Application of micro-analytical technologies for in situ biogeochemical sensors

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Ocean Technology And Engineering Group
National Oceanography Centre, UK
Overview

• **Intro to our labs**

• Oceanography
  – what we measure
  – problems with these measurements
  – what we are hoping to achieve in the future

• Analytical technology
  – Methodology
  – applicability to a broad range of analytes
  – Progress made using theses methods
  – limitations
  – ways to overcome any limitations
  – new directions

• Blatant recruitment advertisement
Research in School of Electronics

- Communication
- Dependable Systems and Software Engineering
- Electrical Power Engineering
- Nano
- Pervasive Systems Centre
- Electronic Systems and Devices
- Intelligence Agents Multimedia
- Optoelectronics Research Centre
- Science and Engineering of Natural Systems
- Information Signals Images Systems
Nano Group:

- Electronic Materials & Devices
- Quantum Electronics
- Photonic devices
- MEMS & NEMS
- RF Circuits
- **Bioelectronics**
  - Lead collaborator is Prof. Hywel Morgan
Microfluidics

Microfabrication + Microfluidics = Miniature platforms for chemical, molecular and cellular analysis
• Sensors
  – Chemical
  – Biological
  – Miniature CT-DO
• Engineering
  – Vehicles
  – Lake Ellsworth
• Technology
  – Sterility
  – Biotechnology
  – Analytical sciences
• Sea level measurement systems
• Telemetry
• Landers
• Vehicles and instrumentation
• Instrumentation to measure particles and sediments
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Biogeochemistry: Global impact, hard to measure
Target platform: Argo – global reach and impact
Sensors must have
• low cost
• easy setup
• low buoyancy change
• low weight in water
• long-term stability
• >1 sample / 4 minutes in burst mode
Chemical Targets

- Nutrients (uM coastal / deep, nM open ocean)
- **Trace metals** (n -fM)
- Gases (n-uM)
- Carbonate system (0.001 pH equiv)
- **Small organics, e.g. PCBs (f-pM)**
- Proteins and large organics (copies / L)
- Nucleic Acids (copies / L)
sensors on gliders (initially in shelf seas)
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Methodologies

- **Optical**
  - Nitrate
- **Optodes**
  - Methane
  - Oxygen
  - \( p\text{CO}_2 \)
  - pH
- **Electrochemistry**
  - Oxygen

- **Lab on a chip**
  - Nutrients
  - Trace metals
  - pH, TA, DIC, \( p\text{CO}_2 \)
  - Small organics, e.g. PCBs
  - Proteins and large organics
  - Nucleic Acids
Methodologies Applied on LOC

• Nutrients
  – **Nitrate**: cadmium reduction Griess
  – **Nitrite**: Griess
  – **Ammonium**: OPA
  – **Phosphate**: molybdocvanadophosphoric or molybdate
  – **Silicate**: molybdate / reduction
Nitrate / Nitrite LOC
State of the art operational LOC

A

B
High temporal resolution

See Beaton et al. Env. Sci & Tech 2013
Nutrient LOC

- Float optimisation required!
- Nitrate LOD / precision ≈ 20nM / 7nM
- Phosphate (yellow) LOD ≈ 80nM / 10nM
- Phosphate (blue) LOD ≈ 10nM / < 1nM
Iron and Manganese sensor

Research data and images by Ambra Milani
Methodologies Applied on LOC

**Trace metals**

- **Fe (II, III)**: Ferrozine, LOD \( \approx 20 \text{ nM} \)
  - With chelating resin pre-concentration LOD <1 nM (Nitriloacetic acid).
- **Mn (IV)**: PAN, LOD \( \approx 30 \text{ nM} \)
Methodologies Applied on LOC

- **Carbonate system**
  - **pH**: Spectrophotometry with indicators e.g. Thymol blue, MCP. Precision ≈ 0.001 pH
  - **TA**: Spectrophotometric tracer monitored titration with indicators e.g. BCG precision ≈ 10 uM
Applications: Carbon observations (pH sensor)

- short term precision 0.001 pH (n=20)
- accuracy within the range of a certified Tris buffer (0.004 pH)

Research and data by Victoire Rérolle
Biosensing: Nucleic Acid

- Developing Generic platform for Nucleic Acid Assays
- Initially targeting RNA with Nucleic Acid Sequence Based Amplification (NASBA – above)
- Enables analysis of transcription, and species presence
- Initial target is rbcL gene (codes large subunit of Rubisco holoenzyme)
- Several species specific assays developed
- Can target toxin producing genes

Figure and work by M.N. Tsaloglou
Figure  and work by M.N. Tsaloglou
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Limitations

- We have tackled
  - In situ calibration
  - Interferences
  - Cheap materials
  - Cheap high performance optics
  - Pressure tolerance
  - Reagent consumption
  - Time response
  - Filtering / biofouling

- We are tackling
  - Reagent stability
  - Required user skill
  - Reliability
  - Low cost minature pumps and valves
  - Highly multiplexed systems
  - Preconcentration / ultra low LOD
  - Aggressive fouling
Pressure tolerant electronics

Development led by Ed Waugh
Low-cost high fidelity optics

Floquet et al 2011
Low-cost optical surface finish

Ogilvie et al 2010
Fast measurement with precision

- Fluidics =
  - Dispersion
  - Reaction Kinetics
  - Delay is inevitable
  - High frequency possible with dispersion compensation OR MULTIPLE DETECTION CHAMBERS

- Elastomer based valves and pumps = low cost, many on each chip

Ogilvie et al 2011
Fast measurement with precision

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Ogilvie et al 2011
Advantageous Dispersion

• Dispersion enables measurement to be corrected for pH perturbation induced by indicator

(Rerolle et al. 2012 & 2013)
Proprietary reagent packs

Courtesy TelLab
Preservation of reagents

Tsologlou et al. 2013
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New Directions

• Low-power actuation of pumps / valves
• High frequency (>1Hz) measurement
• New targets, including dissolved organic nutrients, organics and proteins
• Rugged In situ field deployed systems
• Next generation in situ nucleic acid sensors
We are recruiting

• Head of analytical science (up to NERC band 4 approx UoS ERE 6)
• Three research / engineers (NERC 6 approx ERE 4)
• Two electronics software engineers (NERC 6)
• One microfabrication / fabrication engineer (NERC 6)
• PhD studentships
Acknowledgements to the team past and present: http://www.southampton.ac.uk/cmm/