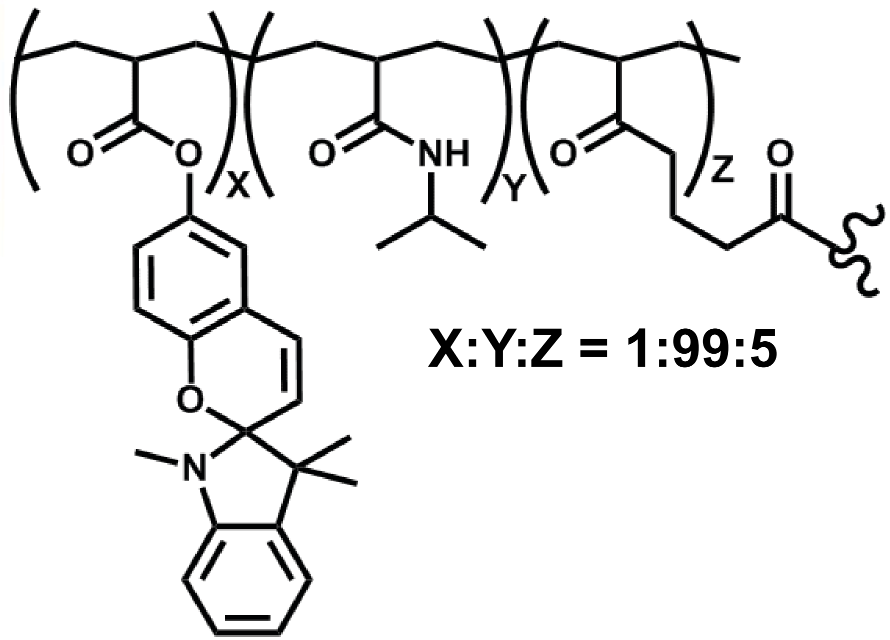


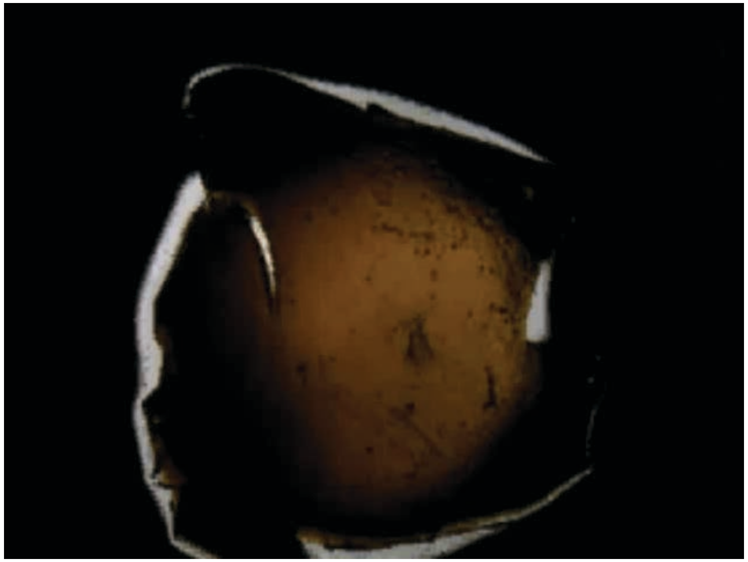
Figure 3. (a, b) Images of the pSPNIPAAm hydrogel layer just after the micropatterned light irradiation. Duration of irradiation was (●, red) 0, (◇) 1, and (■, green) 3 s. (c) Height change of the hydrogel layer in (●) non-irradiated and (○) irradiated region as a function of time after 3 s blue light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

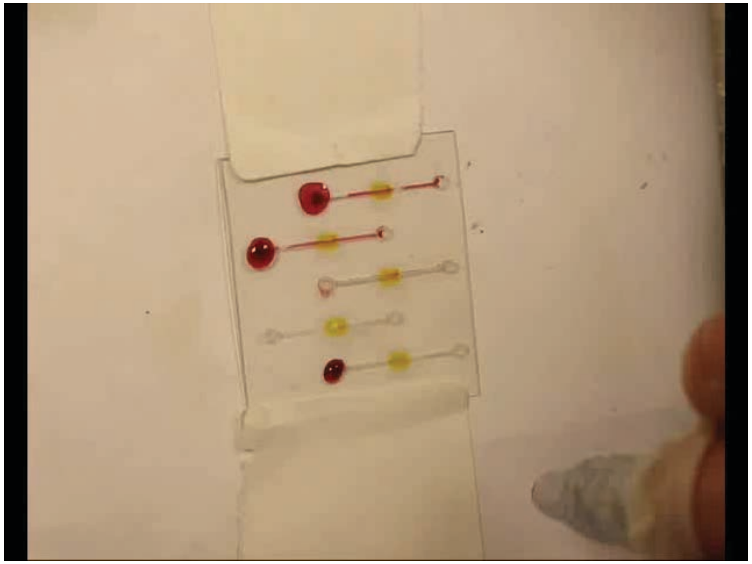


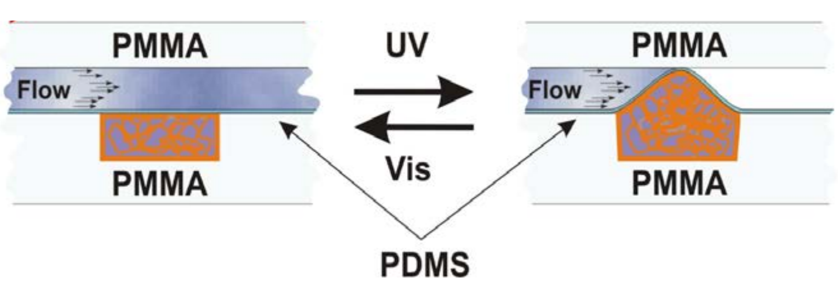
X:Y:Z = 1:99:5

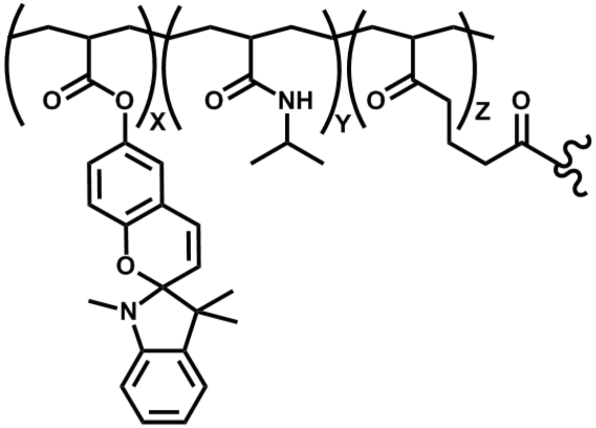
poly(N-isopropylacrylamide) (PNIPAAm)
Formulation as by Sumaru et al[1]
***1) Chem. Mater.*, 19 (11), 2730 -2732, 2007.**

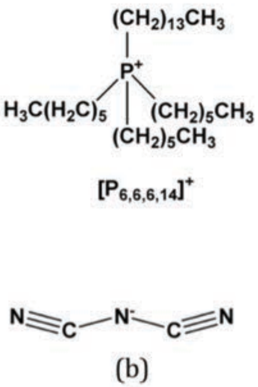
Photo-actuator polymers as microvalves in microfluidic systems







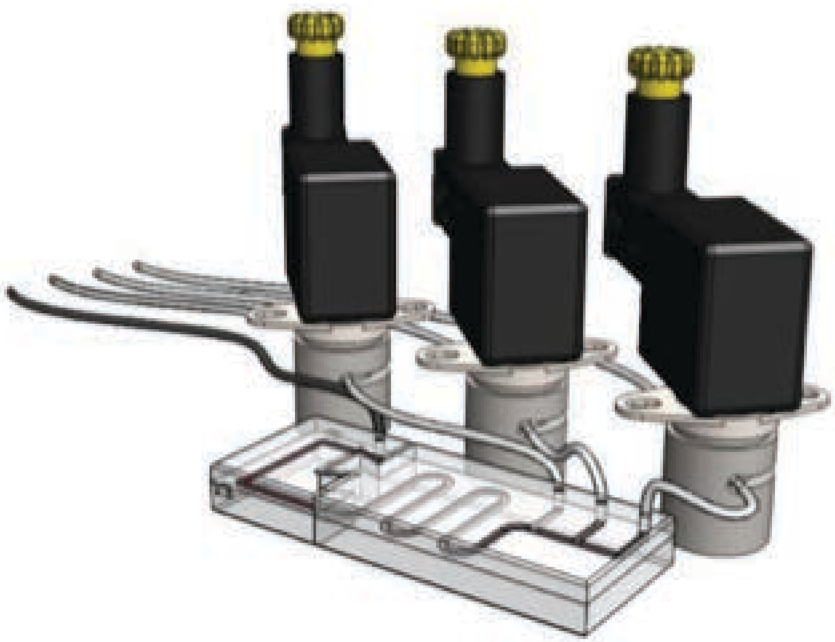




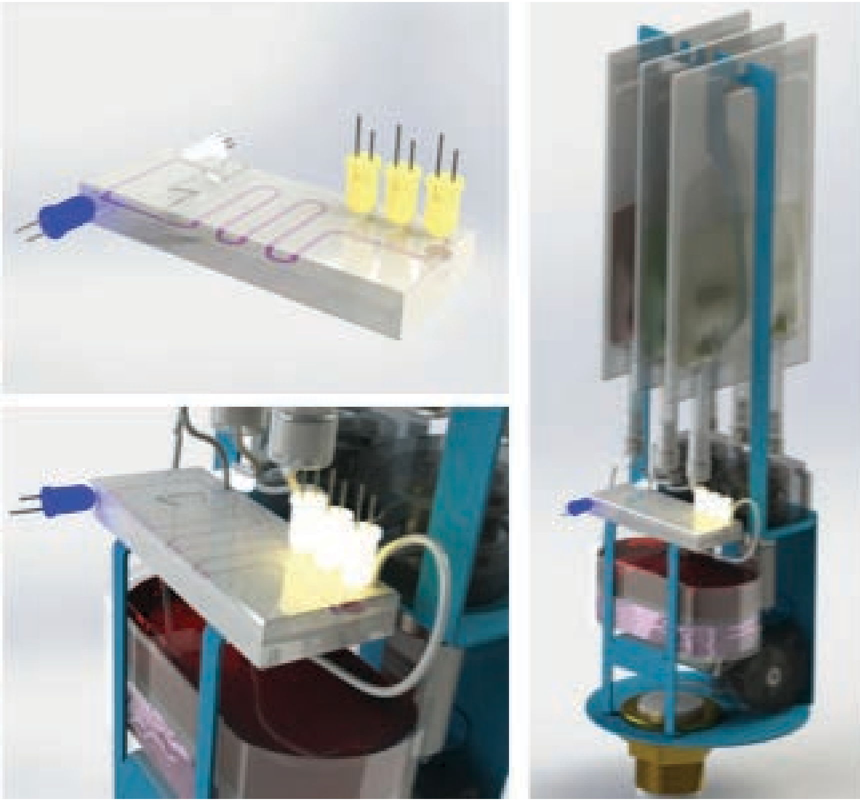
trihexyltetradecylphosphonium dicyanoamide $[P_{6,6,6,14}]^+[dca]^-$

Ionogel-based light-actuated valves for controlling liquid flow in micro-fluidic manifolds, Fernando Benito-Lopez, Robert Byrne, Ana Maria Raduta, Nihal Engin Vrana, Garrett McGuinness, Dermot Diamond, Lab Chip, 10 (2010) 195-201.

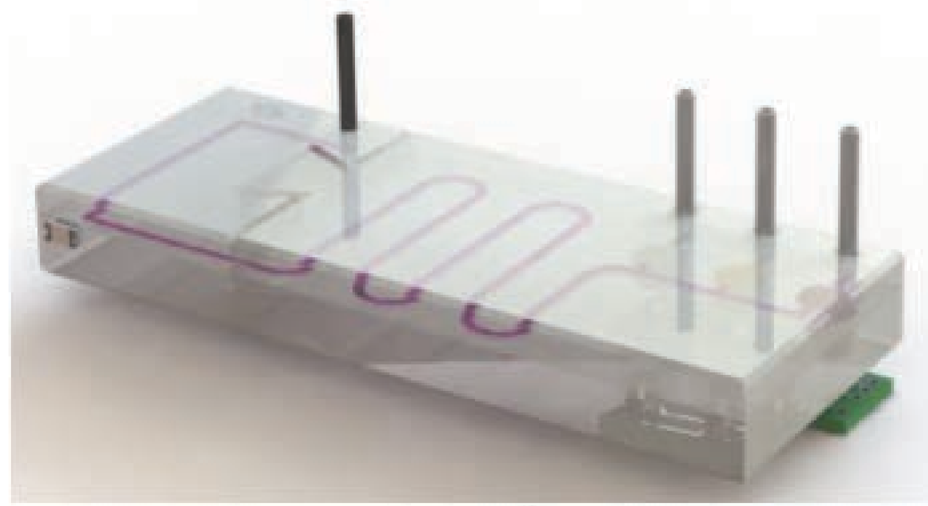
Can we go from this:

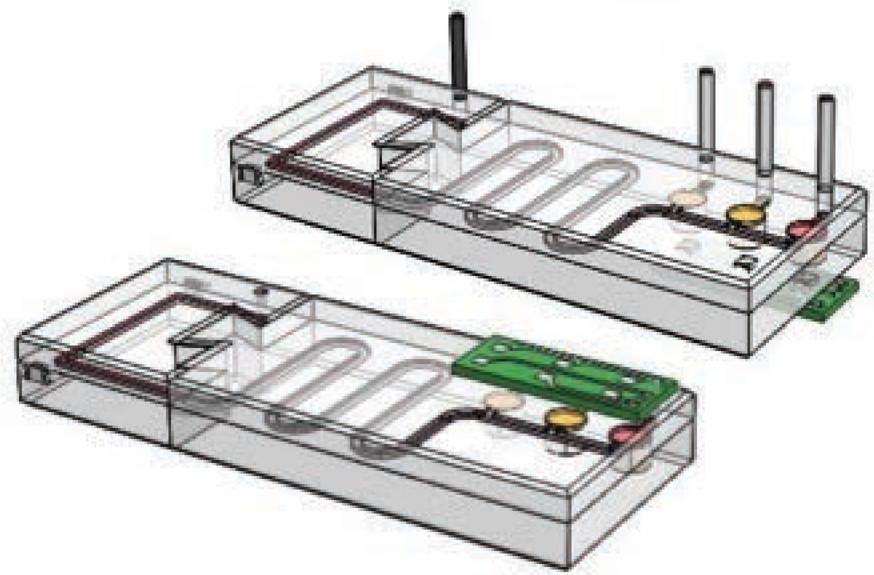


To Photo-Fluidics & Detection



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





- **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/fluoescence measurements**

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…..

RBI
Research
Brazil Ireland
BRIDGE TO PROGRESS

Thanks for the invitation

sfi DCU UCC OÉ Gaillimh NUI Galway UCD DUBLIN