



**COMMON SENSE**

MARINE SENSORS - MARINE MONITORING

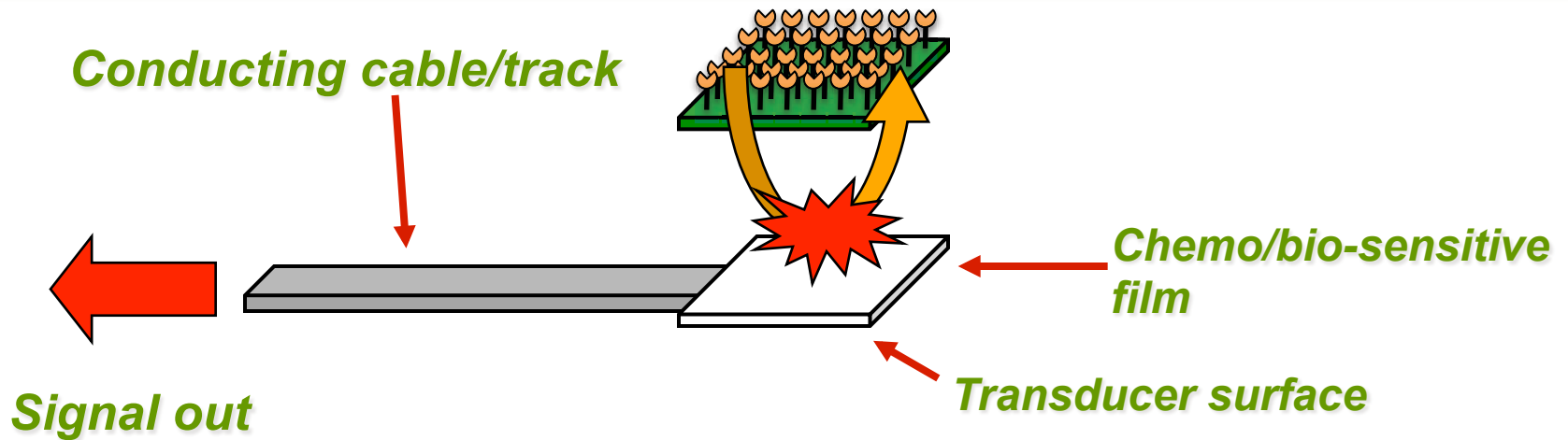
Professor Dermot Diamond, Dublin City University  
**‘Sensor Roadmap: Future Trends on (Marine)  
Chemical Sensor Development’**

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**)



## internet 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 digitalization 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)**



# 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....

**Increasing difficulty & cost**

**Increasing scalability**

**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

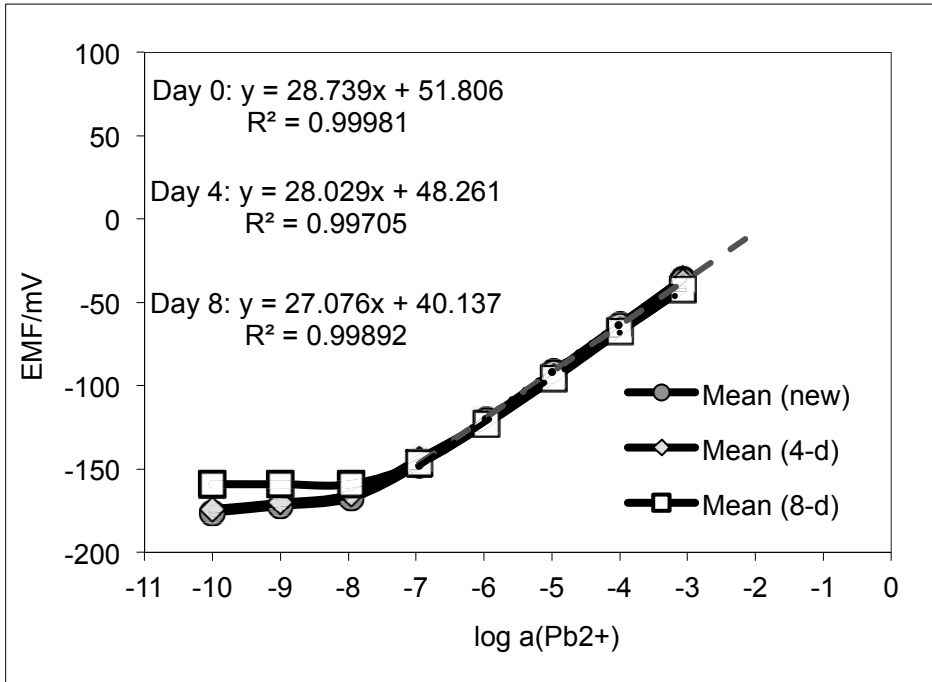




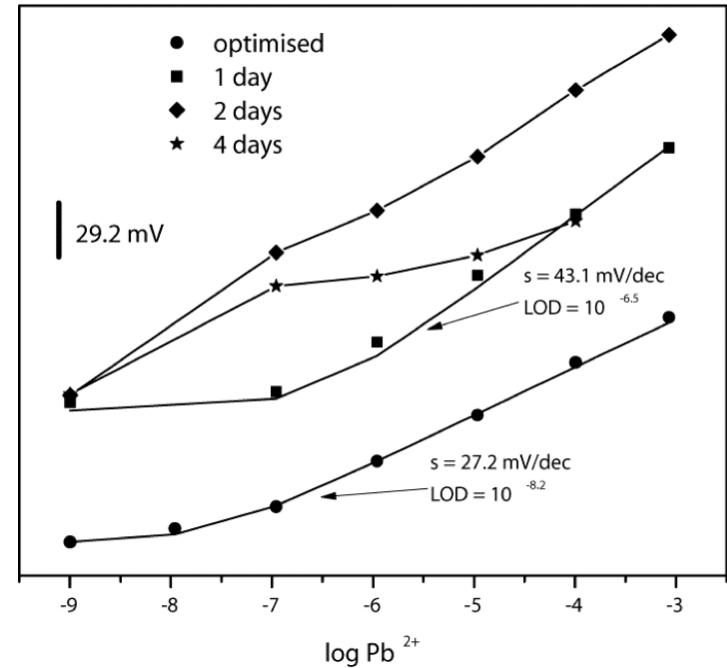
# Change in Electrode Function over Time



See *Electrochimica Acta* 73 (2012) 93–97



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



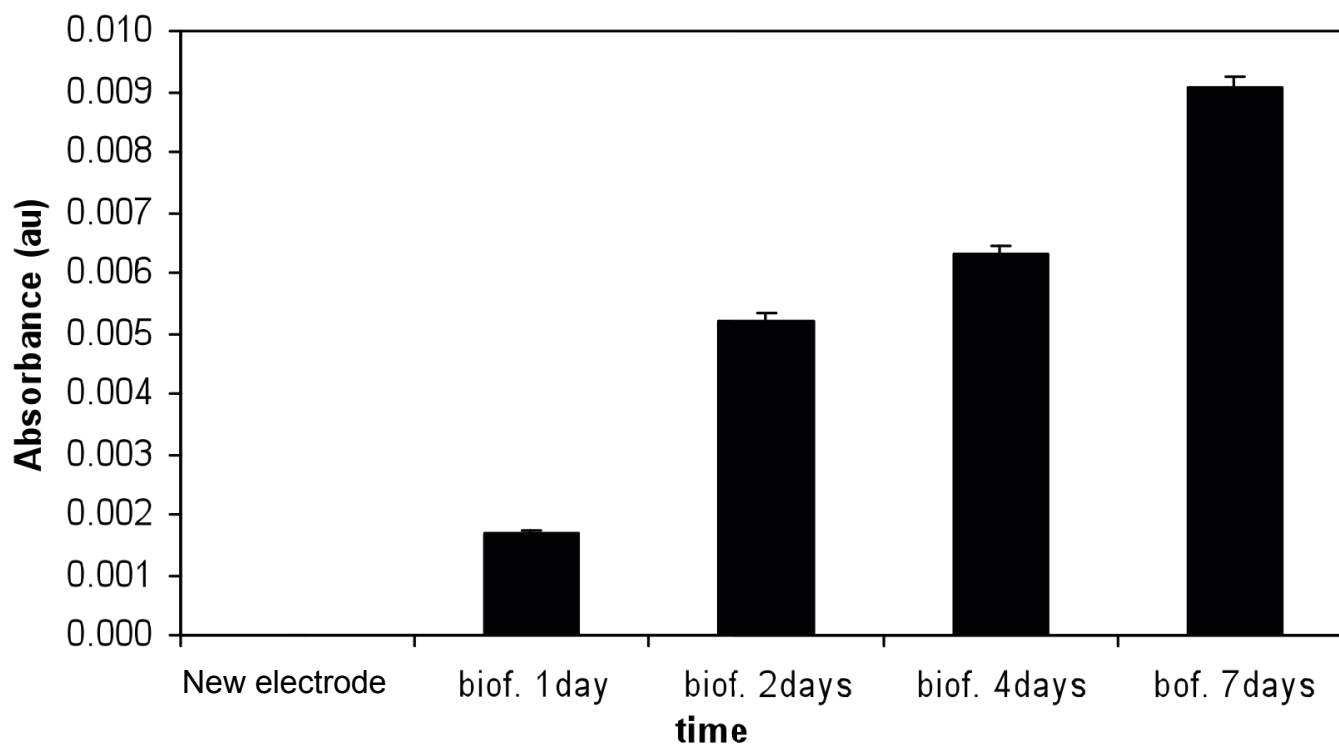
Continuous contact with river water

Conventional PVC-membrane based ISEs





# Biofilm Formation on Sensors

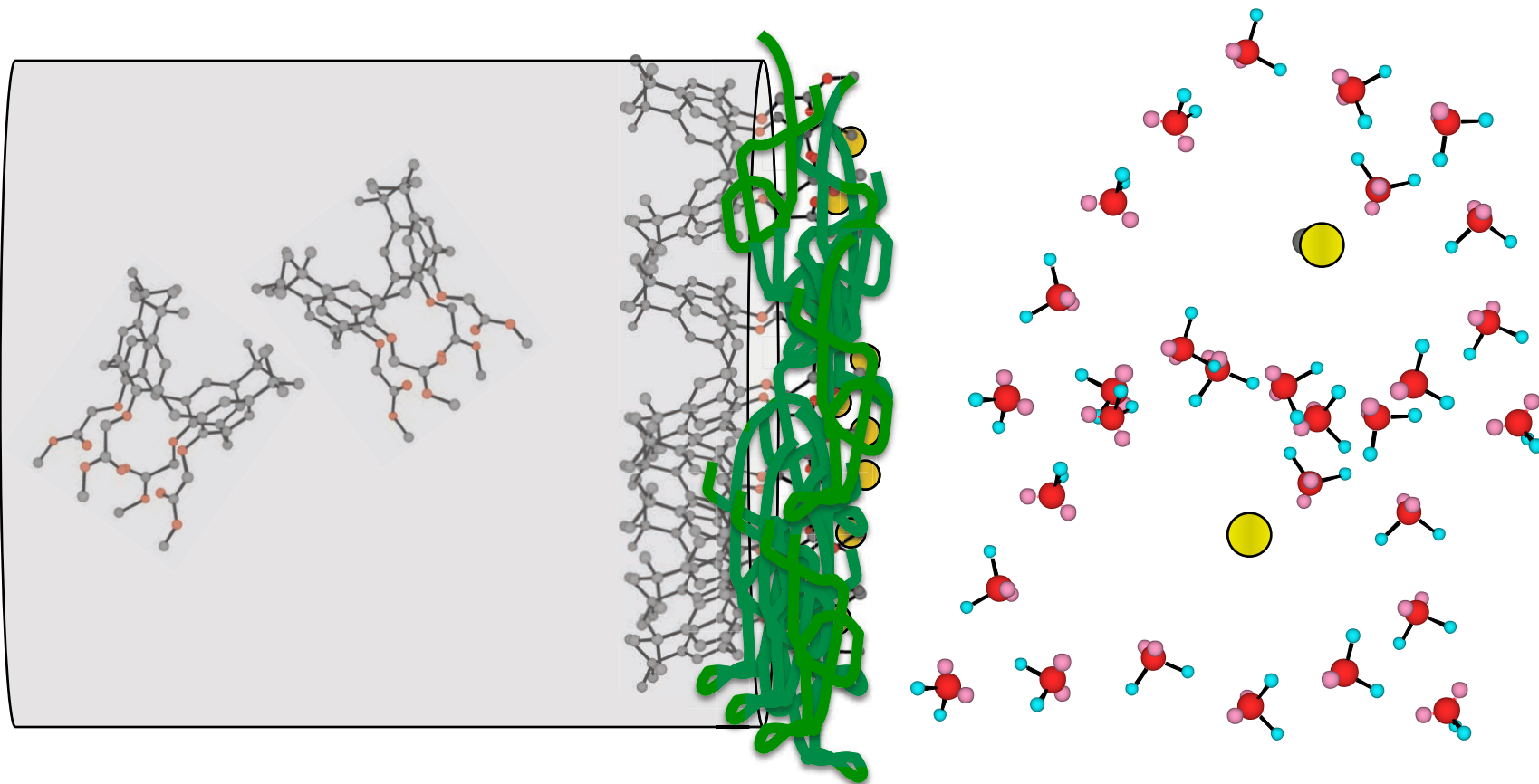


- **Electrodes exposed to local river water (Tolka)**
- **‘Slime test’ shows biofilm formation happens almost immediately and grows rapidly**





# Control of membrane interfacial exchange & binding processes



**Remote, autonomous chemical sensing is a tricky business!**

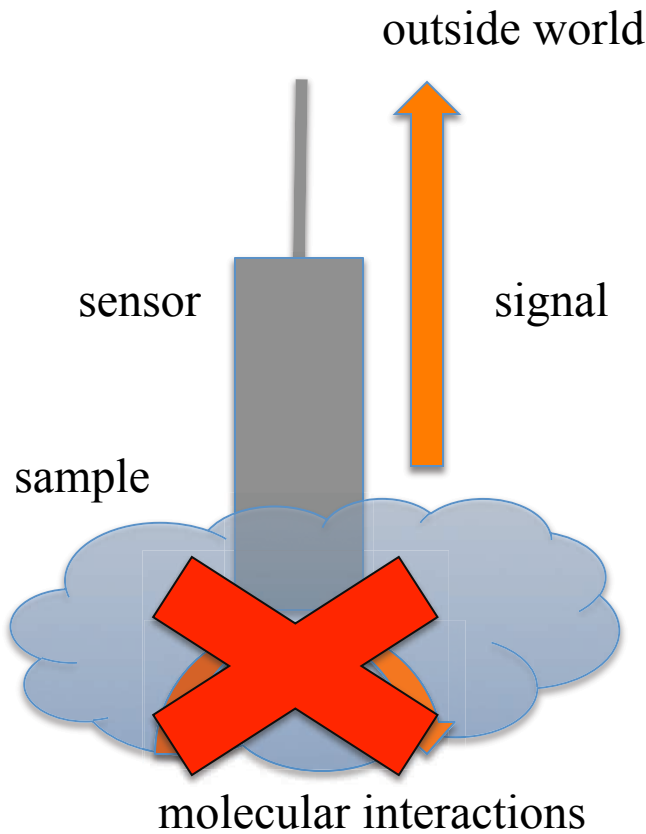




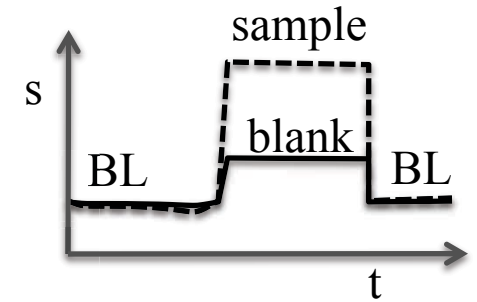
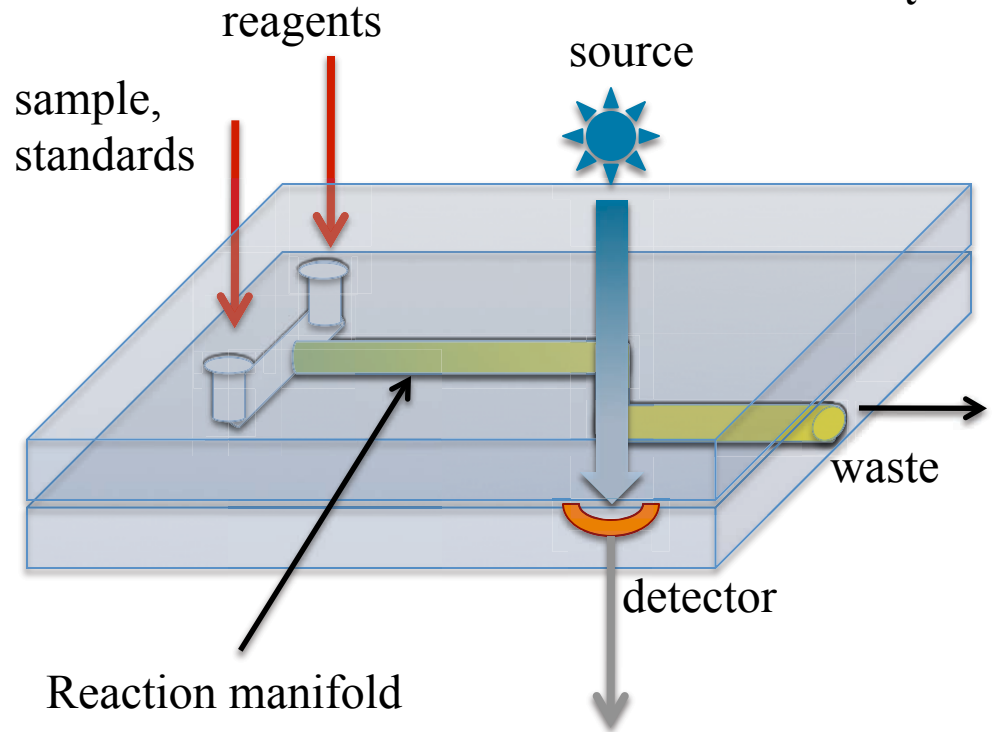
# Direct Sensing vs. Reagent Based LOAC/ufluidics



Direct Sensing



LOAC Analyser







# Osberstown – 3 week deployment

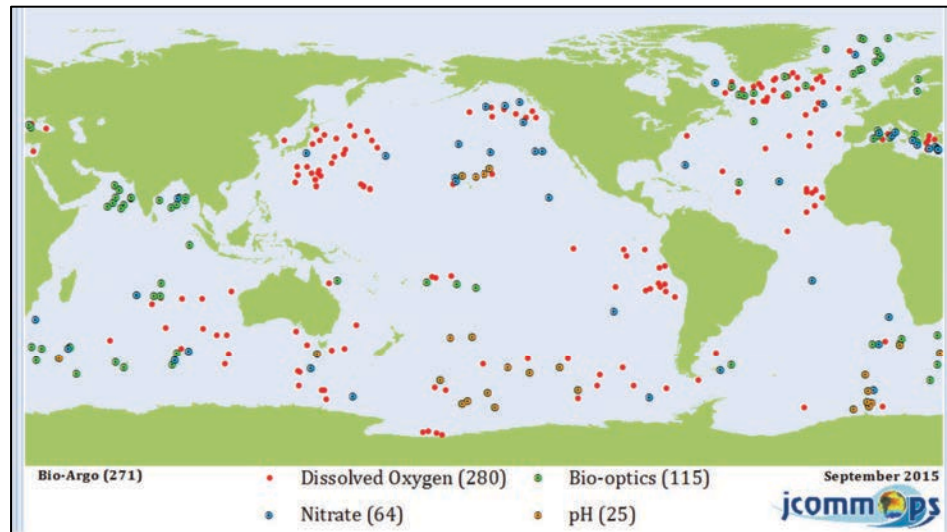
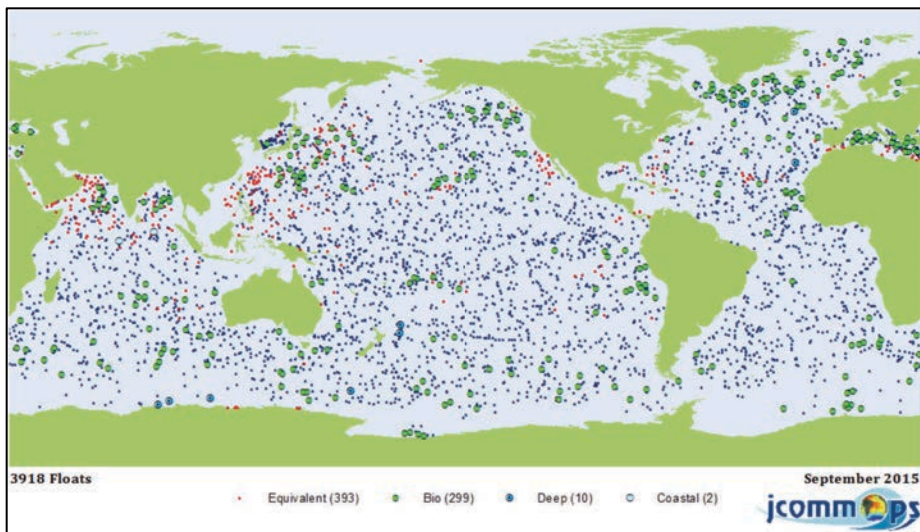


Biofouling of sensor surfaces is a major challenge for remote chemical sensing – both for the environment and for implantable sensors





# Argo Project (accessed March 20 2016)



- 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)

@€60K ea!

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
<b>PHASE 1: Innovation Phase</b>	
Registration opens	January 1, 2014
Early-bird Registration deadline	March 2014
OA Solutions Fair and Kick-Off Event	March 2014



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

## OVERVIEW

### Overview

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

### Competition Guidelines

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.

### Competition Schedule

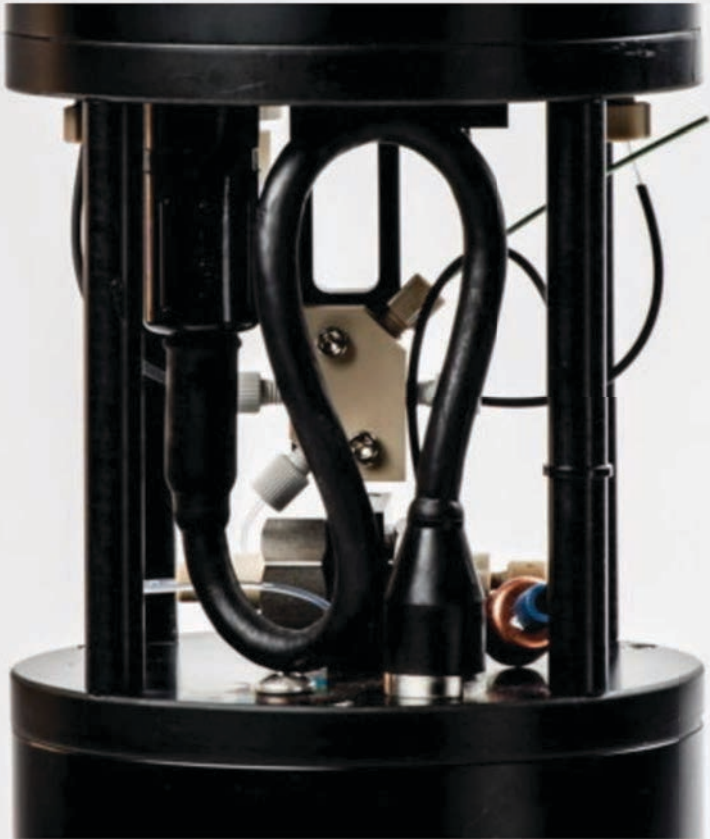
There are two prize purses available (teams may compete for, and win, both purses):

### Registration Process

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.



## SAMI-pH - Ocean pH Sensor



- Measures  $\text{pH}_T$  (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, 25C)
- 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



# And for nutrients....

**ALLIANCE FOR COASTAL TECHNOLOGIES**  
SUPPORTING INNOVATION TO BETTER UNDERSTAND, PREDICT AND MANAGE COASTAL, OCEAN AND GREAT LAKES ENVIRONMENTS.

Home About Tech Database Workshops Evaluations The Sensor Contact

**The Challenge**

- Register Now
- The Problem
- Timeline
- Awards
- Market Information
- Reports
- Provide Your Input
- Registered Participants - Spring 2015
- Frequent Questions

**Nutrient Sensor Challenge**

**A Water Sensor Market Stimulation Challenge**

Federal agencies, the Alliance for Coastal Technologies, and other partners **CHALLENGE YOU** to join the effort to develop affordable, accurate, and reliable nutrient sensors!

**Registration closes March 16, 2015**

**Nutrient Sensor Features**

- Measures dissolved nitrate and/or phosphate
- Provides real-time data
- Easy to use
- Less than \$5,000 purchase price
- Unattended deployments for 3 months
- Highly accurate and precise

**Thinking about registering for the Challenge?**

**Info and Q&A webinar  
12 Feb 2015**





# From 29 to 6 participants...

### The Challenge

- Application
- The Problem
- Timeline
- Awards
- Market Information
- Reports
- Provide Your Input
- Participants
- Frequent Questions

### The Coalition

- Office of Science and Technology Policy
- US Department of Agriculture
- US Environmental Protection Agency
- US Geological Survey
- National Oceanic and Atmospheric Admin
- National Institute of Science and Technology
- Everglades Foundation



## Nutrient Sensor Challenge

#### Participants Selected for Final Verification Testing in 2016

Decagon Devices, Inc.	Real Tech	SYSTEA S.p.A.
National Oceanography Centre	Sea-Bird Coastal	T.E. Laboratories & Dublin City University

Detailed Protocols used for ACT Verification Testing of Next-Generation Nutrient Sensors are available for download [here](#)

#### Registered Participants as of March 2015

USDA Ag Research Service	Sea-Bird Coastal
Turner Designs	Open Photonics Inc.
ASA Analytics	Translume, Inc.
RATES	JAL Engineering
YSI, Inc.	Aquisure
Decagon Devices, Inc.	University of Illinois / MoboSense, LLC.
SYSTEA S.p.A.	Lumense, Inc.
Franklin Thompson	National Oceanography Centre
SUNY Binghamton	Environmental Monitoring Solutions, Ltd.
SubChem Sensor Systems, Inc.	Geekchitecture
T.E. Laboratories & Dublin City University	Katsujinken Foundation
CleanGrow, Ltd.	Water Canary
Blue Legacy International	Ayyeka
UCSD Biodynamics Lab	Real Tech
SRI International, Marine & Space Sensing Laboratory	

## Winners will be announced March 2<sup>nd</sup> 2017 in Hawaii

US Integrated Ocean Observing System

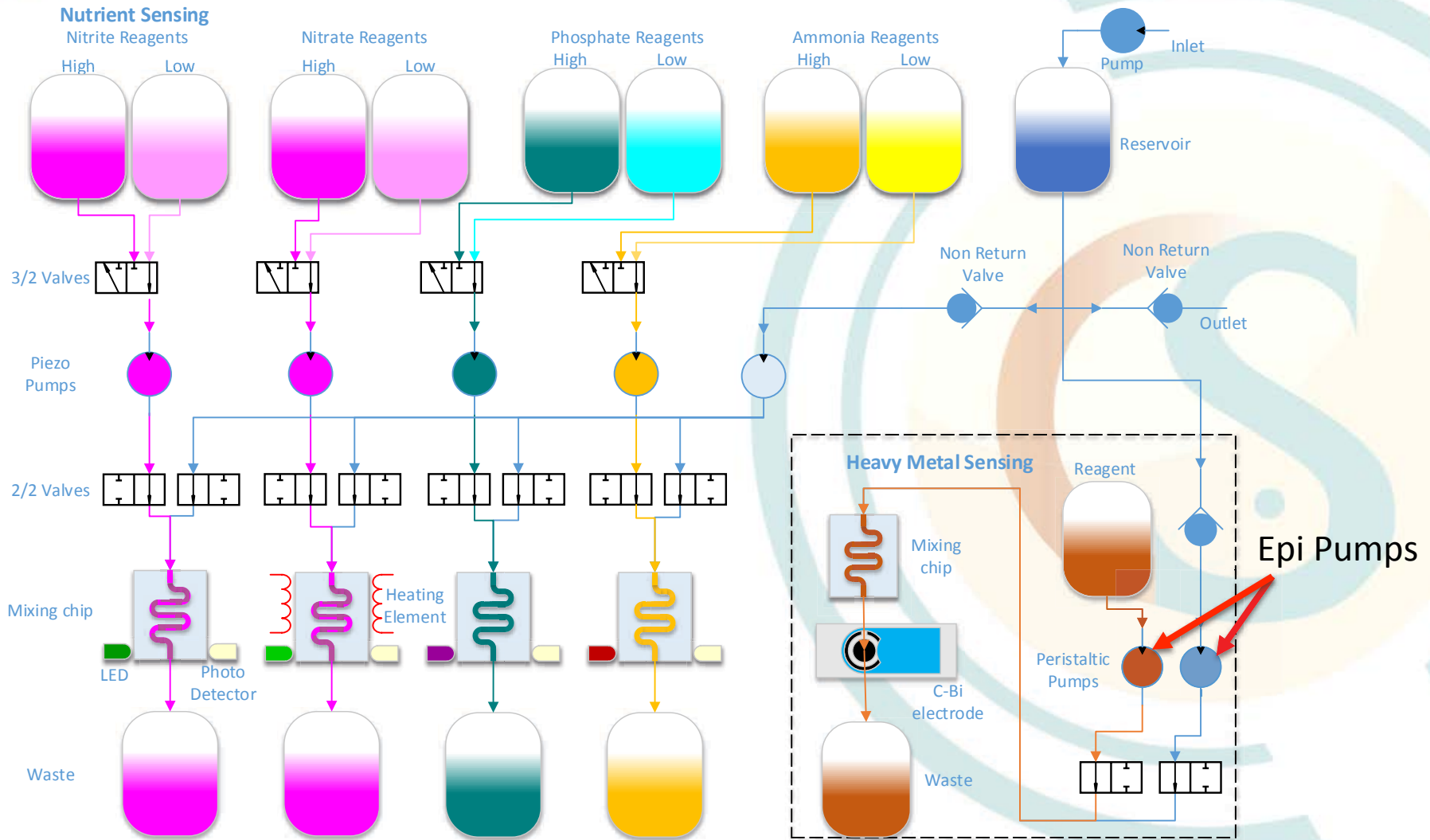




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## Hydraulic schematic



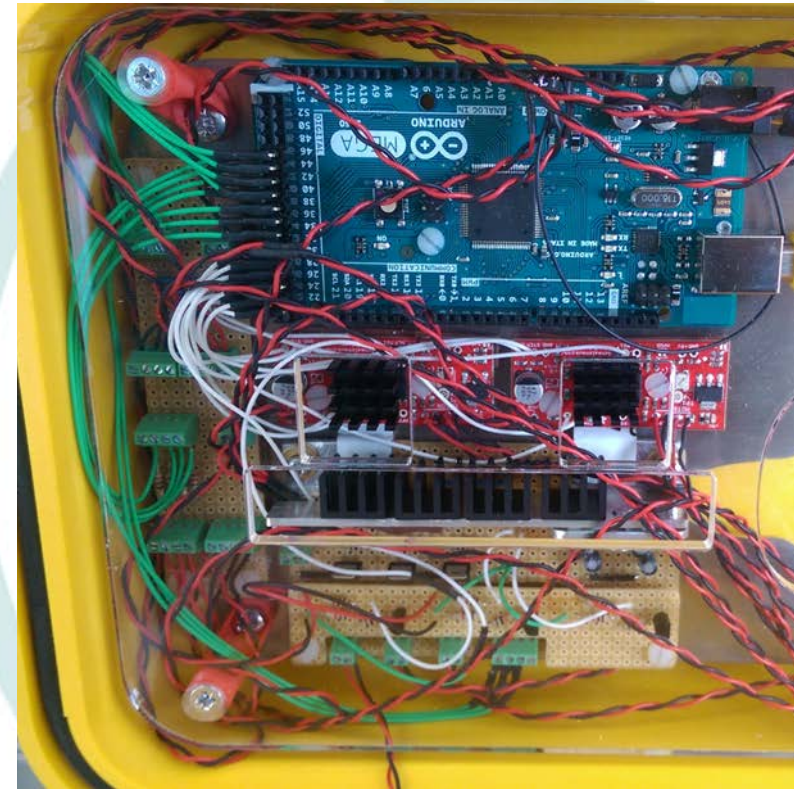
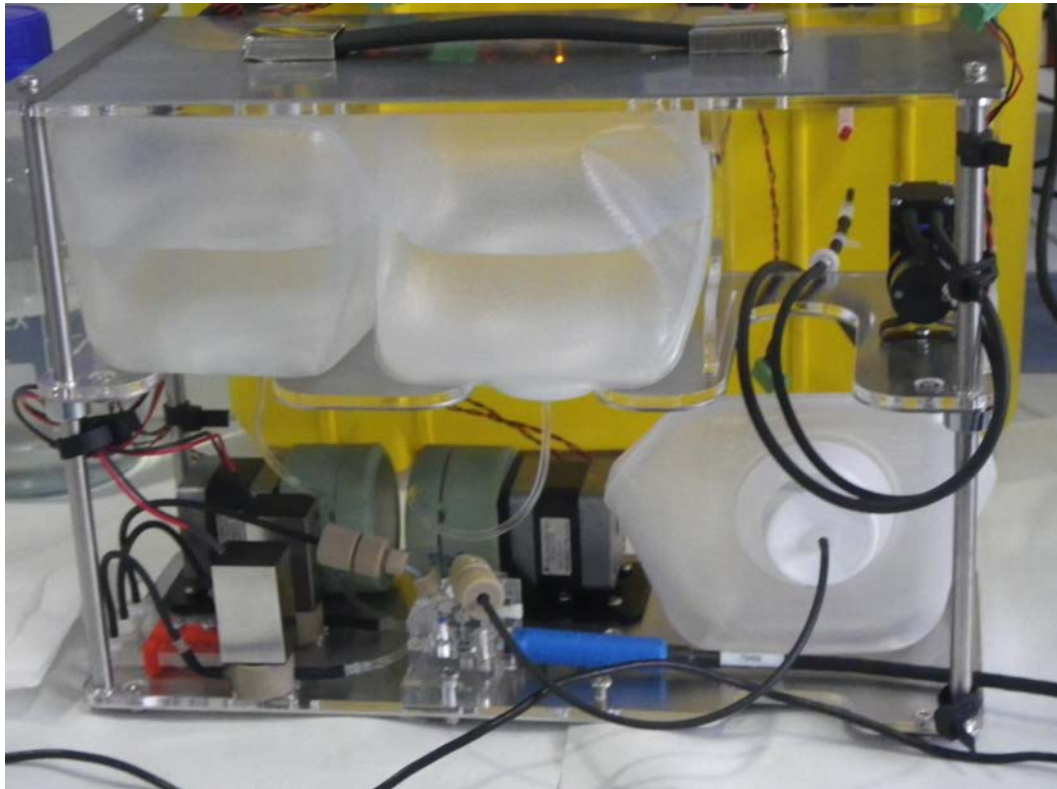
This project has received funding from the European Union's Seventh Programme for research, technological development and demonstration under grant agreement No 614155.

[www.commonsenseproject.eu](http://www.commonsenseproject.eu)



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MARINE SENSORS - MARINE MONITORING

## Heavy Metals Sensing System



This project has received funding from the European Union's Seventh Programme for research, technological development and demonstration under grant agreement No 614155.

[www.commonsenseproject.eu](http://www.commonsenseproject.eu)







# Current State of the Art



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

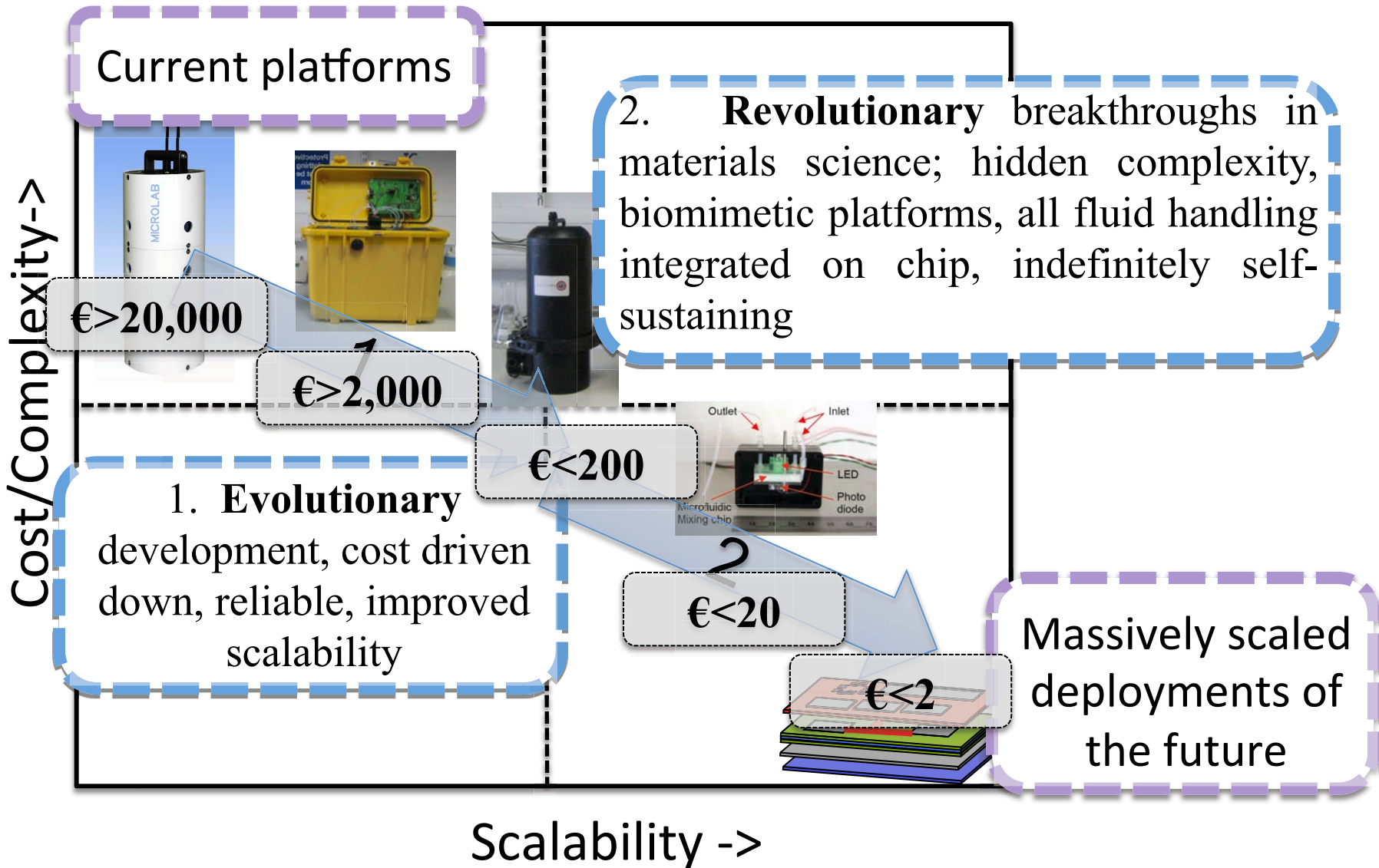
The screenshot shows a web browser window with the URL partech.co.uk. The page features the Partech logo and navigation menu (HOME, ABOUT US, APPLICATIONS, MEASUREMENTS, PRODUCTS, SERVICES, BLOG, CONTACT). The main heading is "MicroMac 1000 Portable Colorimetric Analyser" with a "BACK TO OUR PRODUCTS" button. Below this is a large image of a person in a white lab coat and blue gloves opening a grey rugged case containing the analyser. To the right of the image, the text reads: "Single or Multiparameter Portable Colorimetric Analyser". A paragraph describes the device as a free-standing colorimetric analyser for field use. Another paragraph highlights its portability and use as a portable laboratory. Below the text is a "Share:" section, a call to action "For specialist advice call: +44 (0)1726 879800" with an "ONLINE ENQUIRY" button, and a "RELATED DOCUMENTS" button. At the bottom of the page, there is a cookie consent banner.

This website uses cookies to improve your experience. We'll assume you're ok with this, but you can opt-out if you wish. [Accept](#) [Read More](#)



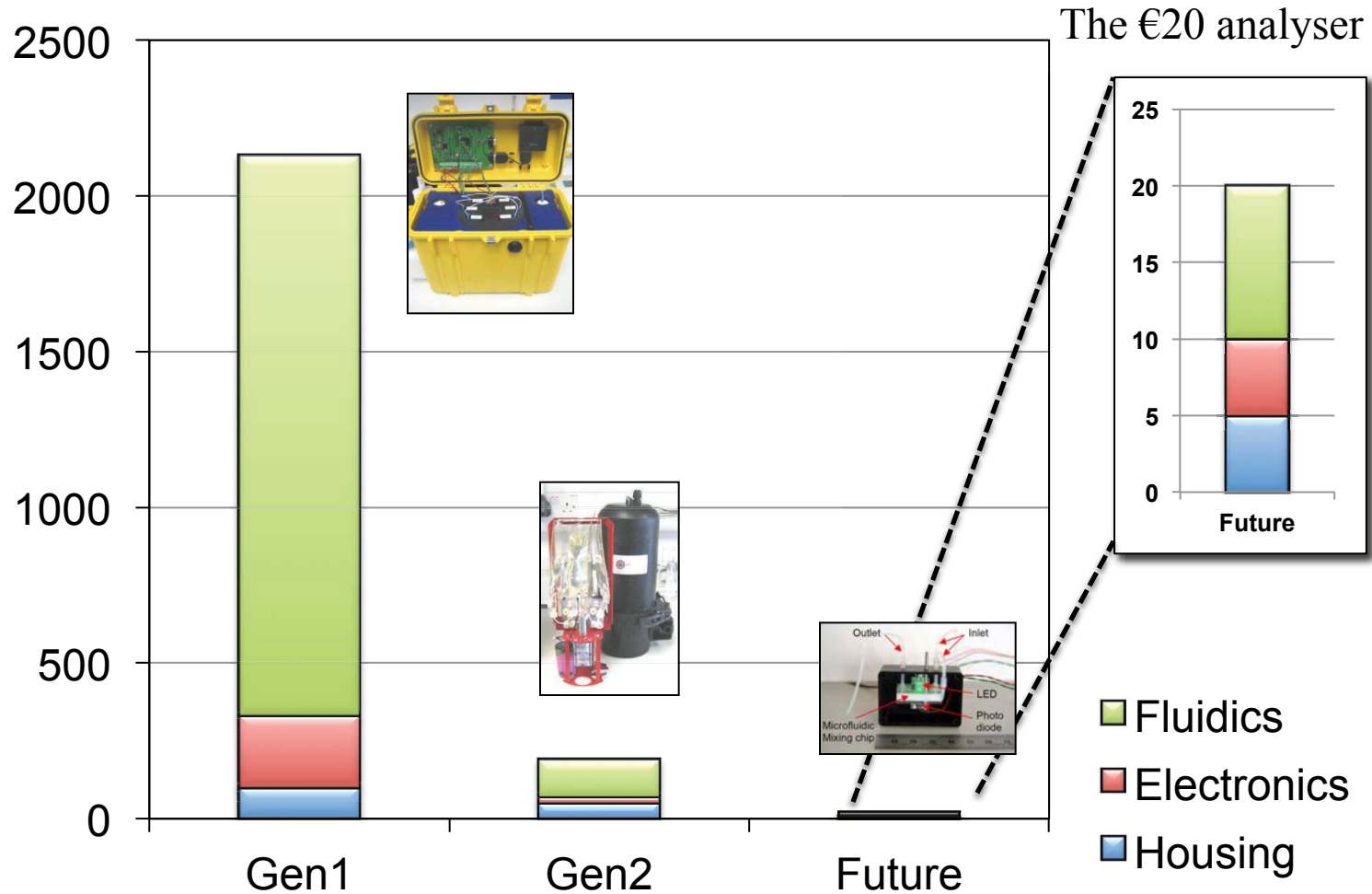


# Achieving Scale-up





# Cost Comparison Analysis (€)

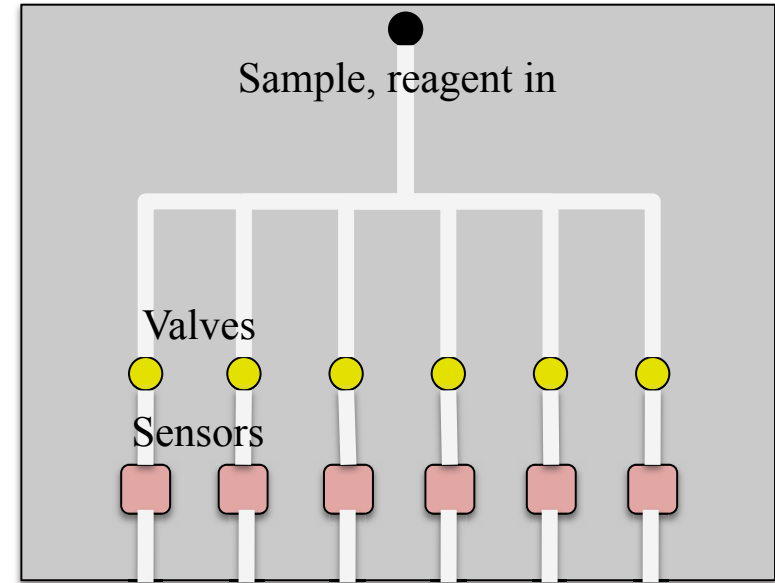




# Extend Period of Use via Arrays of Sensors....?



- 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



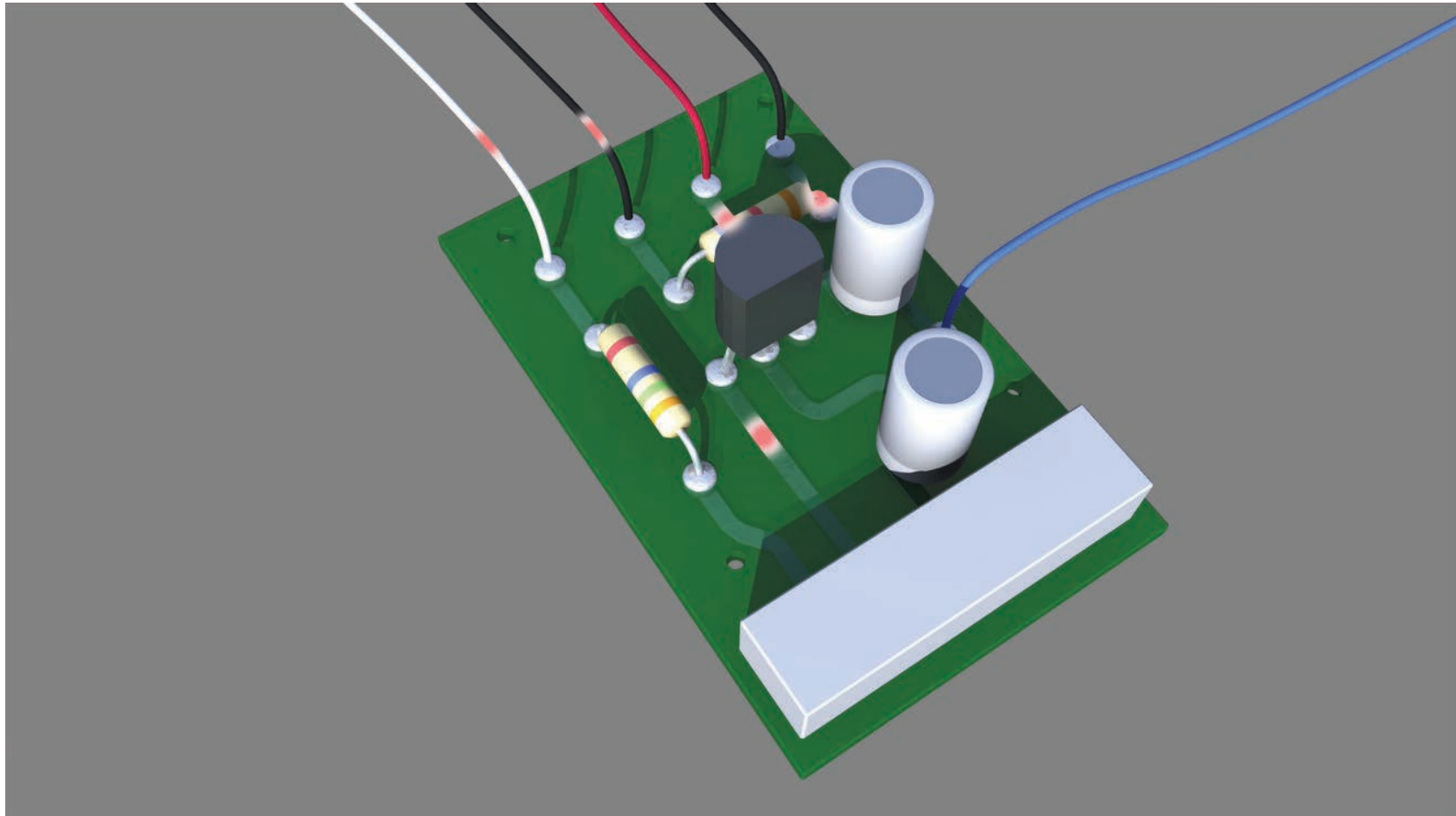
# Microfluidics – Evolution....



Engineering Inspired

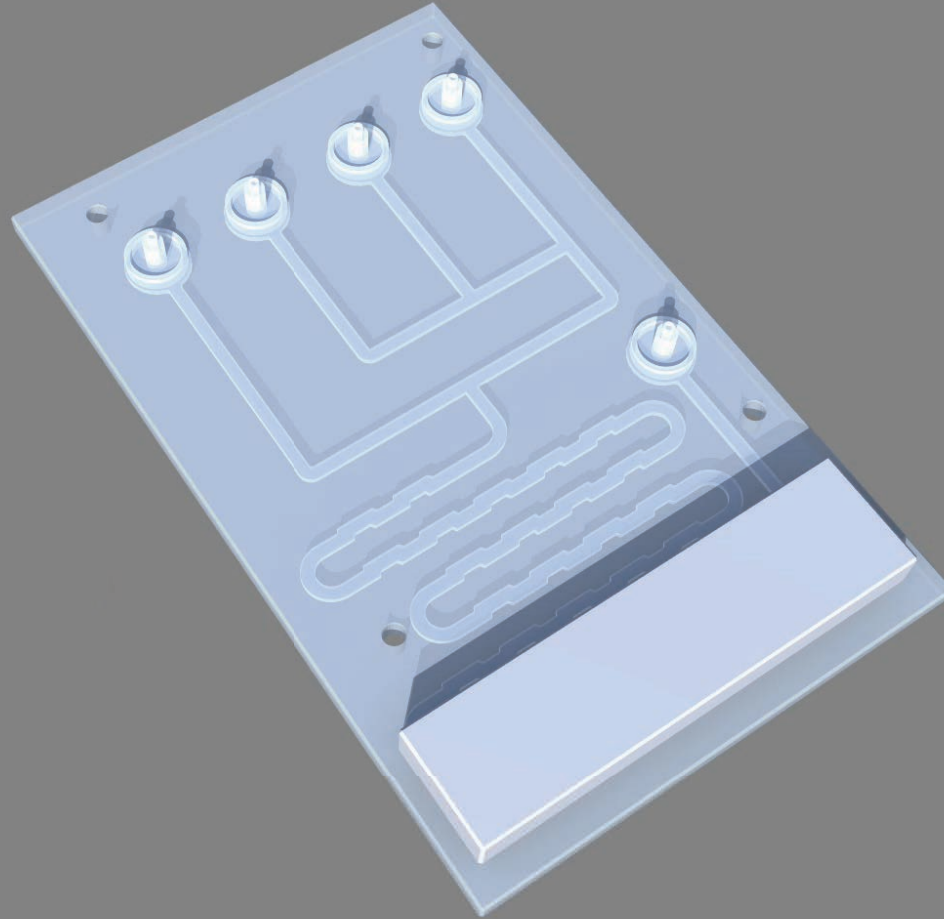


BioInspired



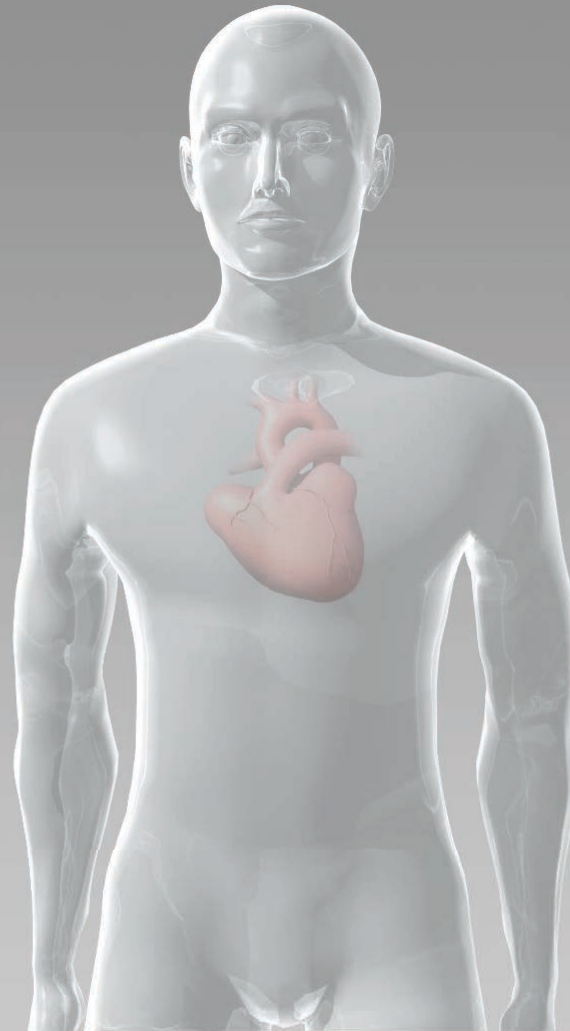


# But not everything is integrated.....

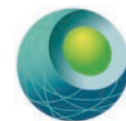




# Bioinspired Fluidics

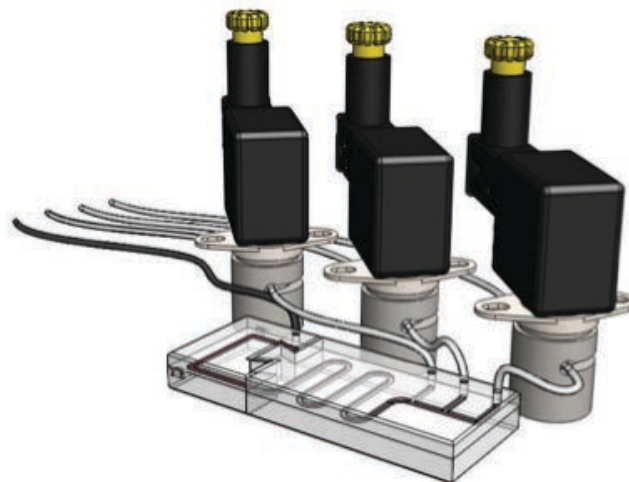






# How to advance fluid handling in LOC platforms: re-invent valves (and pumps)!

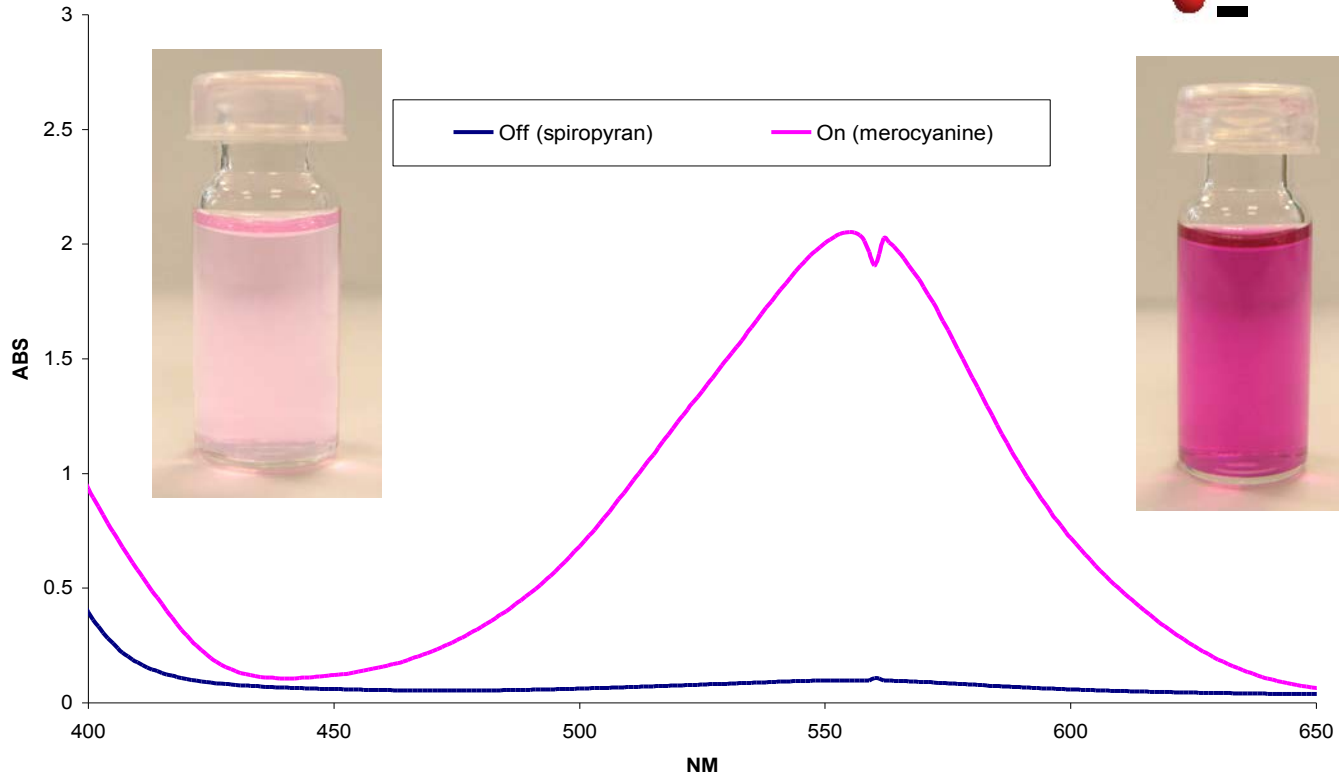
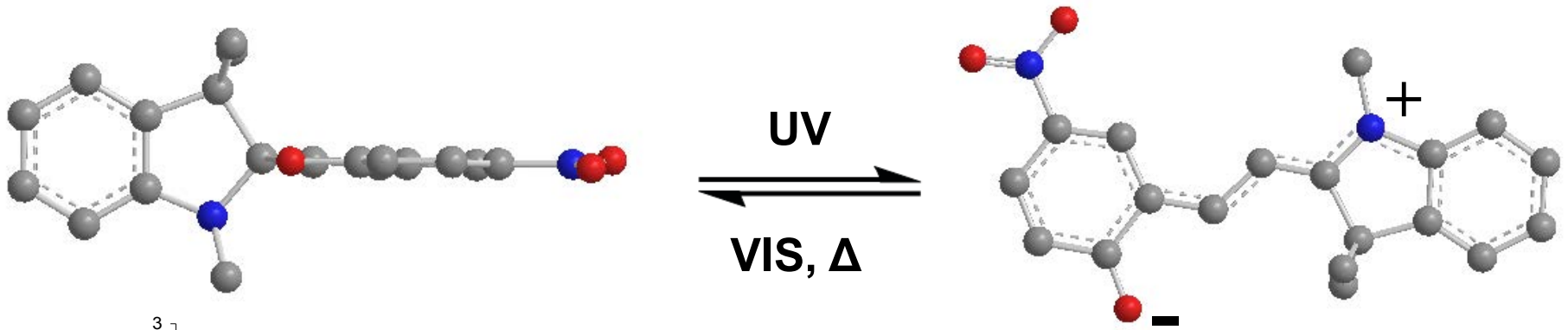
- **Conventional valves cannot be easily scaled down - Located off chip: fluidic interconnects required**
  - Complex fabrication
  - Increased dead volume
  - Mixing effects
- **Based on solenoid action**
  - Large power demand
  - Expensive



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



# Photoswitchable Actuators

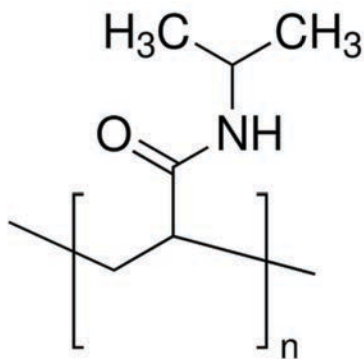




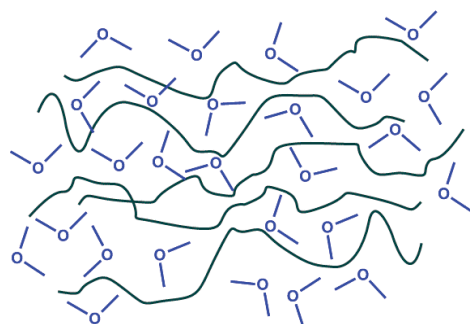
# Poly(*N*-isopropylacrylamide)

- 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

## pNIPAAm



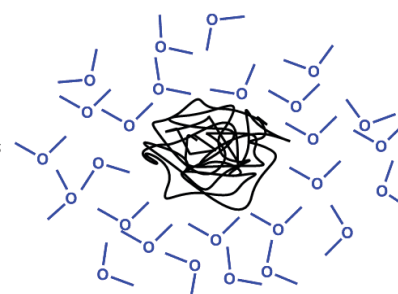
Hydrophilic



Hydrated Polymer Chains



Hydrophobic

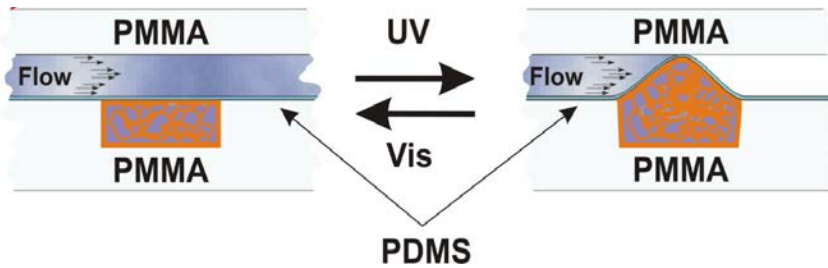
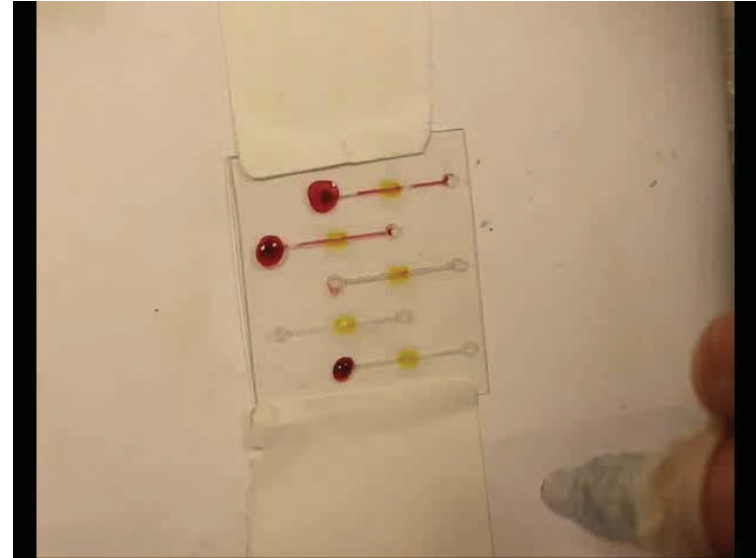
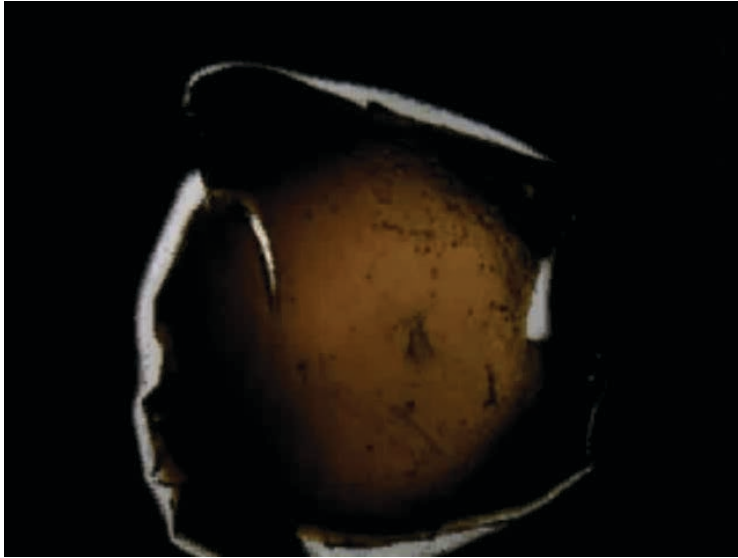


Loss of bound water  
-> polymer collapse

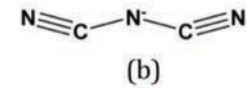
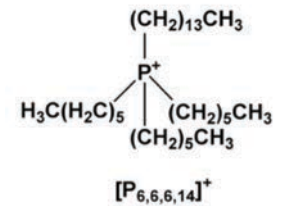
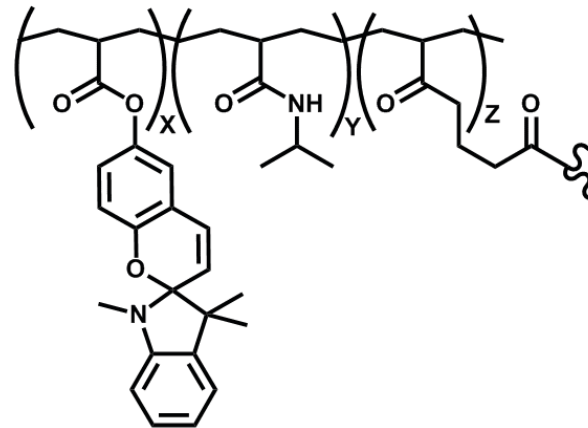




# Photo-actuator polymers as microvalves in microfluidic systems



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

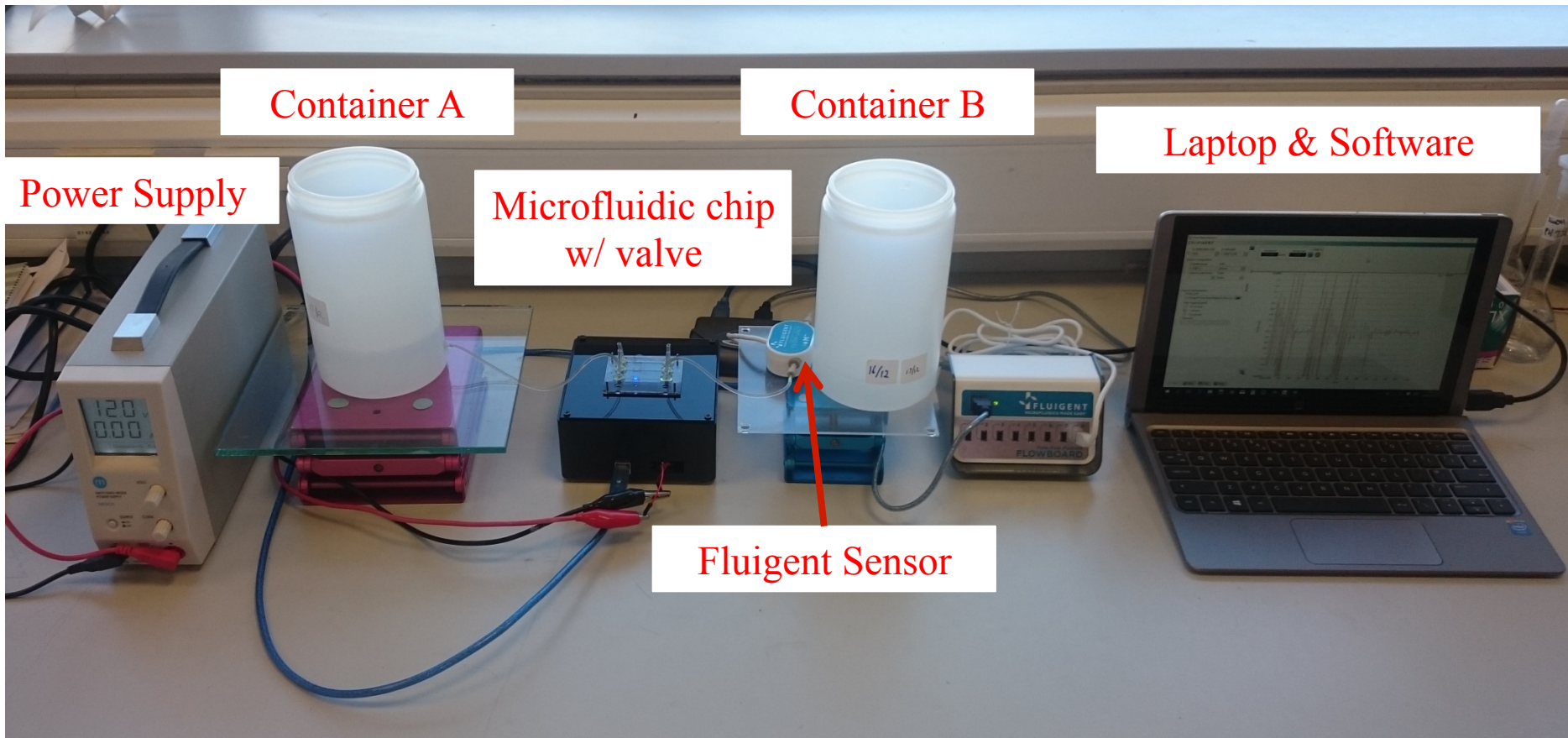


Ionogel-based light-actuated valves for controlling liquid flow in micro-fluidic manifolds, Fernando Benito-Lopez, Robert Byrne, Ana Maria Raduta, Nihal Engin Vrana, Garrett McGuinness, Dermot Diamond, Lab Chip, 10 (2010) 195-201.

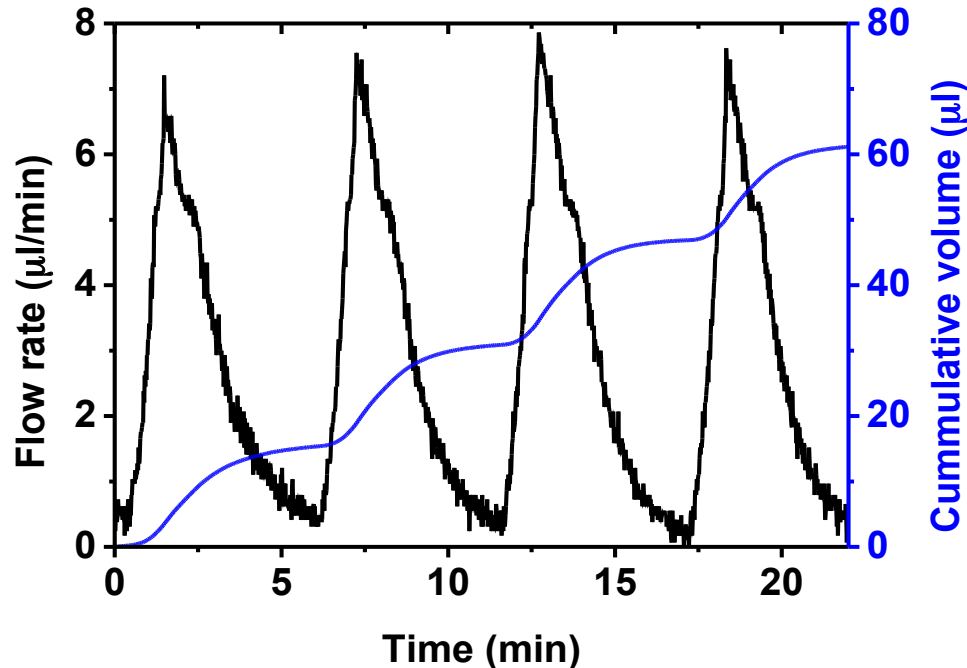




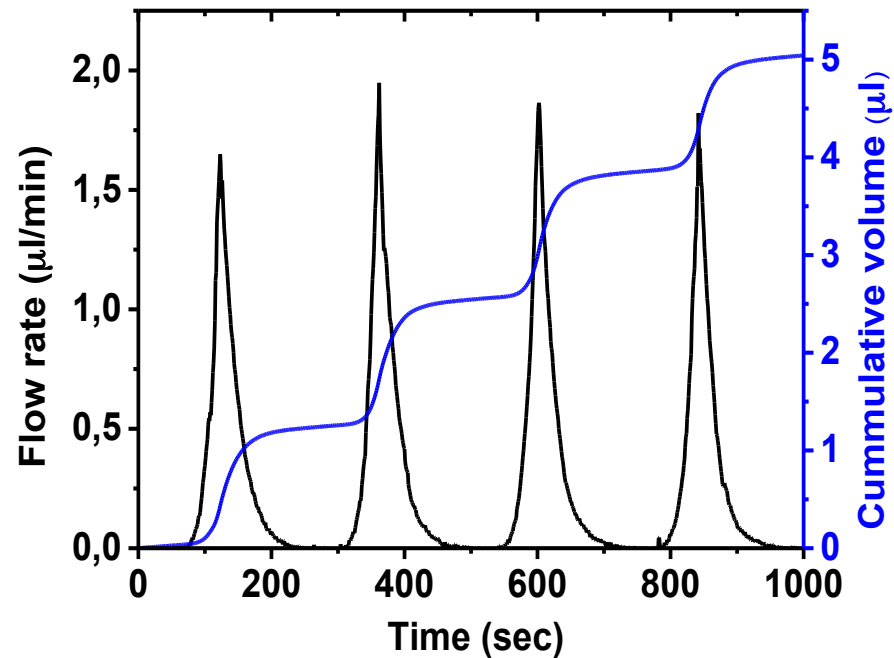
# System Components



# Optimisation of valve dimensions



1.7 mm mask



1.6 mm mask

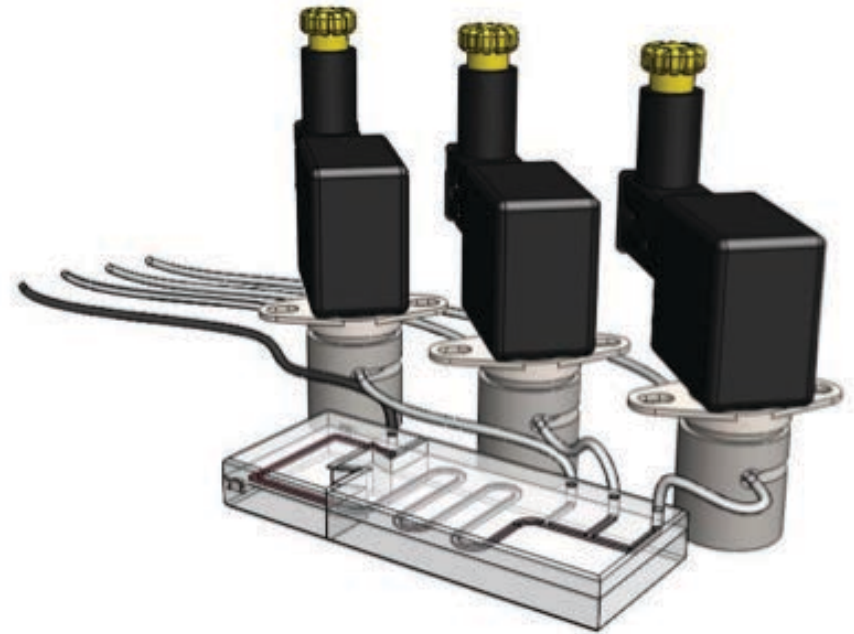
**First example of actuating polymer gels as reusable valves for flow control on minute time scales (> 50 repeat actuations)**

From 'Molecular Design of Light-Responsive Hydrogels, For in Situ Generation of Fast and Reversible Valves for Microfluidic Applications', J. ter Schiphorst, S. Coleman, J.E. Stumpel, A. Ben Azouz, D. Diamond and A. P. H. J. Schenning, Chem. Mater., 27 (2015) 5925–5931. (cover article)



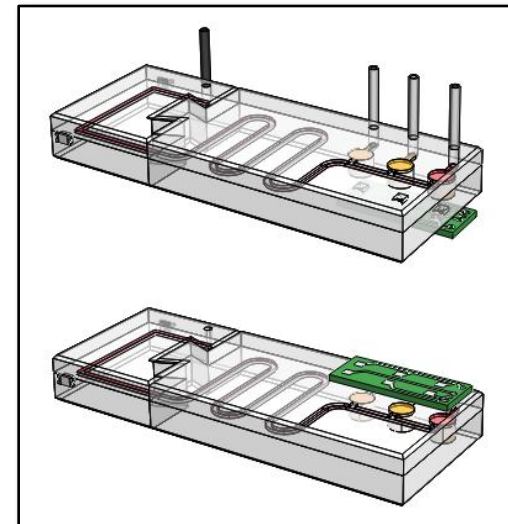
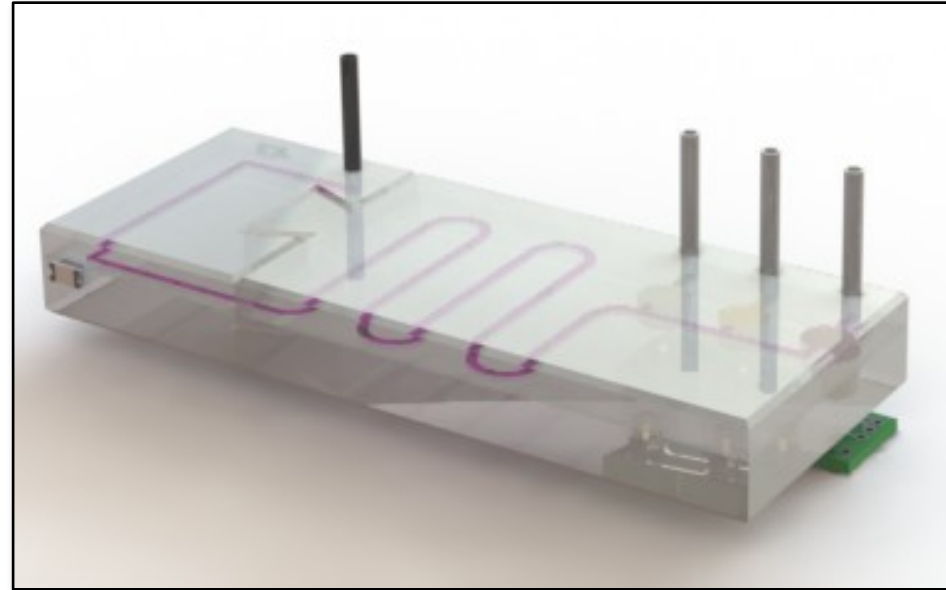
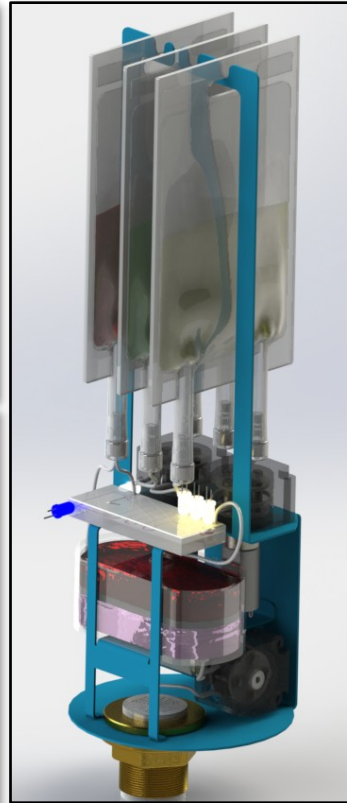
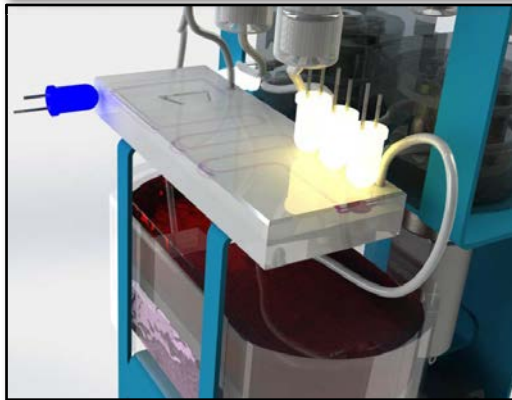
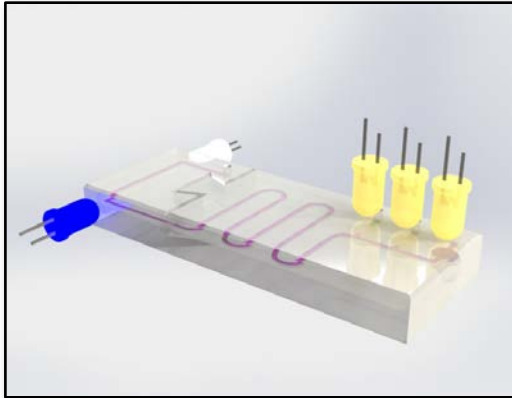


# Can we go from this:





# To Photo-Fluidics & Detection



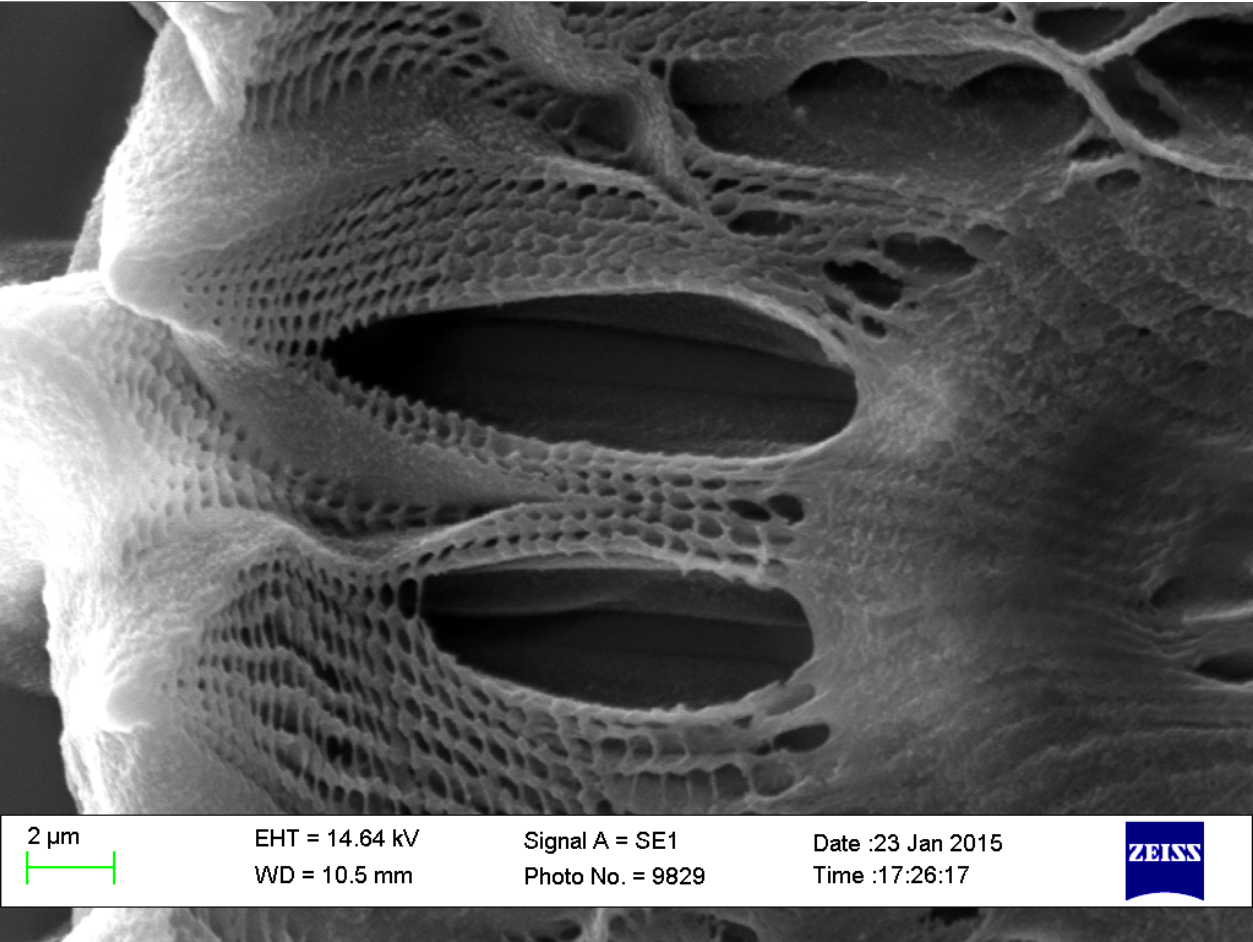
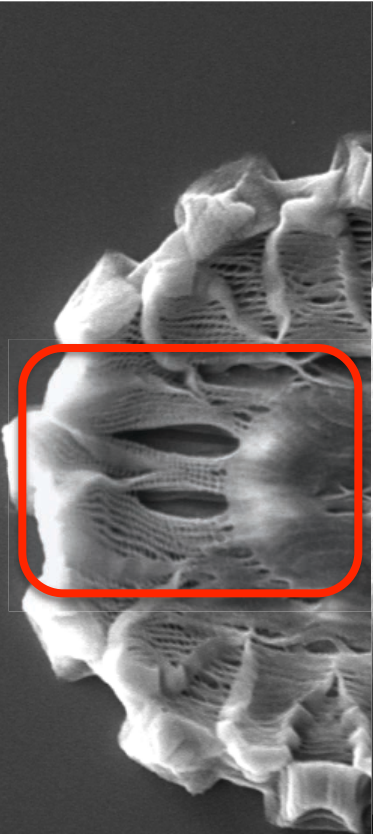
- **Fluidic handling completely integrated into the microfluidic chip**
  - Valves actuated remotely using light (LEDs)
  - Detection is via LED colorimetric measurements
  - Photo-controlled uptake and release







# 'Daisy' – Micro/Nano Scaled Porous Structure



2  $\mu$ m

EHT = 14.64 kV  
WD = 10.5 mm

Signal A = SE1  
Photo No. = 9829

Date :23 Jan 2015  
Time :17:26:17



20  $\mu$ m

EHT = 14.64 kV  
WD = 10.5 mm

Signal A = SE1  
Photo No. = 9826

Date :23 Jan 2015  
Time :17:21:12





# 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

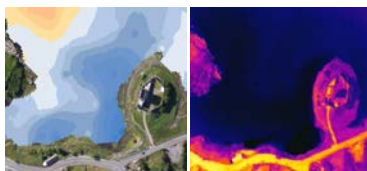
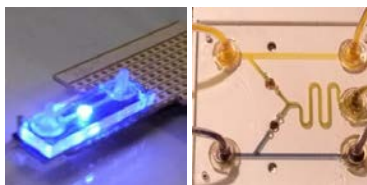
Technologies for monitoring the quality of natural waters and drinking water, and compliance of wastewater with regulatory standards, are set to change dramatically in terms of price and performance. The impact of 'big environmental data' will be truly revolutionary for businesses and for citizens.

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](http://www.napes.eu)), The National Centre for Sensor Research ([www.ncsr.ie](http://www.ncsr.ie)) and the DCU Water Institute .

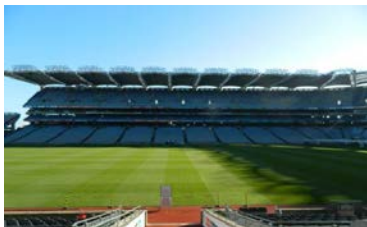
## Confirmed Speakers:

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 Grift, Deltares



Date: 27<sup>th</sup> & 28<sup>th</sup> March 2017

Venue:  
Croke Park, Jones Road, Dublin 3, Ireland.



Contact Details: Angela Lally  
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## NAPES WORKSHOP

Croke Park Convention Centre, Dublin

27/28 March 2017

Contact:

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Cead Mile Failte oraibh uilig!!





- **Members of my research group**
- **NCSR, DCU**
- **Science Foundation Ireland, INSIGHT Centre & Enterprise Ireland**
- **EU Framework Funding**
- **Academic and Industry Research Partners**







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**Thank you for your Attention**

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