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RIAL Real-Time Water Quality Monitoring Workshop June 16th and 17th, 2009

Outline

- Process/treatment and EEM (environmental effects monitoring) systems
- □ Scale of the problem
- Limitations in current approaches
- Microfluidics
 - Advantages over macroscale methods
 - Technological advances
 - Detection methods
- Coatings
- Detection/measurement

- Monitoring process streams, drinking water, and wastewater streams and receiving water bodies critical:
 - Levels of chemicals in process streams can indicate inefficient treatment systems
 - Use of personal care products, pesticides, pharmaceuticals, etc... resulted in rapid increase in number of possible contaminants in drinking water/wastewaters
 - Even at low levels, these contaminants can have significant impacts on human health and the ecosystem of the receiving water body

- Most effluent treatment systems are not designed or operated to remove many of previously mentioned contaminants or their degradation products due to:
 - inability to measure and/or
 - sheer number of contaminants
- **EEM** systems suffer same problems:
 - large number of contaminants of concern but limited ability to target, discriminate, and
 - samples not representative of space and time

Effective Systems

- Efficient design/operation process systems, design EEM, and assessment of impact/risk of industrial/municipal waters requires addressing fundamental issues:
 - Target Contaminant(s) 1000s of compounds
 - Persistence
 - Compounds that are inherently harmful due to the toxicity of the compound itself and/or the toxicity of their degradation products. The toxic effect on the organisms (disease causing, birth defects, etc.) may be acute or chronic in nature.
 - Toxicity
 - Compounds that have a harmful effect on the ecosystem, for example eutrophication of water bodies due to nutrient enrichment
 - Purpose (i.e. process control or EEM)
 - Possible indicator
 - Compounds that are not necessarily harmful but are indicators of other more toxic compounds, of human impact, or process ineffectiveness (e.g. problems in the treatment system or even upstream in the industrial process itself).

☐ Frequency of measurements

- Can be costly but long lag times between measurements may result in inefficient operation of a process or design of EEM
- Detection vs. measurement
 - Ideally want to do both but in some cases detection may be all that is required for appropriate action

Specifics on Current Approaches to Analysis

Point source

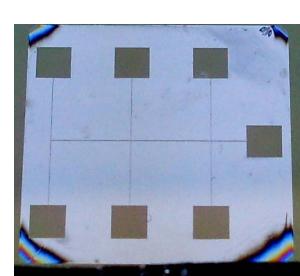
- On-line analysis
 - Bulk properties (e.g. oil in water, pH, etc.)
 - Limitations in specificity and sensitivity
- Sampling with off-line analysis
 - Limited sampling density
 - No real-time data results in delayed response
 - Degradation of sample quality
- Ambient (in-situ)
 - "grab samples" do not reflect spatial and temporal diversity
 - Degradation of sample quality between sampling and analysis
 - Sampling density

Micro-Total Analysis Systems

- µ-TAS or "lab on a chip" devices incorporate all the processes required for sample analysis into one small scale unit which may include:
 - Specialized sample intake and/or handling: filtration, derivitization, preconcentration, etc.
 - Separation in microfluidic channels: need specialized surfaces and flow control
 - Post separation treatment
 - Detection: fluorescence, UV-vis, Raman, mass spectrometry, electrochemical methods, etc.
- Advances in technology have meant scaled-down size and cost
 - More accessible technology, easier to use, more widely deployable
- Our devices focus on microfluidics, flow control, specialized surfaces and innovative detection methods

- Microdevices can offer substantial improvements over these approaches to analysis
- □ Innovative and new proprietary fabrication techniques
- Tailored devices
 - Selective
 - Small (devices the size of a dime)
 - Easy signal recognition
 - o Colour change
 - Field-operable spectrometers
 - o In-lab spectrometer
 - Many variations can be very simple to operate

Robust

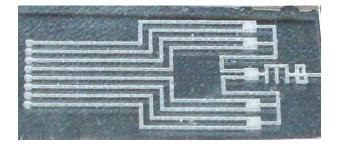


Micro- to nano-scale channels

- Different flow regime (laminar flow) than macroscale
- Better fluid manipulation (controlled input/output/separations)

□ Small footprint:

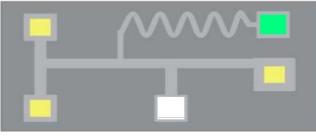
- Lower cost of manufacture
- Lower cost of field deployment
- Higher density of information/measurements
- □ Higher surface area-to-volume ratio
 - Higher sensitivity
 - Faster response



Microfluidics – Technological advances

Microfabrication methods from the semiconductor industry

- Use industry-standard photolithography to create "wires" to channel fluids instead of electrical current
- We have recently acquired a state-of-the-art patterning system with associated thin film deposition equipment
- New methods for "soft lithography"
 - Device fabrication and replication in polymers and plastics
 - Proprietary method for direct polymeric constrution (patent filed)
- More than just tubes
 - Valves, reactive areas, sensing "pads", signal transduction modules (optical windows, electrodes)



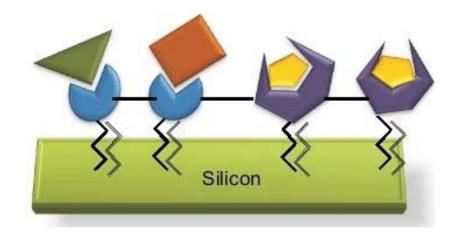
Selective and Sensitive Detection and Quantification

□ Sensitivity:

- On-chip separations
- Selective binding regions
- ❑ Raman spectroscopy
 - Detects organics and inorganics, solutions and solids
 - Highly specific "fingerprint" for each molecule
 - Distinguishes different sizes and functionalities
 - No need to label or otherwise modify sample
- Mass spectrometry
 - Detects a wide range of compounds with varying sizes and functionality
 - Sensitive, selective and quantitative
 - Drawback: compounds must be converted into gas phase ions

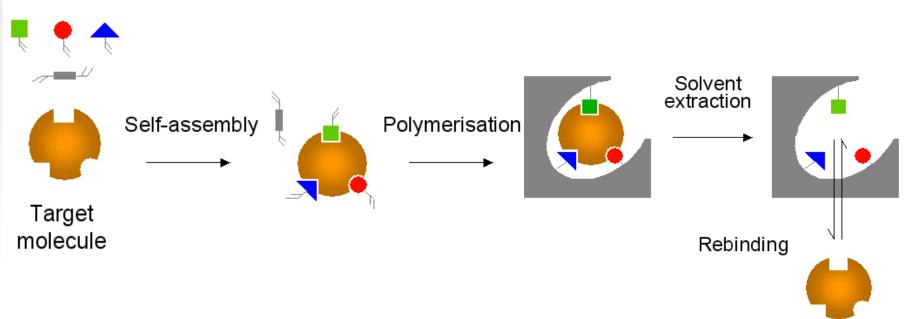
Tailored Coatings for Enhanced Performance

- Separation ("smart filtration"):
 - Different migration times with different coatings
- Binding:
 - Accumulate analytes of interest on a "sensing pad"
 - Separate similar analytes by functional group or shape differences
- Detection:
 - Enhanced signal from binding event
 - Coating can promote signal transduction (*e.g.* by a colour change)



Molecularly Imprinted Polymers (MIPs)

Monomers



- Functional monomer + cross-linker + template molecule = MIP
- □ Attractive material for use in specific molecular recognition
 - Simple to prepare, easy to tailor, and robust
- Detection can be on-chip using optical interrogation (our interest is Raman, but other methods are being explored) or off-chip

Targets of interest based on *indicator* status or *toxicity and occurrence*: 2,4-dichlorophenoxyacetic acid

- Most widely used herbicide in the world, used for the control of broadleaf weeds.
- Present in 1500 different products, many used domestically, e.g. Killex
- Possible human carcinogen
- □Polycyclic aromatic hydrocarbons (PAHs)
 - Found in oil, coal, tar, byproducts of burning oil/gas or biomass
 - Composed of hundreds of different compounds
 - Composition can be used to discriminate between sources
 - Toxicity depends on structure, some fairly benign, others are strong carcinogens, mutagens, etc.

Bisphenol A (BPA)

- Controversial chemical because of widespread use in plastics manufacturing particularly of products used in beverage containers and lining cans used for food
- Suspected endocrine disruptor
- Presence in wastewater an additional route to surface water contamination

Caffeine

- One of the most commonly used drugs worldwide (tea, coffee, chocolate, etc.)
- Commonly found in surface water due to infiltration of wastewater making it an early indicator of contamination

□ Other pharmaceuticals and Contaminants

• e.g. Ibuprofen

The Way Forward

□ Microfluidic and µ-TAS Technology

- Optimization
- Designs for new targets
- Implementation
 - Monitoring in remote/fragile areas
 - Real-time data
 - Optimized processing to minimize impact
 - Rapid detection results in quick response to prevent/mitigate environmental impacts
 - Long-term monitoring of environmental quality Options for on-site reporting, off-site verification
- Validation of technology in real-world environments using traditional analytical approaches

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