20th RACI Research And Development Topics Conference in Analytical and Environmental Chemistry

Featuring: The ACA Editors Symposium

11th-14th December 2012

School of Life and Environmental Sciences,
Faculty of Science and Technology,
Deakin University,
Geelong, Victoria, Australia

Conference Co-Chairs

Danielle Bassanese

Zoe Smith

Special Thanks

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Dr. Jie Zhang - Robert Cattrall Early Career Medal

Prof. Kliti Grice - Environmental Chemistry Medal

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Sarah Laird (La Trobe University)

Judges

A selection of ACA editors will judge the oral and poster presentations

Cover Images

Donna Squire

Welcome Mixer Organising Committee

Brendan Holland

Dave Donaldson

Teo Slezak

Contents

General Information

Name Badges

Please wear name badges at all conference sessions including lunch breaks. Conference volunteers can be identified by their black lanyards.

Oral Presentations

Oral presentations will be held in Lecture theatre *ka3.403*. Delegates presenting oral presentations are requested to contact a conference volunteer during the registration period at the beginning of each day to have their presentations uploaded onto the computer.

Poster Sessions

Poster session 1 will be held on Wednesday (12th) between 3:30 and 5:00 pm in the dining hall (room jb1.102, near the Union Green). Poster session 2 will be held on Friday (14th) between 10:00 and 11:00 am in the foyer outside the lecture theatre. Posters will be set up by conference volunteers; delegates are asked to hand in their posters at the registration desk on the morning of their session. Poster boards will be labelled with the number corresponding to the abstract number in this book. Authors presenting posters are requested to be in attendance at their poster for the duration of the session.

Presentation Of Prizes

Prizes will be awarded at the conference dinner.

Parking

Delegates driving to the conference should enter via entrance 2.
The closest car park to the conference venue is car park 2. This is a permit area and daily tickets are $6.00. Car park 11 is a free car park, and is an approx. 5 min walk to the conference building (see map).

Important Numbers

- Geelong Campus Security: 5227 2222 (or 222 from an internal phone)
- Taxi: 131 008

Emergency Evacuation

Standby alert signal - BEEP BEEP BEEP
Evacuation siren - WHOOP WHOOP WHOOP

Evacuation will happen when the standby alert signal sounds
All building occupants <u>must </u>evacuate on this evacuation signal.
Remember not to use lifts during evacuation.
Please follow the instructions given by Emergency Wardens, Security staff or Emergency Services personnel. At the end of the evacuation, you will be advised when it is safe to return to the building.

Campus Map
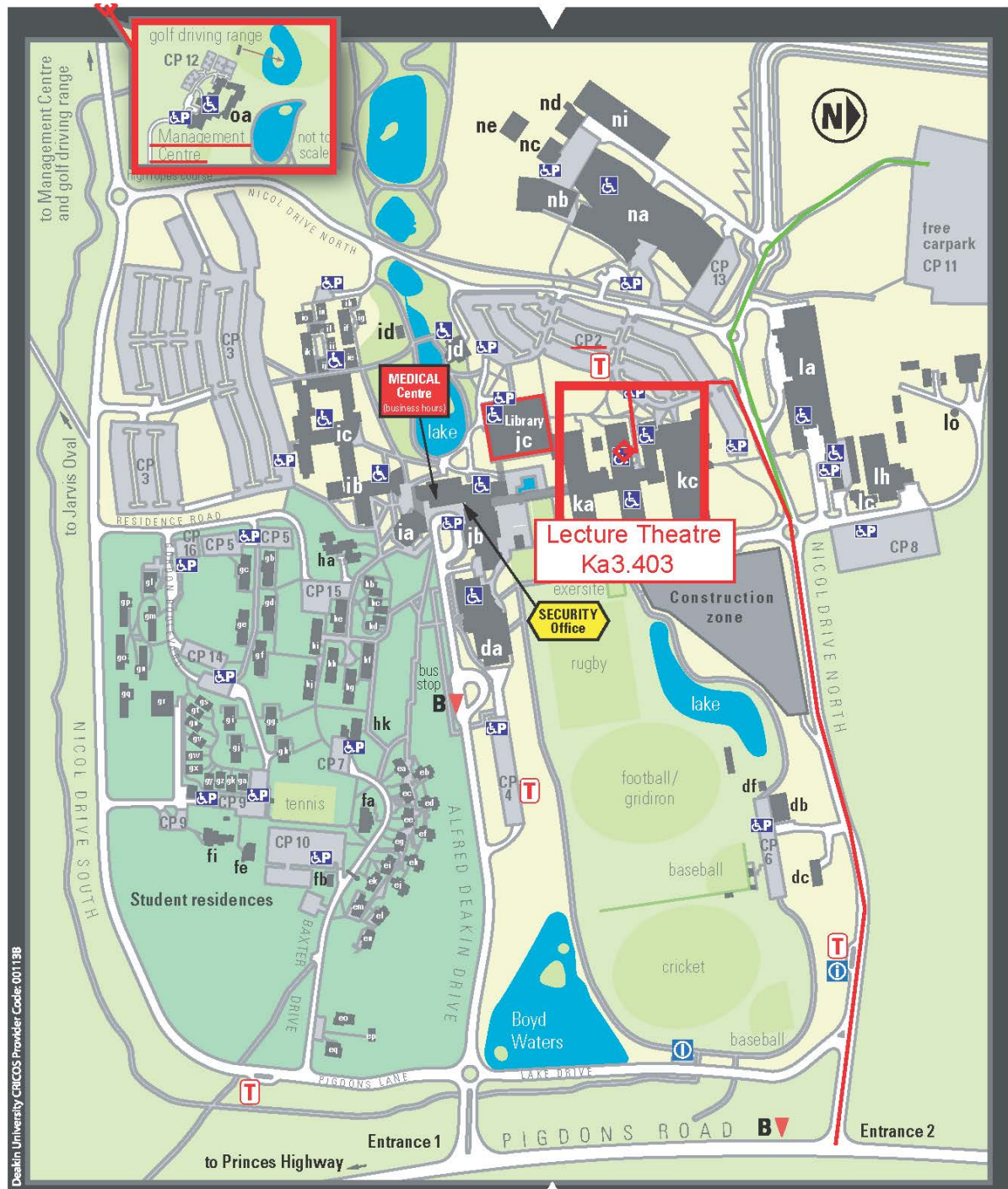
Red Line - Directions to car park 2

Green line - Directions to the free car park (car park 11)

B▼ - Bus Stops

Activities

Welcome Mixer
Tuesday 11th December (following the ACA editors symposium)

Beer and Pizza Night

  Venue: The Union Green

  Time: 6:00 PM

  Cost: $5

Winery Tour: Leura Park Estate
Thursday 13th December

A winery tour and tasting session - transport included

  Cost: $10 to be paid upon registration

  Leaves: 1:00 PM

  Meeting Point: Deakin bus stop at 12.50 PM

  Activity Leaders: Dave Donaldson and Xavier Conlan

End of Conference Dinner
Friday 14th December

  Venue: Le Parisien Restaurant
      15 Eastern Beach Road, Geelong

  Time: 6:30 - 11:30

  Dress: Formal

Sponsor Raffle
In your conference bag you will find your sponsor raffle pass-book. Get stamps by talking to our sponsors at their trade tables. Hand your forms in at the registration desk to go into the running to win a prize each day!

Around Geelong...
In your conference bag you will find a map pointing out local attractions and nightspots so you can enjoy your stay in Geelong!

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Programme At A Glance

Tuesday ACA Symposium	Wednesday	Thursday	Friday
11th December	12th December	13th December	14th December
	8:00AM - 9:00AM **Registration Open**		
8:30AM - 9:45AM **Registration Open**			
		8:50AM - 9:00AM **Registration Open**	**8:50AM - 9:00AM** **Registration Open**
	9:00AM - 9:15AM Conference Opening	9:00AM - 9:30AM Robert Cattrall Medallist	9:00AM - 10:00AM Oral Session 6
	9:15AM - 9.45AM Lloyd Smythe Medallist	9:30AM - 10:30AM Oral Session 4 Chair: Brendan Holland	Chair: Sara Sandron
9:45AM - 10:00AM Opening Comments	9:45AM - 10.45AM Oral Session 1 Chair: Zoe Smith		
10:00AM - 10:30AM Prof. Rick Baldwin			10:00AM - 11:00AM **Poster Session 2**
10:30AM - 11:00AM Prof. Wolfgang Buchberger	10:45AM - 11:15AM Morning Tea / Trade Display	10:30AM - 11:00AM Morning Tea / Trade Display	10:45AM - 11:10AM Morning Tea/Trade display
11:00AM - 11:30AM Morning Tea	11:15AM - 12:35PM Oral Session 2 Chair: Michelle Camenzuli	11:00AM - 12:00PM Oral Session 5 Chair: Elizabeth Murago	11:10AM - 11:40AM Environmental Chemistry Medallist
11:30AM - 12:00PM Prof. Lutgarde Buydens			11:40AM - 12:20PM Oral Session 7 Chair: Kenneth Ogogo
12:00PM - 12:30PM Prof. Purnendu (Sandy) Dasgupta		12:00PM Lunch Trade Display Winery Tour	
12:30PM - 1:30PM Lunch	12:35PM - 1:30PM Lunch Trade Display		12:20PM - 1:30PM Lunch/Trade Display 1:00PM - 1:30PM Technical Seminar
1:30PM - 2.00PM Prof. Ulrich Krull	1:30PM - 2:50PM Oral Session 3 Chair: Scott Meyerink		1:30PM - 2:50PM Oral Session 8 Chair: Sarah Laird
2:00PM - 2:30PM Prof. Liang Li			
2:30PM - 3:00PM A/Prof. Manuel Miró	2:50PM - 3:15PM Afternoon Tea / Trade Display		2:50PM - 3:20PM Afternoon Tea / Trade Display
3:00PM - 3:30PM Afternoon Tea			3:20PM - 4:20PM Oral Session 9 Chair: Leigh Thredgold
3:30PM - 4:00PM Prof. Janusz Pawliszyn	3:30PM - 5:00PM **Poster Session 1** Dining Hall (jb1.102)		
4:00PM - 4:30PM Prof. Paul Worsfold			4:20PM Conference Closing
4:30PM - 5:00PM David Sleeman			
5:00PM - 5:15PM Closing Comments			
6:00PM **Welcome Mixer** Beer and Pizza Night			**6:30PM** **Conference Dinner** Le Parisien

ACA Editors Symposium

Tuesday 11th December

Chair: Prof. Neil Barnett, Deakin University

9:45 AM   Opening comments

10:00 AM   Prof. Richard Baldwin
University of Louisville, USA
CALIBRATION-FREE MICROFABRICATED ELECTROCHEMICAL SENSOR BASED ON
COULOMETRY

10:30 AM   Prof. Wolfgang Buchberger
Johannes Kepler University of Linz, Austria
MODERN PLASTIC MATERIALS IN EVERYDAY LIFE AND THE ROLE OF
ANALYTICAL CHEMISTRY

_____

11:00 AM   Morning Tea and Trade Display

_____

11:30 AM   Prof. Lutgarde Buydens
Radboud University Nijmegen, Netherlands
DATA FUSION FOR A BETTER UNDERSTANDING OF MULTIPLE SCLEROSIS

12:00 PM   Prof. Purnendu (Sandy) Dasgupta
University of Texas at Arlington, USA
REFLECTION ON REFLECTIONS: HOW ALICE MEASURED SO MUCH MORE
ABSORBANCE NEAR THAT DETECTION LIMIT

_____

12:30 PM   Lunch and Trade Display

_____

1:30 PM   Prof. Ulrich Krull
University of Toronto
QUANTUM DOTS AS MULTIPLEXED OPTICAL TRANSDUCERS FOR BIOASSAYS
AND BIOSENSORS

2:00 PM   Prof. Liang Li
                              University of Alberta, Canada
              METABOLOME PROFILING: A MASS SPECTROMETRIST'S DREAM AND
                                      NIGHTMARE

2:30 PM   A/Prof. Manuel Miró
                        University of the Balearic Islands, Spain
              AUTOMATED SAMPLE PROCESSING IN MESO/MICROFLUIDIC PLATFORMS
                        EXPLOITING DISPOSABLE SORPTIVE SURFACES

                    _____
3:00 PM   **Afternoon Tea and Trade Display**
                    _____

3:30 PM   Prof. Janusz Pawliszyn
                             University of Waterloo, Canada
              SPME AND RELATED SOLVENTLESS SAMPLING/SAMPLE PREPARATION
                          TECHNOLOGIES: WHERE DO THEY FIT

4:00 PM   Prof. Paul Worsfold
                              University of Plymouth, UK
              INVESTIGATING THE CHEMISTRY OF THE OCEANS USING FLOW INJECTION
                                        ANALYSIS

4:30 PM   David Sleeman
                                Elsevier Publishing
              RECENTLY PUBLISHED RESEARCH IN ANALYTICAL CHEMISTRY

5:00 PM   Closing Comments

                    _____
6:00 PM   **Welcome Mixer**
                               Beer and Pizza Night
                                   Union Green
                    _____

ACA Editor Abstracts

Tuesday 11th December

CALIBRATION-FREE MICROFABRICATED ELECTROCHEMICAL SENSOR BASED ON COULOMETRY

Mohamed M. Marei[1], Thomas J. Roussel[2], Robert S. Keynton[2], and <u>Richard P. Baldwin</u>[1]

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There currently exists a variety of environmental, industrial, and security applications where long-term remote chemical analysis is desirable, and the development of "smart" sensing devices that require minimal operator intervention and can form the basis of a continuous sensor network is of interest. One obstacle for use of such sensors over time is the issue of calibration, since nearly all instruments require at least periodic calibration. We have therefore been investigating the use of coulometric analysis, based on Faraday's law, which in principal allows absolute determinations to be made. This presentation will describe one approach to the design of microfabricated a coulometric sensing platform and our initial efforts in applying the resulting sensor to heavy metal analysis.

The sensor platform consists of a Au working electrode and a thin-layer micro-cell possessing a volume of less than 2 microliters. Initial evaluation using ferri-/ferrocyanide as a model analyte and fluorescent micro-particle microscopy as a probe showed that, for µL-volume electrolysis, elimination of adventitious flow after sample injection was critical. Once this was achieved, complete sample electrolysis was required less than 60 seconds, in agreement with diffusion models in thin-layer cells. Highly reproducible charges (RSD < 5%) were obtained, with detection limits down to 50µM ferrocyanide levels, both for recycling of individual samples and for repeated sample injections. Subsequently, this approach was applied to the calibration-free quantitation of heavy metals such as copper and mercury. Here, analysis could be carried out directly via the reduction of the metal ion or indirectly via anodic stripping of the electrodeposited metal film. The best analytical results were obtained using the latter approach where the preconcentration effect permitted detection at the picomoles (or micromolar) level. Most important, the resulting assays were reproducible over extended periods over a wide range of environmental conditions.

MODERN PLASTIC MATERIALS IN EVERYDAY LIFE AND THE ROLE OF ANALYTICAL CHEMISTRY

Wolfgang Buchberger, Susanne Beissmann, Ingrid Hintersteiner, Michael Reisinger, Lukas Sternbauer, Martin Stiftinger

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The importance of plastic materials in everyday life is constantly growing as more and more products of daily use are made from synthetic polymers. However, such materials are vulnerable to degradation induced by exposure to sunlight and oxygen. Under these conditions free radicals are formed which may lead to scission of the polymer chains. Possible consequences can range from yellowing to brittleness of the polymer, finally resulting in complete failure of the material. Therefore, stabilizers protecting them against light, thermal and oxidative decomposition are added. Unfortunately these stabilizers can get degraded themselves or simply washed out by different impacts from the environment. For this reason there is an increasing interest in analyzing the type, distribution, and degradation products of stabilizers within a polymeric material.

The comprehensive characterization of plastic materials with respect to stabilizers requires the availability of a range of sophisticated analytical techniques. Ideally, such techniques should not require any sample preparation for the solid sample. This could be realized for a few stabilizers by advanced mass spectrometric techniques like Direct Analysis In Real Time (DART) – MS. A more universal approach is based on an extraction of the stabilizers from the polymer followed by HPLC with APCI- or APPI-MS detection. Using high-resolution MS, degradation products of stabilizers could be identified, leading to a better understanding of the degradation mechanisms during weathering experiments.

Finally, knowledge about depth-profiles of stabilizers in plastic materials may be essential for monitoring the degradation processes starting at the surface and progressing towards the inner of a plastic product. For this purpose, miniaturized methods have been developed that are optimized for analysis of microtome cuts.

This presentation also includes the demonstration of various pitfalls encountered during quantitative determination of stabilizers in real polymer materials.

DATA FUSION FOR A BETTER UNDERSTANDING OF MULTIPLE SCLEROSIS

Lutgarde Buydens

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While Multiple Sclerosis is a major disabling disease of the Central Nervous System (CNS) in young adults, little is known on the real cause of this disease; even diagnosis in an early stage is a non-solved issue.

Cerebrospinal Fluid (CSF) is the bio fluid, which is in closest interaction with the Central Nervous System (CNS). It is therefore the bio fluid that best mirrors the biochemical status and processes in brain and CNS. Biochemical changes are therefore most likely to be found by means of a comprehensive analysis of the CSF Other bio fluids such as plasma may also contain crucial information;

Comprehensive analysis by a large variety of analytical technologies, yield however complex data for which chemometric data analysis and data mining have become crucial tools. Since no analytical platform on its own yields a comprehensive image of the biochemical status, data fusion has become widespread in the last decade. Many methods have been proposed, most of them restrict to a linear fusion strategy However, it is not realistic to assume that all biological or (bio)chemical data display this simple linear behavior. In that case linear methods are bound to fail. In this lecture alternative approaches will be presented. One is based on the hierarchical fusion of mid-level fusion models. Non-linear kernel fusion model allow to cope specifically with nonlinearities [1]. We use our pseudo-sample approach [2,3] to reveal the contribution of the individual variables.

In the lecture we will present results of fusion of CSF and plasma analysis data for a better diagnosis and search for biomarkers for Multiple Sclerosis

[1] S. Yu et al., Kernel-based Data Fusion for Machine Learning. Methods and applications in Bioinformatics and Text mining. Springer: Berlin 2011.

[2] P. Krooshof et al., Analytical Chemistry 82 (2010) 7000-7007

[3] Postma et al. Analytica Chimica Acta 705 (2011) 123-134

REFLECTION ON REFLECTIONS: HOW ALICE MEASURED SO MUCH MORE ABSORBANCE NEAR THAT DETECTION LIMIT

Purnendu K. Dasgupta

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By far the most common quantitation technique in analytical chemistry is optical absorbance measurement. With single path multireflection cells such as a "White Cell", the LOD improves but not the dynamic span. Partially reflective mirrors on each side of a measurement cell were proposed in 1987. This leads to greatly increased effective pathlengths at low absorbance levels. Interferometric principles were originally applied incorrectly to derive the transmission behavior. In 1988 O'Keefe introduced Cavity Ring Down Spectroscopy and in 1998 extended it to CW measurements using the same arrangement proposed in 1987. O'Keefe's derivations of transmission behavior are also approximate. The trouble of using highly reflective mirrors to get gains in a cavity is that very little light gets in to begin with.

Just like Alice though, light can fall through an entrance hole and be reflected and not find its way back out as easily because due to dispersion its footprint gets bigger. We show that the limiting gain is $\sim 1/(1-R)$, R being mirror reflectance. This leads to a simple way to attain substantial gain in detection limits by this technique very inexpensively. We will discuss this and other multipath absorption techniques that lead to strong nonlinear gains at low absorbances. Broadband Cavity Enhanced Absorption spectroscopy is only now coming into being although the feasibility was shown 25 years ago.

QUANTUM DOTS AS MULTIPLEXED OPTICAL TRANSDUCERS FOR BIOASSAYS AND BIOSENSORS

Ulrich J. Krull

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The optical properties of semiconductor quantum dots (QDs) have been widely exploited. Fluorescence Resonance Energy Transfer (FRET) bioassay designs have been described that detect selective binding interactions in close proximity to the nanoparticles. Solid-phase assays using QDs as FRET donors can offer numerous advantages in terms of sensitivity, selectivity and speed of response. A limitation in the widespread implementation of this technology has been the need for custom built fluorescence instruments. Now, a method for solid-phase multiplexed detection of nucleic acids using mixed films of quantum dots (QDs) and oligonucleotide probes in microtiter plates has been developed. Polystyrene microwells were functionalized with multidentate imidazole ligands to immobilize QDs. Oligonucleotide hybridization was transduced using QDs as donors in FRET, with signal being collected by a typically plate reader. A selective two-colour multiplexed assay will be described that uses a 96-well plate format.

Assembly of QDs on the glass walls of microfluidic channels has also been accomplished, with delivery of the QDs and reagents being done by a combination of electroosmotic flow (EOF) and electrophoresis. Quantification of target oligonucleotides that were injected into the microfluidic channels was accomplished using fluorescence intensity changes, but in a novel manner. The quantification was achieved either by measuring the length of the channel that exhibited a "turn-on" signal from the FRET sensitized dye emission, or a "turn-off" signal based on loss of QD emission[1]. The detection of as little as 5 fmol of target DNA was possible using this method. A strategy for quantification of unlabeled target oligonucleotides will be presented. Such multi-color fluorescence sensing in microfluidics channels is being incorporated into a microsystem based on a CMOS field-modulated colour sensor to spectrally detect and differentiate among multiple emission bands.

1. A.J. Tavares, M.O. Noor, C.H. Vannoy, W.R. Algar and U.J. Krull, Analytical Chemistry, 84: 312-319 (2012).

METABOLOME PROFILING: A MASS SPECTROMETRIST'S DREAM AND NIGHTMARE

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Metabolomics can be defined as the high throughput characterization of all the small molecule metabolites (the metabolome) present in a biological system. Metabolites are an important class of cellular components that play significant rules in biological functions. Detailed analysis of the metabolome can provide important and holistic insight into a biological process, as well as facilitate the discovery of disease biomarkers. However, metabolomics is still a relatively young field where there are many challenges, such as difficulty of interpreting the results within a biological context and integration with other omics data. Many of these challenges are largely due to the limitation of current analytical tools for metabolome profiling. Despite great efforts in the past decade or so in developing new or improved techniques for metabolome profiling, generating a quantitative and very comprehensive metabolome profile from a biological system is still very difficult. On the other hand, this young field opens many research opportunities for analytical chemists. In this presentation, the analytical challenges and potential opportunities for technical development in metabolomics will be discussed from a mass spectrometrist's point of view.

AUTOMATED SAMPLE PROCESSING IN MESO/MICROFLUIDIC PLATFORMS EXPLOITING DISPOSABLE SORPTIVE SURFACES

Manuel Miró

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Amongst the new advances in flow analysis methodology, the so-called Lab-on-a-Valve (LOV) [1,2], is currently garnering increasing interest as mesofluidic platform for downscaling and automation of chemical wet assays, along with the simplification of sample processing in both the environmental and bioanalytical arenas.

This lecture overviews the current state-of-the-art of a new μSPE technique, termed Bead Injection Analysis [3], as appealing analytical tool in LOV platforms for overcoming the shortcomings of SPE in a lab-on-a-chip format wherein the sorbent is integrated within the chip as a permanent column component [4]. Bead-injection based procedures feature the automatic disposal of the sorbent material per assay whereby fresh sorptive surfaces are made available for the analytes in each individual sample. This lecture will address and critically pinpoint novel instrumental developments based on the three generations of flow injection, which have been reported for execution of μSPE in a bead injection fashion [1-3]. Also described will be the vast number of alternatives proposed in the literature for immobilization of reactants on beads and for in-line chemical derivatization along with the instrumental detection techniques utilised for on-column optosensing measurements or post-extraction detection [3]. A wide variety of sorbent materials, encompassing reversed-phase, mixed-mode, molecularly imprinted polymers and multimodal beads, has been implemented in a bead-injection fashion for automatic preconcentration and/or sample clean-up of both trace elements and emerging organic pollutants in troublesome matrices. On-line interfacing of bead injection-based sample processing with liquid or gas chromatography and atomic absorption/emission spectrometers will be described in detail. Also included are recent applications in the environmental field for speciation analysis of trace elements in harsh matrices and for assays of drugs, pesticides and UV-filters in raw wastewaters and solid waste leachates [3,4,5-9] but also in the bioanalytical field for cell assays and micro-affinity chromatography [10-12].

[1] M. Miró, E.H. Hansen, Anal. Chim. Acta 750 (2012). DOI: 10.1016/j.aca.2012.03.049
[2] E.H. Hansen, M. Miró, Appl. Spectr. Rev. 43 (2008) 335
[3] M. Miró, S. Kradtap-Hartwell, J. Jakmunee, K. Grudpan, E.H. Hansen, TrAC-Trend Anal. Chem., 27 (2008) 749.
[4] M. Miró, E.H. Hansen, Anal. Chim. Acta 600 (2007) 46.
[5] M. Miró, H.M. Oliveira, M.A. Segundo, TrAC-Trends Anal. Chem, 30 (2011) 153.
[6] J.B. Quintana, W. Boonjob, M.Miró, V.Cerdà, Anal. Chem., 81 (2009) 4822.
[7] W. Boonjob, Y-L. Yu, M. Miró, M.A. Segundo, J.-H. Wang, V. Cerdà, Anal. Chem. 82 (2010) 2052.
[8] H.M. Oliveira, M.A. Segundo, J.L.F.C. Lima, M. Miró, V. Cerdà, J. Chromatogr. A, 1217 (2010) 3575
[9] X.-B. Long, M. Miró, E.H. Hansen, J. Anal. At. Spectrom Analyst, 131 (2006) 132.
[10] Y. Gutzman, A.D. Carroll, J. Ruzicka, Analyst 131 (2006) 809
[11] I. Lähdesmäki, Y. K. Park, A. D. Carroll, M. Decuir, J. Ruzicka, Analyst 132 (2007) 811
[12] H. Erxleben, J. Ruzicka, Analyst 130 (2005) 469.

SPME AND RELATED SOLVENTLESS SAMPLING/SAMPLE PREPARATION TECHNOLOGIES: WHERE DO THEY FIT

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The talk will focus on development and applications of solvent-free technologies under development in my laboratory, Solid Phase Microextraction (SPME) and Needle Trap Device (NTD). In particular simultaneous deployment of these sampling/sample preparation tools will be highlighted. Combining SPME and NTD extraction allows for the differentiation of free and particulate bound compounds in a gaseous sample matrix. Samples may contain both solid and liquid aerosols in addition to freely dissolved analytes. Where analytes of interest preferentially bind to the aerosols, the free concentration may be significantly lower than expected. The NTDs trap both gaseous chemical compounds as well as particulate matter present in the sample. SPME samples only the freely dissolved analytes. Thus SPME and NTD together can differentiate these and provide a more complete characterization of aerosol samples. Deployment together of two green sampling/sample preparation technologies, SPME and NTD has demonstrated several important advantages for comprehensive gaseous sample analysis such as simplicity, sensitivity, and robustness under both laboratory and on-site field sampling conditions.

To increase sensitivity of the SPME measurement the polydimethylsiloxane (PDMS) thin-film as well as DVB or carboxen particle loaded membranes were used as the extraction phase. This technique is based on a similar principle as the SPME fibre technique with additional advantage of higher surface to volume ratio facilitating much higher extraction rates and higher sensitivities because of high volume of the extraction phase. More specifically, the development of the thin film sampler involved cutting a section of PDMS thin-film into a specific size and shape, and mounting it onto a stainless steel wire (the handle). This technique was used as rapid spot or TWA sampling of environmental samples. For rapid water sampling, an electric drill was used to rotate the thin-film to get higher sampling rate. Passive water sampling can be calibrated through the desorption of a preloaded standard and the variety of the environment, such as turbulence and temperature, can be compensated. It was also found that the extraction rates of Oligochaetes (black worms, Lumbriculusvariegatus) and PDMS thin-film were identical for polycyclic aromatic hydrocarbon (PAH) compounds in water, which indicated that thin-film samplers could mimic the behavior of black worms for passive TWA monitoring.

B. Bojko, et al., "SPME: Quo Vadis?" Analytica Chimica Acta**2012**, *750*, 132-151.

INVESTIGATING THE CHEMISTRY OF THE OCEANS USING FLOW INJECTION ANALYSIS

Paul Worsfold

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To improve our understanding of the linkages between trace element biogeochemistry and marine processes, e.g. eutrophication, climate change, productivity and ocean circulation, a detailed knowledge of their oceanic distribution, sources, sinks and cycling is required. This necessitates reliable and accurate methods for the determination of trace elements in seawater, ideally with a high sample throughput and shipboard deployment capability to provide a high degree of temporal and spatial resolution. Additional analytical challenges include the need for sub-nanomolar detection limits, seawater matrix interferences and the high risk of contamination. This presentation overviews the application of flow injection (FI) techniques [1] to the determination of important trace elements, e.g. phosphorus, iron, cobalt, zinc, aluminium and plutonium, in marine waters. Shipboard and laboratory based FI methods are considered with spectrophotometric, luminescence and ICP-MS detection. Analytical method development and the linkages between flow injection data and other physico-chemical and biological parameters are discussed. The benefits of intercomparison exercises and more detailed uncertainty estimates for all aspects of the analytical process are also considered.

[1] E.A.G. Zagatto, C.C. Oliveira, A. Townshend and P.J. Worsfold, Flow analysis with spectrophotometric and luminometric detection, Elsevier Handbooks in Analytical Science Series, 471 pp, Elsevier, 2012.

RECENTLY PUBLISHED RESEARCH IN ANALYTICAL CHEMISTRY

David Sleeman

Elsevier Ltd., The Boulevard, Langford Lane, Kidlington, Oxford, OX5 1GB, United Kingdom

E-mail: D.sleeman@elsevier.com

Presenter Biography:

David Sleeman has worked for Elsevier since 1988, although he took a five year break in 1997 to set up a small technical publishing company with his wife. Returning to the company in January 2001 he has a comprehensive knowledge of Elsevier and has managed and developed several journal portfolios, major reference work programmes (multi-volume encyclopaedias and comprehensive subject-specific titles), monographs, textbooks, handbooks, newsletters, magazines and market research reports.

David comes from a publishing background and began his professional life working for local newspapers and magazines and still writes football reports for the UK press as a hobby. He has countered his lack of any higher level scientific knowledge by masking his confusion with a deadpan expression when talking to his editors and always offering to buy the first round. This has led to begrudging acceptance, but a bar bill that is starting to spiral out of control.

Abstract:

This presentation will focus on recently published research information by the analytical chemistry community globally, but also look at research published in Australia and at Deakin where other disciplines will also be considered. The presenter will also be happy to take questions about the future of scientific and technical publishing in relation to constantly changing technical developments and topics such as Open Access.

Oral Programme

Wednesday 12th December

9:00 AM   Prof. Jane den Hollander
                         Vice-Chancellor, Deakin University
                            OPENING OF CONFERENCE

9:15 AM   A/Prof Noel Davies
                           University of Tasmania
                         Lloyd Smythe Medallist
              MASS SPECTROMETRY IN THE AUSTRALIAN LANDSCAPE

Session 1 Chair: Zoe Smith, Deakin University

9:45 AM   Sarah Laird
                            La Trobe University
          UNUSUAL PH DEPENDENT PHOTOPHYSICAL AND ELECTROCHEMICAL
             BEHAVIOUR OF 1,2,4-TRIAZOLE BASED IRIDIUM COMPLEXES

10:05 AM   Sara Sandron
             Dublin City University/Irish Separation Science Cluster (ISSC)
              APPLICATION OF MULTI-DIMENSIONAL CHROMATOGRAPHY TO THE
           SEPARATION AND IDENTIFICATION OF THE COMPONENTS OF DISSOLVED
                            ORGANIC MATTER (DOM)

10:25 AM   Jessica Steele
                          University of Wollongong
        GLUTATHIONE REDOX RATIOS: THE DETECTION OF COPPER INDUCED STRESS
                            IN MARINE MICROALGAE

                    _____
10:45 AM   **Morning Tea and Trade Display**
                    _____

Session 2 Chair: Michelle Camenzuli, University of Western Sydney

11:15 AM

Brendan Holland

Deakin University

DETERMINATION OF SMALL BIOMOLECULES IN COMPLEX BIOLOGICAL
MATRICES USING PERMANGANATE CHEMILUMINESCENCE

11:35 AM

Kenneth Ogogo

Queensland University of Technology

CHARACTERISATION OF ORGANIC POLLUTANTS IN CONTAMINATED
SEDIMENTS OF A DYNAMIC ESTUARINE ENVIRONMENT: AN ASSESSMENT
APPROACH APPLIED TO THE BRISBANE RIVER

11:55 AM

Elizabeth Murago

University of New South Wales

Au@Fe$_3$O$_4$ NANO-ELECTRODES: THEIR ELECTROANALYTICAL PERFORMANCE AS
'DISPERSIBLE ELECTRODES' AND THEIR USE AS SENSORS

12:15 PM

Sung-Tong Ching

Monash University

BETTER SNIFFING – A STORY OF HIGH-RESOLUTION WINE AROMA ANALYSIS

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12:35PM   **Lunch and Trade Display**

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Session 3 Chair: Scott Meyerink, Australian National University/University of Canberra

1:30 PM

Chris Vardangea

University of Wollongong

CHANGES IN METAL BIOAVAILABILITY DURING DISCHARGE OF ACIDIC
DRAINAGE WATERS IN THE RIVER MURRAY

1:50 PM   Leigh Thredgold
                                   Flinders University
              TOWARDS AT SCENE FORENSIC STR ANALYSIS ON A MICROFLUIDIC PLATFORM

2:10 PM   Sui Ching Phung
                                  University of Tasmania
                              ISOTACHOPHORESIS OF CELLS

2:30 PM   Jamie Lindsell
                                   Victoria University
              THE DETERMINATION OF PHTHALATE MIGRATION IN FOOD CONTACT
              MATERIALS COMPARING GRAVIMETRIC AND GC-MS/MS TECHNIQUES

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2:50 PM   **Afternoon Tea and Trade Display**
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3:30 PM - 5:00 PM   **Poster Session 1**
                                Dining Hall (jb1.102)
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Thursday 13th December

9:00 AM   Dr Jie Zhang
Monash University
Robert Cattrall Early Career Medallist
ELECTROCHEMICAL BIOSENSORS

Session 4 Chair: Brendan Holland, Deakin University

9:30 AM   Danijela Kocic
University of Western Sydney
HIGH THROUGH-PUT AND HIGH SENSITIVITY LC-MS ANALYSIS OF AMINO ACIDS
USING SEGMENTED FLOW CHROMATOGRAPHY COLUMNS

9:50 AM   Bradley Stringer
La Trobe University
EXPLORATION OF THE POTENTIAL ELECTROANALYTICAL APPLICATIONS OF
NEAR-INFRARED EMITTING QUANTUM DOTS

10:10 AM   Elvio Amato
University of Wollongong
ASSESSING THE PERFORMANCE OF DIFFUSIVE GRADIENTS IN THIN FILMS FOR
PREDICTING TRACE METAL BIOAVAILABILITY IN ESTUARINE SEDIMENTS

_____
10:30 AM   Morning Tea and Trade Display
_____

Session 5 Chair: Elizabeth Murago, University of NSW

11:00 AM   Jacqui Delaney
La Trobe University
HOW TO USE A MOBILE PHONE AS A POTENTIOSTAT

11:20 AM   Tiffany Reeves
Flinders University
DIFFERENTIATION OF BINDERS IN ABORIGINAL AND EUROPEAN PAINTED
WORKS USING PYROLYSIS GAS CHROMATOGRAPHY MASS SPECTROMETRY

11:40 AM   James Brady
                            Queensland University of Technology
                    HEAVY METALS IN THE SEDIMENTS OF DECEPTION BAY, QUEENSLAND
                                            AUSTRALIA

                    _____

12:00 PM   **Lunch and Trade Display**

1.00 PM   **Winery Tour**
                                    Leura Park Estate
                    _____

Friday 14th December

Session 6 Chair: Sara Sandron, Dublin City University

9:00 AM   David Bower
La Trobe University
CO-REACTANT ELECTROGENERATED CHEMILUMINESCECE (ECL) FROM CARBON
DIOXIDE IN IONIC LIQUIDS

9:20 AM   Sangeeta Goundar
The University of the South Pacific
SOIL PHOSPHORUS REQUIREMENTS OF DIFFERENT SOILS IN THE SUGARCANE
BELT OF FIJI

10:00 AM   Bing Chen Chai
Victoria University
DEVELOPING A RAPID LIQUID CHROMATOGRAPHY TANDEM MASS
SPECTROMETRY (LC-MS/MS) METHOD FOR THE ANALYSIS OF PARALYTIC
SHELLFISH TOXINS (PST)

_____
10:00 AM - 11:00 AM   Poster Session 2
Foyer outside Ka3.403

10:45 PM   Morning Tea and Trade Display
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11:10 AM   Prof. Kliti Grice
WA-OIGC/ Curtin University
RACI Environmental Chemistry Medallist
CONSISTENT CHANGES IN MOLECULAR FOSSILS (MICROBES, FLORA,
EXTREMOPHILES) AND STABLE ISOTOPES ACROSS SEVERAL OF MAJOR
EXTINCTION EVENTS OF OUR PLANET: A FIGHT FOR SURVIVAL AND
RESURGENCE OF LIFE

Session 7 Chair: Kenneth Ogogo, Queensland University of Technology

11:40 AM   Christopher Desire
                                University of Tasmania
        SEPARATION AND CHARACTERISATION OF HUMAN IMMUNOGLOBULIN G
    VARIANTS UTILISING A POLY(ETHYLENE GLYCOL)-BASED MONOLITHIC COLUMN

12:00 PM   Edward Nagul
                            The University of Melbourne
        FLOW ANALYSIS OF ORTHOPHOSPHATE USING POLYMER INCLUSION
        MEMBRANES FOR ON-LINE SEPARATION AND PRECONCENTRATION

                    _____
12:20 PM   Lunch and Trade Display

1:00 PM   Bio-Rad Technical Seminar
                            Dr. Adam Lowe
                    _____

Session 8 Chair: Sarah Laird, La Trobe University

1:30 PM   Lachlan Carter
                            University of New South Wales
        NANOPARTICLE-MEDIATED ELECTROCHEMICAL GATING: APPLICATION TO
                                ELECTROANALYSIS

1:50 PM   Matthew Jacobs
                                University of Tasmania
        ANALYSIS OF ANTARCTIC PETROLEUM SPILL SITES BY RESISTIVELY HEATED GAS
                                CHROMATOGRAPHY

2:10 PM   Leigh Crilley
                        Queensland University of Technology
        AEROSOL MASS SPECTROMETRIC ANALYSIS OF ORGANIC AEROSOL IN
                                BRISBANE SCHOOLS

2:30 PM   Ziqing Weng
Deakin University
CHIRAL GOLD NANOPARTICLES FOR METAL ION DETECTION

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2:50 PM   Afternoon Tea and Trade Display
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Session 9 Chair: Leigh Thredgold, Flinders University

3:20 PM   Scott Meyerink
Australian National University/University of Canberra
SWITCHING ON THE LIGHTS IN DIATOM CELL WALLS: USING PDMPO TO
INVESTIGATE SILICON UPTAKE IN DIATOMS

3:40 PM   Michelle Camenzuli
University Of Western Sydney
HIGH SPEED SCREENING OF NATURAL PRODUCTS USING HIGH PERFORMANCE
LIQUID CHROMATOGRAPHY WITH MULTIPLEXED DETECTION

4:00 PM   Sunny Kim
Monash University
A RATIONAL APPROACH TO QUANTITATIVE PREPARATIVE GAS
CHROMATOGRAPHY WITH NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

4:20 PM   Final Comments
Close of Conference

6:30 PM   End of Conference Dinner
Le Parisien Restaurant
15 Eastern Beach Road
Geelong, Australia

Poster List

Poster Session 1 (Wednesday)

W1	David Donaldson *Deakin University*	An Investigation into Nitramine Explosives Detection and Munitions Stability
W2	Tristan Kilmartin *Flinders University*	Characterisation of Temporal Inter-Pulse Delay Effect of Double-Pulsed Laser-Induced Breakdown Spectroscopy
W3	Umairah Mokhtar *University of Technology Malaysia & Monash University*	Application of Dispersive Liquid-Liquid Microextraction Based on Solidification of Floating Organic Droplet to the Analysis of Antidepressant Drugs in Water Samples
W4	Jessica Pandohee *Deakin University*	Determination of Cannabinoids using Two-Dimensional Liquid Chromatography Coupled with Permanganate Chemiluminescence Detection
W5	Sahar Farzadnia *Macquarie University*	Characterisation of Antarctic Aqueous Fulvic Acid by a New Simplification Approach Prior to Chromatographic Analysis
W6	Helen Price *University of Wollongong*	The Effect of Bioturbation on Sediment Porewater Concentrations of As, Se, PO_4^{3-} and V(V)
W7	Taiwo Akanbi *Deakin University*	Lipase-Catalysed Synthesis of Omega-3 Fatty Acid Concentrate from Fish Oil
W8	Alexander Weremfo *University of NSW*	Characterisation and Optimisation of Electrochemically Roughened Platinum Microelectrode for Neural Stimulation
W9	Runqing Li *Deakin University*	Functionalisation of Boron Nitride Nanotubes: Preparation, Underlying Mechanism and Potential Bio-Applications
W10	Edward Ogabiela *Monash University*	Fabrication of Polypyrrole Based Ultra-Sensitive Phosphate Biosensors Using Pyruvate Oxidase
W11	Karen Bruce *Flinders University*	Detection of "Red Tide" Forming Dinoflagellate Species: Towards an Early Warning System for Harmful Algal Bloom Formation
W12	Eamon McGuire *Monash University*	Use of Multidimensional Gas Chromatography Techniques to Detect Illegal Doping with Beta-2 Agonists
W13	Zahra Khamseh Safa *Macquarie University*	The Use of Eucalyptus Biomass for Removal of Arsenic and Selenium from Coal Fly Ash Leachate

W14	Danielle Taylor *University of Western Sydney*	Characterization of Gellan Gum by Capillary Electrophoresis
W15	Renée Webster *Monash University/DSTO*	Multidimensional Gas Chromatographic Analysis of Jet Fuel Oxidation Products
W16	Zoe Smith *Deakin University*	Chemiluminescence Detection of Biologically Important Thiols and Disulfides in Mouse Striatum
W17	Larissa Schneider Guilhon *University of Canberra*	Analysis of Volatile Selenium Fluxes in Lake Macquarie
W18	Caitlyn Rogers *Flinders University*	Improving Toxicological Analysis in Drug-Facilitated Sexual Assault: Through Enzymatic Hydrolysis and Extraction
W19	Kirsteen Smith *Deakin University*	Interactions Between Polycyclic Aromatic Hydrocarbons and Wine Phenolics with Graphene Based Chromatography Columns
W20	Daniel Gstoettenmayr *University of Tasmania*	Development of a Novel Ultrasensitive Capillary Electrophoresis-Mass Spectrometry System for the Analysis of Environmental Pollutants
W21	Mohd Zulkhairi Abdul Rahim *Monash University*	Amperometric Detection of Cholesterol With a Nanocomposite Polypyrrole-Cholesterol Oxidase Biosensor Infused with Multiwalled Carbon Nanotubes
W22	Nitika Mishra *Queensland University of Technology*	Airborne Concentration of Volatile Organic Compounds in Urban Schools
W23	Polly Dobson *Deakin University*	Enzymatic Synthesis and Characterisation of Lipid Mediators of Inflammation
W24	Christine Close *RMIT University*	Passive Sampling: Quantification and Qualification of Pharmaceuticals and Personal Care Products (PPCPS) in Victorian Surface Waters
W25	Rachel West *Flinders University*	Surface Assisted Laser Desorption Ionisation for the Analysis of Propellants
W26	Danielle Bassanese *Deakin University*	Investigating Surface Coverage of a Mixed Mode Monolithic Column Using Multi-Location Peak Parking
W27	Cassandra Smith *University of Wollongong*	Using Immobilised Metal Affinity Chromatography (IMAC) to Compare Protein Profiles in Control And Copper Exposed Marine Algae

W28	Sercan Pravadali	Selectivity in Detection: the Analysis of Alkaloids and Phenols using HPLC with Mass Spectral, UV, and Chemiluminescence Detection
	University of Western Sydney	
W29	Ala Alhusban	Online Organic Acids Characterization and Monitoring from Bioprocess Using Sequential Injection Capillary Electrophoresis
	University of Tasmania	
W30	Shahid Hussain	Fabrication Of A Novel Sulfite Nanobiosensor By Modification Of Polypyrrole Nanowires Array With Platinum Nanoparticles And Sulfite Oxidase
	Monash University	
W31	Benjamin Savareear	Multiplexed Dual-Secondary Column Comprehensive Two-Dimensional Gas Chromatography
	University of Tasmania	
W32	Jiewu Cui	Construction of a Potentiometric Nitrate Biosensor Based on Gold Nanowires Array
	Monash University	
W33	Pat Sacchetta	Analysis of Fat Soluble Vitamin Capsules Using Ultraperformance Convergence Chromatography
	Waters Australia	
W34	Pat Sacchetta	USP Methods Transitioned to MS and MSMS Detection
	Waters Australia	
W35	Dianne Purcell	Rapid Detection of Harmful Algal Blooms (HAB) in Coastal Waters using Molecular Tools
	University of Canberra/ANU	
W36	Tom Kazarian	Characterisation of Mixed-Mode Phases for the Comprehensive Analysis (APIS, Excipients and Inorganic Ions) of Binary and Ternary Pharmaceutical Preparations
	University of Tasmania	
W37	Blagoj Mitrevski	Evaluation of Comprehensive Two-Dimensional Gas Chromatography with Flame Photometric Detection: Potential Application for Sulfur Speciation in Shale Oil
	Monash University	
W38	Blagoj Mitrevski	Fast Profiling of Fatty Acids of Safflower Oil by Using Comprehensive Two-Dimensional Gas Chromatography
	Monash University	
W39	Jacky Watson	A New Accurate Mass Screening Solution Incorporating the UNIFI Scientific Information System for Analysis of Pesticide Residue at Regulatory Limits in Food
	Waters Australia	
W40	Jacky Watson	Quantification of the Hormones Progesterone and Cortisol in Whale Breath Samples Using Novel, Non-Invasive Sampling and Analysis with Highly-Sensitive ACQUITY UPLC and Xevo TQ-S
	Waters Australia	

Poster Session 2 (Friday)

F1	Celale Kirkin	The Influence of Gamma Irradiation and Modified Atmosphere Packaging on Essential Oil Yield of Various Spices
	Istanbul Technical University & Monash University	
F2	Mari Egeness	Comprehensive Two-Dimensional Liquid Chromatography for the Separation of Organic Acids
	University of Tasmania	
F3	Winston Doherty	Polypyrrole-Penicillinase Based Biosensor for Potentiometric Detection of Penicillin
	Monash University	
F4	Zurahanim Anual	Mercury Associations in Fish
	University of Canberra	
F5	Roya Tavallaie	A Selective Electrochemical DNA Sensor Using a Methylene Blue Intercalator
	University of NSW	
F6	Rachel Brokenshire	Characterisation of Patterned Copper Sulphide Thin Films by SECM And Profilometry
	CSIRO/Deakin University	
F7	Fidelis Nitti	Preconcentration of Mercuric Ions From Waste Waters Using Polymer Inclusion Membranes
	The University of Melbourne	
F8	Motilal Mathesh Shanmugam	Molecular Tuning of Graphene Oxide-Inciting Conductivity
	Deakin University	
F9	Yada Nolvachai	Molecularly Imprinted Polymer in Tips for the Extraction of Flavonoids, with High Resolution GC Analysis
	Monash University	
F10	Yufei Sun	VOC Exposure in a Research and Teaching Facility
	RMIT University	
F11	Jessica James	Quantitative Analysis of Renaissance Paints and Pigments by Portable X-Ray Fluorescence (PXRF)
	Flinders University	
F12	Noah Kebede	Possible New Co-Reactants for Tris(2,2'-Bipyridine)Ruthenium(II) Electrogenerated Chemiluminescence
	Deakin University	
F13	Thishakya de Silva	Method Development and Analysis of Neutraceutical Compounds in Victorian Strawberry Varieties
	RMIT University	
F14	Manori Jayawardane	The use of a Polymer Inclusion Membrane in the Development of a Paper-Based Microfluidic Sensor for the Selective Determination of Cu (II)
	The University of Melbourne	

F15	Chamani Marasinghe Wadige *University of Canberra*	Molonglo River Sediment Metal Contaminants and Their Effects on Bivalve Health by Linking Organism Metal Exposure-Dose-Response
F16	Annie Xu Zeng *Monash University*	Integrated Multidimensional and Comprehensive Two-Dimensional Gas Chromatography Analysis of Fatty Acid Methyl Esters
F17	Laura Tendone *University of Messina*	Application of Multiple Headspace Solid Phase Microextraction (MHS-SPME) Technique to the Quantitative Analysis of Fragrance and Flavour Compounds
F18	YaYa Bonggotgetsakul *The University of Melbourne*	The Preparation of a Monolayer Silver Nanoparticles on the Surface of a Polymer Inclusion Membrane
F19	Darren Koppel *University of Wollongong*	Bioavailability of Arsenic From Soils to Earthworms and Lettuce
F20	Mark Roderick *Deakin University*	A Comparison of Enhancement Techniques for Permanganate Chemiluminescence
F21	Rima Raffoul Khoury *University of NSW*	Study of Copper (II) Complexes of Tripeptides Containing Glu, Gly and His Using Potentiometry, UV-Vis Spectroscopy and Generalized Multiplicative Analysis of Variance
F22	Heide Rabanes *University of Tasmania*	Synergistic Effect of Field Enhanced Sample Injection on Micelle to Solvent Stacking in Capillary Electrophoresis
F23	Chadin Kulsing *Monash University*	The use of Eigen System Peaks for Improvement of Chiral Resolution in Separations with Porous Layer Open Tubular Capillary Columns
F24	Ana Martins *RMIT University*	Mechanical Mixing Techniques for Chemiluminescence Detection
F25	Yukie O'Bryan *The University of Melbourne*	Transport of Thiocyanate Using a Polymer Inclusion Membrane Based on Interpenetrating Polymer Network of PVDF-CO-HFP And PEG-DMA
F26	Kate Brough *Queensland University of Technology*	Studies of Brisbane Municipal Water Quality Using Inductively Coupled Plasma-Mass Spectrometry and Chemometrics
F27	Elizabeth Zammit *Deakin University*	Evaluation of Selected Platinum Group Metal Complexes as Chemiluminescence Reagents

35 | P a g e

Poster Abstracts

Wednesday 12th December

~ W1 ~

AN INVESTIGATION INTO NITRAMINE EXPLOSIVES DETECTION AND MUNITIONS STABILITY

David Donaldson[1], Neil Barnett[1], Chad Prior [2,3], Paul Francis[1]

[1] *School of Life & Environmental Sciences, Deakin University, Waurn Ponds 3216, VIC, Australia*

[2] *Centre for Expertise in Energetic Materials (CEEM), Australia*

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A simple controlled chemical reduction of RDX and various other nitramine compounds with zinc amalgam, allowed formation of species eliciting intense chemiluminescence with tris(2,2'-bipyridine)ruthenium(III). This process extends the widely used chemiluminescence reagent to a new class of analyte, while also supplying a solid foundation for a presumptive chemical screening test for nitramine explosives. Headway has been made into miniaturisation of the system, as well as characterisation of the species of interest. Comparison studies have indicated that for the reduction to elicit intense chemiluminescence, the presence of an aliphatic nitrogen-nitrogen bond is required. Examination of the chemiluminescence profiles under stopped-flow conditions has implied that multiple transient species contribute to the amount of light produced over differing time periods, allowing for further tailoring of a detection device.

An investigation has also been undertaken to determine the shelf life of standard munitions. Over time, the propellants used in munitions degrade, causing levels of various nitro compounds to be formed. High levels of these nitro-compounds can cause self ignition, causing potentially catastrophic situations. A separation procedure has been developed to accurately determine levels of these compounds in a given sample.

~ W2 ~

CHARACTERISATION OF TEMPORAL INTER-PULSE DELAY EFFECT OF DOUBLE-PULSED LASER-INDUCED BREAKDOWN SPECTROSCOPY

Tristan Kilmartin[1], Benjamin Rogers[2], Benjamin Hall[2], Jamie Quinton[1]

[1] *Flinders University, Sturt Road, Bedford Park 5042, SA, Australia*

[2] *Defence Science and Technology Organisation, West Avenue, Edinburgh, 5111, SA, Australia*

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Laser Induced Breakdown Spectroscopy (LIBS) is a spectroscopic technique which utilises a single laser pulse to ablate and ionise a sample surface, leading to the formation of plasma and the subsequent emission of characteristic line spectra, which in turn allows for determination of the localised elemental composition of the sample. LIBS has both rapid analysis and long-range (standoff) capabilities, as it requires minimal sample preparation and generates a large amount of emission spectra, which can then be collected at distance. LIBS is therefore a subject of great interest for such purposes as in-situ quality control in industrial manufacturing and long range detection of explosives.

 Introduction of a second pulse with a temporal delay in relation to the first pulse causes a large enhancement in signal intensity compared with a single laser pulse of equivalent power and energy. This variation on traditional LIBS is known as Double-Pulsed Laser Induced breakdown Spectroscopy (DP LIBS). The temporal inter-pulse delay resulting in signal enhancement can range from nano- to micro- seconds. However, the mechanisms causing this enhancement are not yet fully understood and are therefore difficult to optimise.

This project aims to characterise the effects of the inter-pulse delay in the microsecond time scale using a pure aluminium target through a combination of optical spectroscopy, Scanning Electron Microscopy (SEM) and high-speed shadowgraphy. Determination of electron densities, coupled with crater analysis and high speed imaging of plasma evolution has led to a clearer understanding of the role of the inter-pulse delay in the signal enhancement as well as an optimised time delay for analysis of aluminium.

~ W3 ~

APPLICATION OF DISPERSIVE LIQUID-LIQUID MICROEXTRACTION BASED ON SOLIDIFICATION OF FLOATING ORGANIC DROPLET TO THE ANALYSIS OF ANTIDEPRESSANT DRUGS IN WATER SAMPLES

Siti Umairah Mokhtar[1], Mohd Marsin Sanagi[2,3], Wan Aini Wan Ibrahim[3],

Hassan Y. Aboul-Enein[4]

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[2] *Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Malaysia*

[3] *Department of Chemistry, Faculty of Science Universiti Teknologi Malaysia, 81310 UTM Bahru, Malaysia*

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A simple and rapid sample preparation method based on dispersive liquid-liquid microextraction-solidification of floating organic drop (DLLME-SFO) combined with gas chromatography-mass spectrometry (GC-MS) method was developed for the analysis of antidepressant drugs in water samples. This method uses organic solvent with low density and reduced toxicity. In the method, the disperser solvent (0.5 mL acetonitrile) containing 30 µL of *n*-hexadecane was rapidly injected using a syringe into 5.0 mL of water sample in a glass tube. After centrifugation for 7 min at 3500 rpm, the mixture was cooled in an ice bath for 5 min. The solidified *n*-hexadecane was transferred into a conical vial, where its melts rapidly at room temperature and an aliquot of 2 µL is injected into a gas chromatograph for analysis. Under optimized conditions, the method showed good linearity in the range of 0.04 - 0.12 µg mL^{-1} for amitriptyline and chlorpromazine with correlation of determination (r^2) in the range of 0.992 - 0.995. The limits of detection (LODs) were in the range 0.0085 - 0.029 µg mL^{-1}. The extraction recoveries of amitriptyline and chlorpromazine from water samples at a spiking level of 0.08 µg mL^{-1} were 71.34 - 73.52% and 73.83 - 91.09%, respectively, with relative standard deviations (RSDs) in the range of 4.97 - 6.85% for amitriptyline and 4.84 - 7.49% for chlorpromazine. The method was successfully applied to the determination of the analytes in drinking water, lake water and tap water samples.

Key words: Dispersive liquid-liquid microextraction-solidification of floating organic; Gas chromatography-mass spectrometry; Antidepressant drugs; Water samples.

~ W4 ~

DETERMINATION OF CANNABINOIDS USING TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY COUPLED WITH PERMANGANATE CHEMILUMINESCENCE DETECTION

Jessica Pandohee[1]

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With the increase in bacterial multidrug-resistance, there has been an urgent need in new antibacterial agents for decades. Cannabis is a plant that has been known to possess antibacterial properties. However due to the huge number of constituents it is difficult to attribute the benefits to a specific compound or groups of compounds in hemp. A comprehensive two-dimensional liquid chromatography methodology coupled with selective acidic potassium permanganate chemiluminescence detection has been developed to efficiently separate cannabinoids in industrial-grade bark, hurd and leaf cannabis extracts of both sexes. The chemical profiles obtained allowed for the detection of a total of 125 components and identification of 11 cannabinoids. This analytical approach can be further applied in areas such as phytochemical, pharmacological and forensic studies where chemical matrix characterisation is required for the identification, classification and individualisation of cannabis plants.

~ W5 ~

CHARACTERISATION OF ANTARCTIC AQUEOUS FULVIC ACID BY A NEW SIMPLIFICATION APPROACH PRIOR TO CHROMATOGRAPHIC ANALYSIS

Sahar Farzadnia, Christopher R. McRae

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Fulvic acids are complicated mixture of organic compounds that accounts for about half of the Natural Organic Matter (NOM) in fresh water and 15-20 % of the NOM in marine waters. Because of the relatively small size of fulvic acids molecules they can readily enter plant roots, stems, and leaves. As they enter these plant parts they carry trace minerals from plant surfaces into plant tissues. Fulvic acid composition and structure are quite variable depending on the geographic location but it is believed consist of weak aliphatic and aromatic organic acids which are soluble in water at all pH conditions. Study of fulvic acid structure is difficult due to complexity and heterogeneity, so despite of many decades of research their chemical structures is still ill-defined. However, chemical characterisation of fulvic material from Antarctic region where cold climate and absence of higher order plants has the advantage of simpler mixture contribution, can assist with the interpretation of more complex fulvic acid found in non-Antarctic waters. Generally, microbial degradation of biomolecules like proteins, carbohydrates and lipids is the natural process responsible for the occurrence of humic substances including fulvic acids in the environment. Carbohydrates as an important family of biomolecules has been widely qualitatively and quantitatively studied in dissolved organic matter and especially in humic substances because of their significant contribution.

Based on the useful information available from previous studies and after preliminary identification of carbohydrate moieties in standard Antarctic fulvic acid by GC/MS, we exposed the sample under periodate oxidation to selectively oxidise and eliminate carbohydrates. The low-molecular weight oxidation products (mostly formaldehyde, formic and acetic acid) were simply separated from components of interest by solid phase extraction using a C18 cartridge. The extract obtained is a simplified fulvic material being investigated with both gas and liquid chromatography techniques.

~ W6 ~

THE EFFECT OF BIOTURBATION ON SEDIMENT POREWATER CONCENTRATIONS OF As, Se, PO_4^{3-} AND V(V)

<u>Helen L. Price</u>[1], Dianne F. Jolley[1], Peter Teasdale[2], Victoria Helmsley[3]

[1] *University of Wollongong, 2522, NSW, Australia*

[2] *The Australian Rivers Institute, Griffith University, Gold Coast, QLD, Australia*

[3] *University of East Anglia, UK*

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Contaminants such as As and Se are mobilised from sediment particles to the dissolved phase in the suboxic zone of the sediment. This is driven the reductive dissolution of iron and manganese (oxyhydr)oxides[1] and leads to sediments acting as a source of metals and oxyanions to porewaters and overlying waters and hence are labile and a source for biological uptake.

The diffusive gradients in thin films (DGT) and diffusive equilibrium in thin films (DET) techniques are *in situ* techniques that have been used to measure trace element contaminants in sediments[2]. DGT is able to provide simultaneous porewater flux data for several analytes at high spatial resolution. This study evaluates the ability of DGT and DET to identify variations in porewater profiles of As, Se, V, P, Mn and Fe due to bioturbation. Bioturbation was achieved by placing bivalves, *Tellinadeltoidalis*, into sediments 8 weeks prior to DGT probe deployment.

Variations due to bivalve bioturbation were clearly detected in the DGT-labile flux of As, Se(IV), V(V),PO_4^{3-}, Fe(II) and Mn(II). Differences in DGT analyte depth profiles associated with bioturbation could arise due to reductive dissolution resulting in (1) resupply from the sediment solid phase to porewaters (2) removal from porewaters to solid phase and (3) change in speciation as a result of redox reactions. This highlights the differences in sediment chemistry of each analyte.

This study undertook a performance evaluation of two binding gels, ferrihydrite and Metsorb™. Comparable capability and affinities were identified under the conditions studied here.

The importance of dual DET and DGT deployments was highlighted by the high proportion of DET labile anions which were present in much lower concentrations on the DGT. These differences were attributed to redox-driven transformations within the suboxic and anoxic regions of the sediments, converting oxyanions to non-DGT labile forms.

1. Edenborn, H.M., *et al*., *Observations on the diagenetic behaviour of arsenic in a deep coastal sediment.* Biogeochemistry, 1986. **2**(4): p. 359-376
2. Davison, W., *et al*.,eds. *Dialysis, DET and DGT: in situ diffusional techniques for studying water,sediments and soils*. In Situ Monitoring of Aquatic Systems –chemical analysis and speciation, ed. J. Buffle and G. Horvai. 2000, IUPAC,Wiley: Chichester. 495-569.

~ W7 ~

LIPASE-CATALYSED SYNTHESIS OF OMEGA-3 FATTY ACID CONCENTRATE FROM FISH OIL

Taiwo O. Akanbi, Jacqui Adcock, Colin Barrow

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Clinical benefits of concentrates of omega-3 fatty acids, such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), in the treatment and prevention of health disorders such as cardiovascular, Alzheimer's and Parkinson's diseases have made them the subject of intensive research. Current techniques for the production of omega-3 concentrates are expensive and environmentally unfriendly involving fractional distillation and urea complexation techniques. In pursuit of cheaper, milder and greener techniques for concentrating omega-3 fats, we investigated the use of a commercial lipase for concentrating EPA and DHA via fish oil hydrolysis. Monitoring percent hydrolysis using capillary chromatography with flame ionization detector (Iatroscan) and omega-3 concentration using gas chromatography (GC) indicated that during hydrolysis DHA primarily remained on the glycerol backbone, while EPA was progressively removed. ^{13}C nuclear magnetic resonance (NMR) data showed a clear increase in DHA at all positions (*sn*-1,3 and *sn*-2) which resulted in a 2-fold increase in its concentration.

~ W8 ~

CHARACTERISATION AND OPTIMISATION OF ELECTROCHEMICALLY ROUGHENED PLATINUM MICROELECTRODE FOR NEURAL STIMULATION

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The design of next-generation high-resolution and site-specific neural prostheses requires greater numbers of microelectrodes. However for a fixed charge, reduction in electrode size increases charge density. If charge density exceeds the reversible charge injection limit, undesirable and irreversible electrochemical reactions occur which damage both stimulating electrodes and neural tissues. Platinum is the most widely used electrode material for neural stimulation due to its ability to resist corrosion and inject charge using reversible reactions that do not harm tissues [1]. However, due to low charge injection limits, smooth Platinum are often disregarded as a neural stimulation microelectrode materials [2,3]. An effective way to increase the charge injection limit and maintain low impedance of electrodes is to increase the surface roughness. Electrochemically roughened (HiQ) Pt electrodes with high real surface area (~75 times greater) than standard Pt electrode of same geometric size, showed low polarization, impedance and residual direct current [4]. However HiQPt electrodes lose effectiveness when exposed to atmosphere but maintain their effectiveness when stored in water. The intention of this work is to characterise and optimise the electrochemically roughened microelectrode surfaces and determined the cause of surface area decrease when exposed to atmosphere. The measured impedance, capacitance and charge injection limits of roughened electrodes with various surface roughness factors will be presented

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~ W9 ~

FUNCTIONALISATION OF BORON NITRIDE NANOTUBES: PREPARATION, UNDERLYING MECHANISM AND POTENTIAL BIO-APPLICATIONS

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Boron nitride nanotubes (BNNTs), which possess a similar morphology as carbon nanotubes (CNTs)[1], but unique properties of their own, appear to be potential nanomaterials for biomedical applications due to their stability in dispersion in solution. Unlike CNTs, whose electronic structure and properties vary widely based upon tube helicity, concentric layers, and so forth, the BNNTs are semiconducting regardless of their diameter and chirality. Importantly BNNTs are also found to be nontoxic to health and environment due to their chemical inertness and structural stability, and therefore, they are more suitable for medical applications such as biosensor and drug delivery.[2]

Functionalised BNNTs with biomolecules has been reported recently [3], which led to excellent individual dispersion and potential hierarchical self-assembly. However, the interactions between BNNTs and biomolecules have been less studied in spite of their potential biomedical applications.[4] Herein, we present how to functionalised BNNTs by using proteins into aqueous media, and investigated the strong interactions between BNNTs and proteins using ultraviolet−visible absorption, circular dichroism, fluorescence spectroscopies and computational chemistry.[4c, 4d] These new understanding not only may help to establish effective ways for functionalised BNNTs in aqueous media but also may offer potential opportunities for functionalizing BNNTs and expanding their future applications.

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~ W10 ~

FABRICATION OF POLYPYRROLE BASED ULTRA-SENSITIVE PHOSPHATE BIOSENSORS USING PYRUVATE OXIDASE

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Phosphate is an essential nutrient for plants and animals. It forms part of important life sustaining molecules that are common in the biosphere. Even though it is an essential nutrient for plants and various organisms, the presence of phosphorus or orthophosphate at higher than expected concentrations can cause various environmental problems, such as eutrophication and involvement in the outbreak of blue-green algae, as well as causing health concerns when ingested in excessive amount in foods. For these reasons, there has been a considerable interest in the determination of phosphate in water and wastewaters. One of the approaches that have gained considerable interest in this area is the use of enzyme-based biosensors. In particular, phosphate biosensors are normally based on mono- or multi-enzymatic reactions where phosphate acts as inhibitor or substrate. Enzymes such as purine nucleoside phosphorylase (PNP) and xanthine oxidase (XOD), alkaline phosphatase and glucose oxidase, phosphorylase A, phosphoglucomutase and glucose-6-phosphate dehydrogenase, and pyruvate oxidase have been used for fabrication of phosphate biosensors. An ultra-sensitive biosensor which has been developed for phosphate detection will be presented in this paper. This biosensor is based on the entrapment of pyruvate oxidase into polypyrrole films. The presence of the enzyme is confirmed by electrochemical methods and SEM. The optimisation of the biosensor for successful potentiometric detection of phosphate and possible applications to water and wastewater will be discussed.

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~ W11 ~

DETECTION OF "RED TIDE" FORMING DINOFLAGELLATE SPECIES: TOWARDS AN EARLY WARNING SYSTEM FOR HARMFUL ALGAL BLOOM FORMATION

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Harmful algal blooms (HABs) resulting from an increased growth of natural phytoplankton or microalgae can have devastating effects on the marine environment, releasing toxins that can enter the food chain of marine organisms. Accumulation in the food web is apparent with an increased level of toxins being present higher up the trophic levels[1]. Shellfish poisoning is one example of toxin accumulation side effects. The symptoms from this poisoning can vary from amnesia, diarrhoea, neurological degeneration and respiratory paralysis [2]. These dangerous side effects, which can lead to death in extreme cases, have led to increased interest in detection methods suitable for use as an early warning system for algal bloom formations. These early warning systems will allow early stage intervention prior to toxin build up.

Red tides are commonly associated with increased numbers of dinoflagellates, thus they are a good target for early detection strategies. Detection of specific dinoflagellates using DNA hybridisation techniques where complimentary single stranded DNA is attached to a surface that is then hybridised with a solution containing extracted rRNA has been demonstrated [3,4]. This project aims to extend this approach by covalently immobilising single stranded DNA to surfaces, initially cellulose. Once achieved species of dinoflagellates will be grown, the rRNA extracted, and the surfaces tested in a "dipstick" device. This will hopefully provide species specific detection of the dinoflagellates as well as estimation of cell numbers present based on these results.

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~ W12 ~

USE OF MULTIDIMENSIONAL GAS CHROMATOGRAPHY TECHNIQUES TO DETECT ILLEGAL DOPING WITH BETA-2 AGONISTS

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Beta-2 agonists are a class of drugs which are most commonly used to treat respiratory illnesses in humans and other animals. They bind and activate the beta-2 receptors, which leads to relaxation of the smooth muscles in the respiratory tract, which aides in normal breathing. However, they are also thought to have anabolic effects, as well as repartition energy stores in cattle, which leads to farm animals growing much more muscle and much more quickly than they otherwise would have. For these reasons there is a blanket ban on beta-2 agonists by the World Anti-Doping Agency (WADA)[1] and they are almost entirely banned for use in farm animals for growth promotion purposes, particularly throughout Australia and the European Union (EU).[2] Since steroids were banned in the mid-1980s the use of beta-2 agonists has risen. However there have been more strict testing procedures implemented over the past 10-15 years which have been designed to reduce their use, as they can have dangerous consequences if accidentally ingested. From a sports point of view, cyclist Alberto Contador and swimmer Jessica Hardy are two high profile cases of athletes who have been implicated in the use of beta-2 agonists; each was banned from their respective sports within the last five years. The aim of this research is to develop a multidimensional gas chromatography technique, similar to those which have been shown to successfully lower the limits of detection for other performance enhancing drugs such as steroids,[3] to accurately and precisely detect and identify beta-2 agonists in urine samples. Although there are already techniques available which can readily identify the drugs at the minimum detection levels required by WADA,[4] further lowering of the detection limits would signal advancement in the process, in that lower doses of the drugs could be detected longer after administration.

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~ W13 ~

THE USE OF EUCALYPTUS BIOMASS FOR REMOVAL OF ARSENIC AND SELENIUM FROM COAL FLY ASH LEACHATE

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Coal fly ash is generated during the combustion of coal for energy production in Thermal Power Plants (TPP). More than 70% world wide of all coal fly ashes is either stored in stockpiles, or disposed in ash landfills or lagoons. Fly ash is recognized as an environmental pollutant because of its high concentration of toxic metal(oid)s, and the potential for leaching these metal(oid)s into the wider environment. Several methods are reported for element removal from fly ash. However, in this study, the possibility of using bioadsorbents like Eucalyptus biomass (bark/leaves) for removing Arsenic and Selenium from fly ash leachate was investigated.

At first, the mobility of Arsenic and Selenium from two class F fly ashes was studied using batch leaching tests. The concentrations of these elements released in leaching solutions with initial pH values of 4, 7 and 10 were used to evaluate the effect of pH conditions on element mobility from these acidic fly ashes. According to the results, Arsenic and Selenium concentrations increased with time in leachate solutions where pH was greater than 7. It indicates that the leaching behaviour of fly ash strongly depends on the pH of the leaching solution.

Then, batch adsorption for the removal of total Arsenic and Selenium from synthetic solutions was carried out using raw barks of two different Eucalyptus species under various experimental conditions at 25±2ºC. Percentage removal of both elements increased with the decrease in initial concentration and increased with the increase in contact time and dose of adsorbent at optimum pH.

Finally, a high percentage of Arsenic and Selenium was able to be removed from fly ash leachate using E. bark at optimum adsorption conditions of pH, contact time, and bark dosage for each element. This confirmed the possibility of using Eucalyptus biomass to remove As and Se from fly ash leachate.

~ W14 ~

CHARACTERIZATION OF GELLAN GUM BY CAPILLARY ELECTROPHORESIS

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Gellan gum is of great interest in current research due to its many unique properties and its wide variety of potential applications as a multifunctional gelling, stabilizing and suspending agent with uses in food, pharmaceutical, medical and chemical industries.[1,2] Gellan gum is a natural exopolysaccharide produced by the bacterium Spingomonas elodea which is widely distributed throughout nature. With gellan gum's increasingly widespread use its importance has become apparent with its unique properties showing advantages over other naturally occurring polysaccharides. These advantageous properties are its excellent thermal and acid stability, adjustable gel elasticity and rigidity, high transparency and good flavour release. Currently there is no definitive method available to produce identical gellan gum samples.

Gellan gums were characterised for the first time using free-solution capillary electrophoresis (CE) or CE under critical conditions (CE-CC), using a 7100 Agilent Capillary Electrophoresis machine. CE-CC is a fast method that separates the polysaccharide. Gellan gums are shown to be heterogeneous in terms of their electrophoretic mobility at 55°C revealing: oligomer peak(s), broad peaks of polymers with a random coil conformation with different degrees of acylation (composition), aggregates, and polymers with double-helix conformation. CE-CC is complementary with the rheological analysis also performed in this work. Sonication of gellan gums is shown to decrease the viscosity of gellan gum mainly by breaking up aggregates. The effect of sonication is stronger on the high-acyl gellan gum since the latter has a far higher tendency to aggregate.

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~ W15 ~

MULTIDIMENSIONAL GAS CHROMATOGRAPHIC ANALYSIS OF JET FUEL OXIDATION PRODUCTS

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Many modern aircraft utilise fuel as a cooling fluid for avionics and lubrication systems, exposing the fuel to temperatures above 150°C. Contact with heated parts of the engine induces thermal stress and fuels begin to oxidise through reaction with dissolved oxygen. The initial (primary) oxidation to hydroperoxides is well characterised and triggers a series of further (secondary, tertiary etc.) reactions[1]. The formation of secondary and tertiary oxidation compounds is less well understood, with the mechanistic details remaining largely unknown. The end result of these oxidation reactions is the formation of insoluble deposits and gums[2] which have the potential to block engine parts and cause failures. Increased interest and uptake of alternatively derived fuels from biological (algae, plant or animal oils) or synthetic (Fischer-Tropsch) sources further complicates the issue, as even those fully certified for use have a different molecular composition to those derived from crude oil sources. Therefore, different oxidised species tend to form, and different mechanisms of insoluble formation are possible. Analysis of secondary and tertiary oxidation products in thermally stressed fuels will help to elucidate the mechanism of formation by identifying the heteroatomic compounds formed in thermal oxidation reactions. The analysis of trace heteroatomic species like oxygenates in the fuel matrix has traditionally been difficult, time-consuming and insufficient in terms of selectivity and detection limits. The increased separating power of multidimensional gas chromatography is ideal for resolving trace oxidation products from the extremely complex fuel matrix[3]. Heteroatomic species containing oxygen are key indicators of the progress of oxidation reactions in thermally stressed fuels and their identification and quantification is an important step towards mitigating the effects of oxidative deposits. Here, the separation of tertiary oxidation products formed in thermally stressed jet fuel using multidimensional gas chromatographic techniques is described.

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~ W16 ~

CHEMILUMINESCENCE DETECTION OF BIOLOGICALLY IMPORTANT THIOLS AND DISULFIDES IN MOUSE STRIATUM

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Biological aminothiols such as cysteine, homocysteine and glutathione (GSH) are endogenous compounds which occur widely in animal fluids and tissues and play important roles in physiological processes. The compounds exist mainly in their reduced form, however conditions of oxidative or nitrosative stress can initiate their conversion to the corresponding disulfide. GSH and its oxidised form glutathione disulfide (GSSG) form a redox couple of particular biological importance, as a change in the ratio of GSH/GSSG is one of the first indications of an overproduction of reactive oxygen species.

The potential for diagnosing and monitoring pathological and physiological conditions related to oxidative stress *via* determination of GSH/GSSG, has led to the development of numerous analytical methodologies. These methods usually require derivatisation (as the analytes lack strong chromophores or fluorophores) followed by a chromatographic/electrophoretic separation.

Our research group has recently reported several methods for the direct detection of thiols and disulfides in biological samples with chemiluminescence detection following chromatographic separation [1,2]. This poster describes the use of a method which incorporates thiol blocking and disulfide bond reduction steps to allow for the quantification of both thiol and disulfide species in mouse striatum. We also investigated the use of a formaldehyde enhancer, which improved sensitivity by over an order or magnitude.

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~ W17 ~

ANALYSIS OF VOLATILE SELENIUM FLUXES IN LAKE MACQUARIE

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The removal mechanisms that govern Se concentrations in Lake Macquarie are unknown despite this lake having received inputs from coal-fired power stations for 30 years. The volatilization fluxes of Se from this lake have not been previously measured due to challenges of analysis and the price and effort to develop appropriate methods. In order to quantify the amount of Se volatilised from sediments in Lake Macquarie, a mass balance for Se incorporating Se loads and removal from a contaminated "hot spot" in the lake was undertaken. Measurement of volatile Se fluxes involved using a cryofocusing trap system to concentrate dimethyl Se and dimethydi Se which were transported to the Ecochemistry Lab at the University of Canberra and analysed by inductively coupled plasma mass spectrometry.

~ W18 ~

IMPROVING TOXICOLOGICAL ANALYSIS IN DRUG-FACILITATED SEXUAL ASSAULT: THROUGH ENZYMATIC HYDROLYSIS AND EXTRACTION

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There are a wide range of pharmaceuticals that are known to be commonly used in drug-facilitated sexual assaults (DFSA's), including a selection of benzodiazepines, opioid analgesics, anti-depressants, anti-psychotics and many others [1]. Benzodiazepines are a particular concern due to their sedative and hypnotic effects as well as being readily available [2-5]. There are three main issues associated with the analysis of DFSA samples taken from alleged victims. Firstly, many of these drugs are conjugated to undetectable glucuronides during metabolism in the body, which requires hydrolysis to detect the parent drug [6]. Another issue associated with analysis is the extensive range of drugs associated with DFSA's, as any drug producing a similar central nervous system (CNS) depressant effect, ranging from narcotics to antihistamines, can be used [1]. These are usually administered as a single dose, resulting in low concentrations of the target analyte at time of analysis [7, 8]. The final issue is, due to the rate of metabolism and elimination, urine is the preferred choice of sample. However, analysis of urine samples is only useful within a few days of taking the drug, due to low concentrations [4, 8]. Therefore a high sensitivity analysis method is required.

Presented here is an optimised method of enzymatic hydrolysis of phase II metabolites in urine, and subsequent extraction and analysis of 71 drugs, including a selection of benzodiazepines, opiates and non-narcotic analgesics, anti-depressants, anti-psychotics and over-the-counter drugs. Optimal hydrolysis conditions for codeine and selected benzodiazepines were found to be incubation for 5 hours at 55°C, using 10,000 units of β-Glucuronidase enzyme (extracted from *Haliotis rufescens*, the Red Abalone), at pH 5.0. Liquid chromatography-tandem mass spectrometry (LC-QTOF) was used to analyse the hydrolysed and extracted samples. To verify the final method, a number of parameters were tested, including LOD, specificity, matrix effects, and a selection of authentic DFSA were analysed and compared to existing methodology.

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~ W19 ~

INTERACTIONS BETWEEN POLYCYCLIC AROMATIC HYDROCARBONS AND WINE PHENOLICS WITH GRAPHENE BASED CHROMATOGRAPHY COLUMNS

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There has been great interest in graphene based structures since the Nobel Prize for Physics was awarded to Andre Geim and Konstantin Novoselov in 2010[1][2]. In order to fully realise the potential of graphitic based structures for separation science, applications of some key fundamental aspects need to be better understood.

Here we describe that the π-π interactions involved in polycyclic aromatic hydrocarbons and wine phenolics on a graphene based chromatography column are one of the main mechanisms responsible for retention. In order to study this phenomenon, a selected set of polycyclic aromatic hydrocarbons (benzene, naphthalene, anthracene, 2,3-benzanthracene and pentacene) and several phenolic compounds (coumaric acid, cinnamic acid, vanillic acid and vanillin) have been investigated.

This study displays the importance of the planar structure and the polarity of side chains on this type of separation mechanism. These results are better able to inform the optimisation of separations on commercial porous graphitic carbon chromatography columns for commercial applications.

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~ W20 ~

DEVELOPMENT OF A NOVEL ULTRASENSITIVE CAPILLARY ELECTROPHORESIS-MASS SPECTROMETRY SYSTEM FOR THE ANALYSIS OF ENVIRONMENTAL POLLUTANTS

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The aim of this work is to develop new sensitive methods for the analysis of pharmaceutical and personal care products (PPCPs) in water samples. Some of these compounds were previously undetected or had not been considered as a risk, but there are a number of well documented cases of the impact that these new pollutants have had upon our environment. Based on their potential hazardous effects as well as their frequency of occurrence nine PPCPs that can be found in environmental water samples were chosen to be investigated. Finally, capillary electrophoresis hyphenated with mass spectrometry, will be used for the determination of these pollutants since it is a highly attractive analytical separation technique that offers exceptional performance with regard to speed and flexibility. While its flexibility and versatility are perhaps its greatest strength, the concentration detection limits are one of the most significant limitations of this technique. Within this work, a continuous flow interface was developed which connects a flow injection with the capillary electrophoresis components. The effects of on line preconcentration when using a continuous flow interface on the sensitivity enhancement were investigated. Further a number of innovative approaches will be combined to develop a highly sensitive analytical system that will offer a unique ability to scientists and regulatory authorities to detect and monitor emerging pollutants.

~ W21 ~

AMPEROMETRIC DETECTION OF CHOLESTEROL WITH A NANOCOMPOSITE POLYPYRROLE-CHOLESTEROL OXIDASE BIOSENSOR INFUSED WITH MULTIWALLED CARBON NANOTUBES

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Carbon nanotubes (CNTs) is one of the important nanomaterials that have gained considerable interest in recent years for the development of ultrasensitive electrochemical biosensors due to their special properties such as the ability to promote electron transfer, facilitate low-potential amperometric measurement of H_2O_2, increase specific surface area and increase surface free energy.[1] The unique property of conducting polymers such as polypyrrole along with the possibility to entrap enzymes during electrochemical polymerization has also generated a great interest.[2] Recently, nanocomposites of conducting polymers and nanomaterials have received considerable attention because it can combine properties together and acquire new properties that are useful for fabrication of biosensors. On the other hand, the determination of cholesterol is of great significance in clinical diagnosis of coronary heart disease, arteriosclerosis, myocardial infarction, brain thrombosis, etc.[1c,3] In this paper, the fabrication of a novel amperometric cholesterol nanobiosensor based on the galvanostatic embedment of multiwall carbon nanotubes (MWCNTs) together with cholesterol oxidase (COx) into polypyrrole films will be discussed. The results obtained for the investigation of the influence of film formation parameters such as MWCNT concentration, applied potential, polymerization time, enzyme concentration (COx), pyrrole concentration, current density, electrolyte (KNO_3) concentration, and mediator ($Fe(CN)_6^{4-}$) concentration will be presented. Also, the optimization of measurement conditions, such as pH and buffer concentration, will be discussed. Other analytical benefits of CNTs, PPy and incorporation of COxon platinum electrode will be highlighted.

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~ W22 ~

AIRBORNE CONCENTRATION OF VOLATILE ORGANIC COMPOUNDS IN URBAN SCHOOLS

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There is an increased concern about airborne particles not only because of their environmental effects, but also due to their potential adverse health effects on humans, especially children. Despite the growing evidence of airborne particles having an impact on children's health, there have been limited studies investigating the long term health effects as well as the chemical composition of ambient air which further helps in determining their toxicity. Therefore, a systematic study on the chemical composition of air in school environment has been carried out in Brisbane, which is known as "Ultrafine Particles from Traffic Emissions on Children's Health" (UPTECH). This study is also a part of the larger project focusing on analysis of the chemical composition of ambient air, as well as source apportionment and the quantification of ambient concentrations of organic pollutants in the vicinity of schools. However, this particular paper presents some of the results on concentration of different Volatile Organic Compounds in both indoor and outdoor location from different schools.

The database consisted of 750 samples (500 outdoor and 250 indoor) collected for VOCs at 25 different schools. The sampling and analysis were conducted following the standard methods. A total of 90 individual VOCs were identified from the schools studied. Compounds such as toluene, acetic acid, nonanal, benzaldehyde, 2- ethyl 1- hexanol, limonene were the most common in indoors whereas isopentane, toluene, hexane, heptane were dominant in outdoors. The indoor/ outdoor ratio of average sum of VOCs were found to be more than one in most of the schools indicating that there might be additional indoor sources along with the outdoor air in those schools. However, further expansion of the study in relation to source apportionment, correlating with traffic and meteorological data is in progress.

~ W23 ~

ENZYMATIC SYNTHESIS AND CHARACTERISATION OF LIPID MEDIATORS OF INFLAMMATION

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This study describes the synthesis and chemical characterisation of a range of novel lipid mediator analogues, termed resolvins and protectins. These hydroxylated compounds are derived from various omega-3 and omega-6 polyunsaturated fatty acids, and are potential mediators of anti-inflammatory pathways within the body.

A lipoxygenase enzyme isolated from soybean is used to catalyse the double dioxygenation reactions of the fatty acid substrates, producing a range of mono- and di-hydroxylated compounds. A better understanding of the activity of the soybean 15-lipoxygenase enzyme is achieved by examining the effect of various experimental conditions on the progression of the reaction as well as the formation of different products. As a result, two methods for the specific synthesis of separate mono- and di-hydroxy products are developed in order to obtain suitable yields for full characterisation studies.

The dioxygenation reaction of the starting material by soybean 15-lipoxygenase is a stereoselective and enantioselective process, targeting the *cis,cis*-1,4-pentadiene moiety of the polyunsaturated fatty acids. The addition of a hydroxy substituent to this pentadiene system results in the rearrangement of *cis* double bonds to form conjugated *cis,trans*-dienes, possessing unique UV-visible absorbance spectra. A further dioxygenation reaction at a position ten or seven carbons from the first dioxygenation position enables the formation of two related conjugated *cis,trans* dienes or a conjugated *trans,cis,trans* triene system, respectively.

The specific geometry of the conjugated double bonds are determined using ^{1}H- and ^{13}C-NMR spectroscopy experiments, while the exact position of the hydroxyl substituents are determined by GC-MS analysis following the development of a derivatisation method. Full characterisation of all reaction products is obtained by NP-HPLC, GC-MS, NMR spectroscopy, high-resolution MS and UV-visible spectroscopy.

~ W24 ~

PASSIVE SAMPLING: QUANTIFICATION AND QUALIFICATION OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS (PPCPS) IN VICTORIAN SURFACE WATERS

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The widespread use of pharmaceuticals and personal care products (PPCPs) and the continuous release of these compounds into our aquatic environment has been cause for concern over the last couple of decades.[1] As PPCPs have been designed to have specific biological effects and are not selective on the organisms they impact, they can be potentially detrimental to the aquatic environment even at concentrations as low as ng/L.[2]

Wastewater treatment plants (WWTPs) are known to be significant contributors of PPCPs to the aquatic environment.[2] Conversely, controlled discharge of treated wastewater can also be beneficial to the health of a creek or river through improved environmental flows.

In recent years, passive sampling devises have been determined as a reliable means by which PPCPs can be quantified and qualified in the aquatic environment.[3] They work by accumulating compounds onto sequestering material by the process of passive diffusion. Once the sampler has been taken back to the laboratory, these compounds can be di-sorbed from the sequestering material and measured using traditional analytical methods including, but not limited to, HPLC/MS, GC/MS, and HPLC/MS/MS.[2]

The purpose of this research is to investigate the occurrence and fate of pharmaceuticals in the receiving waters downstream of a Victorian WWTP. The proposed research aims to: 1. Optimise and validate an appropriate passive sampling device for use in Victorian surface waters. 2. Produce a thorough environmental risk assessment to determine the likelihood of further environmental degradation occurring due to the unintentional release of PPCPs into an urban creek.

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~ W25 ~

SURFACE ASSISTED LASER DESORPTION IONISATION FOR THE ANALYSIS OF PROPELLANTS

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Matrix Assisted Laser Desorption Ionization (MALDI) is an ionization technique best known for its ability to investigate biological and large molecules. The Matrix involved absorbs the laser energy, passing it onto the analyte, resulting in desorption, without the high energies regularly required for vaporization. The particles of sample desorbed are ionized and subsequently analysed by time of flight Mass Spectrometry. Recently there has been a lot more interest in the use of MALDI to analyse smaller non-biological samples. Unfortunately the matrix molecules are often in the same range as the target molecules, thus limiting the usefulness of MALDI for low mass samples. This interference means that alternative matrices are being researched, including a variety of surfaces and the technique of Surface Assisted Laser Desorption Ionization (SALDI). Conductive tapes are useful surfaces when looking at solid samples as they serve two purposes, both as an adhesive and a method of desorption/ionization assistance.

Previous SALDI work has been focussed on low mass samples such as drugs and inks. This project applies this technique to the analysis of propellants. Little work has been done with energetic materials and MALDI and most propellant analysis has been limited to chromatographic methods.

By predetermining the components of a variety of unknown propellants using HPLC, they could be more efficiently analysed when targeted by MALDI. The propellants were looked at in both solid and dissolved forms and on a variety of surfaces. One of the advantages associated with analysis in solid form is that there is less sample preparation and no time required for a liquid sample to set and dry, leading to a quicker analysis time.

~ W26 ~

INVESTIGATING SURFACE COVERAGE OF A MIXED MODE MONOLITHIC COLUMN USING MULTI-LOCATION PEAK PARKING

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The major drawback of gradient elution in the second dimension of two dimensional high performance liquid chromatography (2D-HPLC) is the time required to re-equilibrate the column to the starting gradient conditions prior to injection of subsequent fractions. In 2D-HPLC the aggregate analysis time, including separation time and column re-equilibration, must be as short as possible to prevent the wrap around effect and minimise analysis time. In an attempt to eliminate the need for column re-equilibration, and still maintain the advantages of gradient elution over an isocratic approach, a gradient stationary phase has been developed by chemically binding cyano and phenyl ligands at different densities along the length of a silica monolith column (100 x 4.6 mm). However, it is impossible to know the exact ligand density of the different sections without destroying the column. Gritti and Guiochon[1] recently demonstrated that axial diffusion was slower in columns with a higher surface coverage. With this in mind a multi-location peak parking experiment was designed such that a series of thiourea peaks were 'parked' at designated locations along the column surface; peaks were parked by stopping the mobile phase flow for a period between 0 and 480 minutes. We found that peak variance increased with the parking distance from the column inlet, suggesting non-uniform surface coverage along the length of the column was achieved. These results were compared to an Onxy C18 monolithic column (100 x 4.6mm) for which the manufacturer claims uniform surface coverage where a constant peak variance along the length of the column was found.

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~ W27 ~

USING IMMOBILISED METAL AFFINITY CHROMATOGRAPHY (IMAC) TO COMPARE PROTEIN PROFILES IN CONTROL AND COPPER EXPOSED MARINE ALGAE

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Although it is widely known that metals are toxic to life in the aquatic environment, the levels required to cause an effect can vary widely between species. The cause of this interspecies variation is not known. This project aims to investigate differences in metal sensitivity at a molecular level in aquatic organisms, in particular copper in marine microalgae. Copper is an increasingly important mineral resource in Australia, the exploration budgets rose to $261 million in 2010.[1] There is, therefore, an increased incentive to improve the understanding of mechanisms of copper toxicity.

This study investigated copper induced changes in protein profiles in four marine microalgae species (*Dunaliellatertiolecta*, *Tetraselmis* sp.,*Nitzschiaclosterium* and *Phaeodactylumtricornutum*). Proteins were captured through immobilized metal affinity chromatography (IMAC). Proteins were loaded onto a $CuSO_4$ charged IMAC column. Unbound proteins were washed through with a Tris buffer at pH 7.5, membrane bound proteins hindered further analysis and were removed by elution with a 0.1% Triton X-100 solution. Proteins bound to the column were eluted with a 0.2M imidazole solution in Tris buffer at pH 7.5, then collected, concentrated and separated further by 1D SDS-PAGE (1-dimension sodium dodecyl sulfate polyacrylamide gel electrophoresis). Excised sections of the gel were analysed for protein identification using MALDI-qTOF (matrix assisted laser desorption/ionization-quadrupole time of flight) mass spectrometry. Differences in protein expression and intensity were found between the four species of algae. When these algae were exposed to copper only two species *Nitzschiaclosterium* and *Tetraselmis* sp. showed distinguishable differences, these proteins were analysed by mass spectrometry to achieve identification. Profiles of the four marine microalgae will be presented.

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~ W28 ~

SELECTIVITY IN DETECTION: THE ANALYSIS OF ALKALOIDS AND PHENOLS USING HPLC WITH MASS SPECTRAL, UV, AND CHEMILUMINESCENCE DETECTION

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Due to the complexity of many natural products and the extensive range of compounds, characterisation using a single detection mode, for example LCMS would be highly complicated, arduous and expensive, and difficult to isolate a single compound. In this study we use the analysis of tobacco to illustrate the complexity of sample characterisation using various HPLC-hyphenated modes of detection. A number of detection modes were used to systematically reduce the complexity of the sample whilst obtaining comprehensive chemical information. The detection modes included mass spectrometry, UV-absorbance, Chemiluminescence (Acidic potassium permanganate, manganese (IV), tris(2,2'-bipyridine)ruthenium(III)) and DPPH radical scavenging. The analysis showed that a number of compounds were observed *via* all detection modes and some were selective to one system. Due to detection selectivity it is possible to establish some compound functional properties such as antioxidant potential. The methodology generates a great amount of information about the sample without the arduous analytical process of interpreting complex data.

~ W29 ~

ONLINE ORGANIC ACIDS CHARACTERIZATION AND MONITORING FROM BIOPROCESS USING SEQUENTIAL INJECTION CAPILLARY ELECTROPHORESIS

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A rapid Sequential Injection Capillary Electrophoresis (SICE) with capacitively coupled contactless conductivity detection (C^4D) will be developed for the analysis of lactic and other important organic acids. The SICE system was developed in our group [1] and allows for electrokinetic and pressure injection from a sample flow. In this work, the optimisation of parameters including background electrolyte, capillary length, applied voltages and flow rates will be discussed.

The analysis of lactic acid and other organic acids is important for characterization and monitoring of cell culture, where the chemical composition of media and/or fermentation broth provides significant and critical information on the changes occurring within these complex and dynamic systems. CE is a powerful and reliable separation technique because of its high efficiency, complementary, selectivity and shorter analysis time when compared to other separation methods, and therefore well suited for monitoring applications.

The method developed here will be applied to analyse the lactate production during cell culture. Variation of fluid levels will affect the cells respiration process leading to anaerobic metabolism and noticeable increase in lactate production in correlation to amount of oxygen diffused to the cells.

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~ W30 ~

FABRICATION OF A NOVEL SULFITE NANOBIOSENSOR BY MODIFICATION OF POLYPYRROLE NANOWIRES ARRAY WITH PLATINUM NANOPARTICLES AND SULFITE OXIDASE

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Sulfite is a versatile additive and preservative used in a variety of food, pharmaceutical and beverage industries to prevent spoilage by oxidation and bacterial growth during production and storage [1-3]. Despite its known benefits, it has been found to result in mild to severe skin, respiratory, and gastrointestinal reactions [3 - 4]. For these reasons, the US Food and Drug Administration has recommended the labelling of products containing more than 10 ppm (125 µM) of sulfite since 1986 [3]. This has, in turn, prompted considerable interest in the reliable determination of sulfite.

Although a number of methods are available for sulfite determination, there is still an on-going interest in the development of a more reliable, sensitive, and easy to employ methods such as can be achieved with biosensors for rapid determination [3]. When coupled with nanomaterials, such as nanowires which are known to have unique physical and chemical properties, significant improvement in the sensitivity and specificity of biosensors can be realized [4]. In fact, it has been shown that the achievement of nanometer scale spatial resolution provides accurate real-time information of concentration of a specific analyte and corresponding information on other analytes [5].

In this paper, we will describe the fabrication of a novel sulfite nanobiosensor based on the adsorption of sulfite oxidase (SOx) onto a polypyrrole nanowires array (PPyNWA) decorated with platinum nanoparticles (PtNPs). The resulting PtNPs-PPyNWA-SOx nanobiosensor has a low over potential, improved sensitivity and selectivity. Electrochemical behaviour of the biosensor was characterized by amperometry and cyclic voltammetry (CV), while the morphology and microstructure of the PPyNWA were investigated by SEM. The influence of important parameters, such as deposition of PtNPs, enzyme concentration, applied current density, polymerization period and pH, on the performance of the biosensor will be discussed. The successful application of the biosensor to the determination of sulfite in beer and wine samples, as well as comparison with spectrophotometric method will also be presented.

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~ W31 ~

MULTIPLEXED DUAL-SECONDARY COLUMN COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY

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A comprehensive two-dimensional gas chromatograph has been developed that splits the primary column effluent into two second-dimension columns with different stationary phase chemistry. The resulting technique, multiplexed dual-secondary column comprehensive two-dimensional gas chromatography (GCx2mGC), produces a pair of two-dimensional chromatograms for each run and avails retention data from three stationary phases using a single detector. GCx2mGC is a powerful approach for qualitative characterisation of complex mixtures since the instrument configuration leads to less likelihood of co-elution and provides retention times (or indices) on three stationary phases.

MS detection is undisputedly the best choice for qualitative characterisation of complex mixtures GCx2mGC is amenable to coupling to mass spectrometry. This presentation will introduce a new modulation regime that permits GCx2mGC. A detailed description of this novel technique and analysis results will be described in this poster presentation.

~ W32 ~

CONSTRUCTION OF A POTENTIOMETRIC NITRATE BIOSENSOR BASED ON GOLD NANOWIRES ARRAY

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Nitrate is a ubiquitous contaminant in ground water and streams, but its pollution has resulted in serious environmental problems and health hazard, such as eutrophication, blue baby syndrome and gastrointestinal cancer in the past two decades [1-3]. Therefore, the monitoring of nitrate concentration is of significant importance and has attracted considerable interest in recent years. One of the approaches for nitrate determination that is gaining increasing interest is the development and use of biosensors with the advantage of good selectivity due to the specificity of nitrate reductase and excellent sensitivity [4-7]. In the past decade, nitrate biosensors have gained considerable attention because of its portability without the need for large and expensive equipment. Also, the recent interest in the synthesis of nanowires array provides an excellent platform for fabrication of novel nitrate nanobiosensors, which will be more sensitive to nitrate due to the properties of nanowires array, such as high specific surface area, high surface activity and three-dimensional morphology.

In this paper, the fabrication of a novel nitrate nanobiosensor based on the use of gold nanowires array via a chemical cross-linking method with bovine serum albumin (BSA) and glutaraldehyde (GLA) will be described. The morphology and microstructure of gold nanowire arrays are characterized by SEM, TEM and XRD. Parameters for construction of the nitrate nanobiosensor, such as concentrations of BSA and GLA, drying time, concentration of buffer solution and pH, are optimised. Subsequently, the performance of the nitrate nanobiosensor is characterised by potentiometric method. The nitrate nanobiosensor fabricated under optimum conditions achieved very low detection limit and high sensitivity due to the advantages of the electrochemical detection and presence of gold nanowires array.

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~ W33 ~

USP METHODS TRANSITIONED TO MS AND MSMS DETECTION

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The analytical methods that are included in USP monographs are preferred for the development and quality control of drug substances and products. While the chromatographic methods are typically robust and often include the common related substances, they can be difficult to validate where confirmation of peak identity is required. Further, identification of unexpected components can prove difficult. These complications arise because the specified mobile phases often contain high concentrations of buffer salts. These conditions compromise ionization for mass spectral detection and can complicate collection of fractions for use in complementary techniques. A systematic protocol has been developed for using MS detection directly with these methods and for guiding the transition to generally useful separations eliminating non-volatile buffers.

~ W34 ~

ANALYSIS OF FAT SOLUBLE VITAMIN CAPSULES USING ULTRAPERFORMANCE CONVERGENCE CHROMATOGRAPHY

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The analysis of fat-soluble vitamin (FSV) formulations, often from oil filled capsules, powder filled capsules, and pressed tablets, can be a challenging task. Most often, analysis of these formulations employ normal phase chromatographic methods using traditional normal phase solvents (hexane, tertiary butyl alcohol, ethyl acetate, dichloromethane and others) which can be expensive to procure and dispose of. Other techniques include reversed phase liquid chromatography, gas chromatography, thin layer chromatography, and colorimetric techniques for these analyses. The use of Ultra Performance Convergence Chromatography (UPC^2) in fat-soluble vitamin analysis provides a single viable technique that is cost-effective, sustainable, and a green technology alternative that lowers the use of organic solvents, provides fast analysis times, and maintains chromatographic data quality. Using the ACQUITY UPC^2 system (figure 1), a series of FSV formulations were analyzed. The formulations examined (table 1) contained Vitamin A only, Vitamins A + D3, Vitamin E, Vitamin D3 only, Vitamin K1 only, and Vitamin K2 only. Results from these experiments show UPC^2 has the potential to replace many of the separation methods in use today as the sole technique with no compromises.

~ W35 ~

RAPID DETECTION OF HARMFUL ALGAL BLOOMS (HAB) IN COASTAL WATERS USING MOLECULAR TOOLS

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Harmful algal blooms (HAB) are a serious ecological and socio-economic problem. The main cause of bloom proliferation is eutrophication of water sources. Anthropogenic effects contribute significantly to the increased levels of nutrients within the marine environment. Toxins released from blooms can pose a serious health hazard for humans and marine life, therefore early bloom detection is essential. Dinoflagellate blooms are commonly known as red tides due to the discolouration of the water. *Kareniamikimotoi* is a significant dinoflagellate blooming species around the British Isles, but has also detected off Norway, the U.S. east coast and was first described in 1935 in Japan. Bloom identification using traditional methods of microscopy; pigment analysis and remote sensing cannot always identify to species level, especially when species have similar morphological features. Molecular biological techniques now provide a rapid, species specific identification solution. We have developed a nucleic sequence-based amplification (NASBA) assay for isothermal RNA detection of the rbcL gene of Dinophyceae *Kareniabrevis*, *Kareniamikimotoi*, and Chlorophyceae *Tetraselmissuecica*, and the luc gene for Dinophyceae *Alexandriumtamarense* and *Lingulodiniumpolyedrum.* The assay was used to identify two localised HAB's, in UK coastal waters. Water samples from five sites in the English Channel were collected in July 2010, and were compared with brackish samples from Scottish Lochs Mull and Scridain in September 2011. All samples tested positive for *K. mikimotoi*and *T. suecica*, while they were negative for the rest of the targets. This confirms previous microscopy identification of the *Karenia* species in both locations. Our molecular biology approach offers a reliable and rapid RNA-based identification method, which is a measure of viable cells only. It could also be used for identification of bloom-forming potential and algal toxin monitoring with the added benefit of detection sensitivity of as little as 10 cells per sample.

~ W36 ~

CHARACTERISATION OF MIXED-MODE PHASES FOR THE COMPREHENSIVE ANALYSIS (APIS, EXCIPIENTS AND INORGANIC IONS) OF BINARY AND TERNARY PHARMACEUTICAL PREPARATIONS

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This study aims to develop chromatographic methods to address the comprehensive analysis of binary and ternary pharmaceutical preparations. Mixed-mode stationary phases based on ion-exchange and reversed-phase functionalities are investigated including Acclaim Trinity P1, IonPac AS11-HC and IonPac CS10 with the ultimate goal of simultaneous determination of active pharmaceutical ingredients their organic and inorganic counter ions and excipients. Particular attention is given to the tri-modal stationary phase (anion/cation-exchange, reversed-phase), Acclaim Trinity P1, which was characterised on the basis of pH, ion-exchange and hydrophobicity studies while its physical architecture was evaluated using scanning electron micrographs. The column was later subjected to a mixture of neutral, anionic, cationic and permanently charged active pharmaceutical ingredients, excipients organic and inorganic ions revealing excellent peak shapes and retaining a baseline separation as a consequence of its unique selectivity.

~ W37 ~

EVALUATION OF COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY WITH FLAME PHOTOMETRIC DETECTION: POTENTIAL APPLICATION FOR SULFUR SPECIATION IN SHALE OIL

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Global shortages of fossil fuel and continuing price increases are powerful incentives for exploration of new sources, and use of alternative fuels. Oil shale is a promising source because of large and widespread deposits, and the relative ease with which the organic matter can be extracted. However, shale oil differs in its chemical characteristics from conventional fossil fuels, so that characterisation of shale-derived fuel is important in view of the different applications for which the fuel is used. However a thorough evaluation of shale-derived fuel requires advanced analytical methods due to the shale oil complexity, and the presence of high heteroatom sulfur content. This can include S- and N-compounds. For high S-shales, de-sulfurization requires precise group type characterization in order to apply the most effective process. Flame photometric detection coupled with gas chromatography (GC-FPD) is a common method for sulfur characterization. However, single-column methods have shown to be insufficient for differentiation of sulfur components from other hydrocarbons, or to adequately speciate different classes of sulfur components. This study focuses on evaluation of flame photometric detection coupled to comprehensive two-dimensional gas chromatography (GC×GC-FPD), and its potential application in sulfur speciation in shale oil. Method performance parameters (linearity, reproducibility, limit of detection/quantification) in GC×GC format have been tested. The proposed approach offers much better separation of the three main classes of sulfur components (thiophenes, benzothiophenes and dibenzothiophenes) compared to GC-FPD, linearity over the range 15-2500 ppb, and excellent reproducibility of <5% RSD on average.

~ W38 ~

FAST PROFILING OF FATTY ACIDS OF SAFFLOWER OIL BY USING COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY

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Safflower oil is one of humanity's oldest crops, with evidence of its use dating back to the Pharaoh Tutankhamun. Today it is a promising alternative feedstock for biofuel and edible oil production. It comprises a range of fatty acids with similar structure, with the C18 cluster being the most abundant. Their separation and full characterization is difficult by using standard gas chromatography (GC) methods, and represents a continuing challenge for analysts, who often resort to the use of 100-200 m long columns with selective GC phases. Here we propose a fast method for separation and characterization of safflower oil samples based on comprehensive two-dimensional GC. A range of different column combinations have been tested, including combinations of two ionic liquid (IL) columns. The best separation, or spread of components over the 2D space, was obtained when an IL-111 column was coupled with IL-59, with these two columns being the most and the least polar respectively, of the IL column family. Interestingly, similar separation was obtained also when IL-59 was replaced with a polyethylene glycol (PEG) column, where the PEG column behaved as a column of lower polar compared to the higher polarity of IL-111 (normally, PEG is well known as one of the most polar column phases). An excellent separation was achieved in 17 min. Two new components have been detected for the first time in this type of samples.

~ W39 ~

QUANTIFICATION OF THE HORMONES PROGESTERONE AND CORTISOL IN WHALE BREATH SAMPLES USING NOVEL, NON-INVASIVE SAMPLING AND ANALYSIS WITH HIGHLY-SENSITIVE ACQUITY UPLC AND XEVO TQ-S

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The aim of this project is to determine if it is possible to detect the presence of hormones in whale blow samples, and see if the hormone levels could be related to stress due to their environmental situation. If successful the project would enable a non-invasive method to be developed to determine the stress levels of species that are difficult to study.

Specific hormones, progesterone and cortisol, were monitored in samples of whale blow from a variety of different whale species. The results showed that both cortisol and progesterone were detected easily in the lowest calibration standard (0.5 pg/μL) suggesting lower detection limits are possible with further method development.

Reproducibility was excellent, %RSD for both compounds were less than 2% for 5 replicates of a 5 pg/μL standard. Linearity for both compounds was excellent; r^2 = 0.999 for cortisol and r^2> 0.999 for progesterone.

Cortisol was detected in the majority (22 of 25) of samples at a level higher than the lowest calibration point. Progesterone was detected in 13 samples higher than the lowest calibration point.

For all samples parallel collection of both MRM & full scan data was obtained and is shown for each of the species types. This set of data enabled other compounds to be simultaneously screened, and any matrix background to be monitored.

~ W40 ~

A NEW ACCURATE MASS SCREENING SOLUTION INCORPORATING THE UNIFI SCIENTIFIC INFORMATION SYSTEM FOR ANALYSIS OF PESTICIDE RESIDUE AT REGULATORY LIMITS IN FOOD

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Current trends indicate that in excess of 500 pesticide compounds are routinely used on a global basis with different countries having different regulations concerning licensing and Maximum Residue Limits (MRLs). With increasing global trade there is a requirement for multi-analyte screening strategies capable of efficiently detecting residue violations to protect consumer safety. Recent advances in MS and separations technology have a potential impact on complex mixture analysis such as enhanced MS ion transmission and increased peak capacity with UPLC.

This study shows the performance of a new bench top Qtof based platform incorporating StepWave[TM] and Quantof technologies (Figure 1) in combination with a new scientific information system, UNIFI v1.6 specifically designed for non- targeted accurate mass screening applications. UNIFI is a revolutionary new scientific information system that enables scientists to test and report more samples for an increasing number of residues and contaminants. UNIFI firstly captures complex high end mass spectrometry and UPLC data in a single platform and then rapidly process the data to confirm and quantify the presence of pesticide residues.

Poster Abstracts

Friday 13th December

~ F1 ~

THE INFLUENCE OF GAMMA IRRADIATION AND MODIFIED ATMOSPHERE PACKAGING ON ESSENTIAL OIL YIELD OF VARIOUS SPICES

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In this study, the essential oil yield of four spices frequently used in Turkey after packaging and irradiation were evaluated. Irradiation is used to reduce microbial counts and the occurrence of spoilage due to the growth of microorganisms. Thyme, rosemary, black pepper and cumin in ground form were packaged under either a modified atmosphere (100% N_2) or ambient atmosphere. After packaging the samples in 200 g pouches, they were gamma irradiated at 5, 10 or 15 kGy. Un-irradiated samples were used as control. The essential oil of each sample was obtained by hydrodistillation method using a clevenger apparatus. The amount of essential oil was measured using the volumetric scale of the apparatus. The essential oil yield of black pepper and cumin were lower in aerobic packages compared to modified atmosphere. The dose of gamma irradiation also affected the yield of essential oil from thyme, black pepper and cumin. It was the highest in 5 kGy irradiated samples of thyme and cumin, whereas gamma irradiation reduced the yield of essential oil from black pepper. Packaging did not affect the essential oil yield of thyme. No effects of irradiation or MAP were observed in rosemary.

This study will be extended to examine whether chemical differences in the oil composition arise from different irradiation treatments, and classical heat (steam) treatment.

~ F2 ~

COMPREHENSIVE TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY FOR THE SEPARATION OF ORGANIC ACIDS

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Organic acids from fermentation processes can be separated by ion chromatography (IC). However, the sample matrix can be too complex to obtain sufficient separation by one dimension. Hyphenation with HPLC is thus a good approach. Brudin and co-workers, (1), have demonstrated the use of IC×LC as a technique compatible with separation of organic acids in food samples such as yoghurt and wine.

The coupling of IC with LC is more or less straightforward with the prerequisite of eluent suppression. The hydroxide eluent gradient in the ion exchange separation is suppressed to water using a membrane suppressor. This enhances conductivity detection and facilitates coupling with other separation dimensions. A 10-port high-pressure valve with two sampling loops is used as an interface between the two separation columns. The second dimension separation is achieved using UHPLC system to maximize speed and efficiency.

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~ F3 ~

POLYPYRROLE-PENICILLINASE BASED BIOSENSOR FOR POTENTIOMETRIC DETECTION OF PENICILLIN

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This study presents a strategy for fabrication of highly sensitive and selective penicillin biosensor. Entrapment of penicillinase into polypyrrole film via galvanostactic electropolymerisation has been successfully achieved for potentiometric biosensing of penicillin. The optimisation of various film formation and measurement conditions to enable sensitive, selective and reproducible potentiometric detection of penicillin is described and supported by experimental results. The most sensitive potentiometric response for penicillin G detection was achieved in 0.05 mM phosphate (H_3PO_4/NaOH) buffer, pH 8 with applied current density of 0.9 mA/cm^2 and a polymerisation time of 20 seconds. The optimum conditions for formation of PPy-P'Nase-Pen G film, include 0.15 M pyrrole, 0.01 M penicillin G and 5 U/mL of penicillinase. Sensitivity was found to be 114 mV/decade in a linear concentration range of 191 – 552 µM with regression coefficient of 0.99. A minimum detectable concentration of 15 µM was obtained for the biosensor.

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~ F4 ~

MERCURY ASSOCIATIONS IN FISH

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Although eating fish has always been associated with health benefits due to high amounts of omega-3 fatty acids (EPA and DHA), consumption of fish is regarded as the major pathway of mercury accumulation in humans. Through biomethylation and biomagnification processes, mercury concentrations in fish at the top predatory level are often higher than fish at the bottom of the food chain. The toxicity of mercury depends on its chemical form and measurement of methyl mercury ($MeHg^+$) and Hg^{2+} has always been a focus, without consideration that mercury exists as MeHgX (X = low-molecular ions, peptides, proteins or other potential binding ligands). As mercury has a high affinity for sulphur, the most likely binding ligand of mercury is free sulfhydryl groups in protein cysteine residues. However, there is limited information on the binding sites of mercury in fish proteins. In this study the biochemical associations of mercury in fish proteins were examined using size exclusion chromatography and SDS-PAGE to determine the molecular weights of protein bound mercury. Ion chromatography and reverse phase chromatography were used to determine the chemical associations of mercury. The implications for the metabolism and toxicity of mercury in fish were further discussed.

~ F5 ~

A SELECTIVE ELECTROCHEMICAL DNA SENSOR USING A METHYLENE BLUE INTERCALATOR

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Methylene blue (MB) is a redox active molecule capable of reversible binding with different affinity to single stranded (ss) and double stranded (ds) DNA. Spectroscopic and electrochemical studies have demonstrated different types of interactions between MB and both ss and ds DNA including electrostatic interaction of positively charged MB with the negatively charged backbone phosphates of DNA [1], interaction with guanine base [2], and intercalation which proceeds through insertion of MB between two successive DNA base pairs due to favourable π-stacking interactions [3, 4].

The different affinity of MB for ss and ds DNA sequences allowed the application of MB as a redox indicator in a variety of electrochemical DNA assays [1-6]. Understanding the MB-DNA interactions is complex however. This is because of the complex nature of interactions, and the large number of parameters that can vary the response by affecting the binding properties of MB such as immobilization procedure, orientation of DNA, DNA length and sequence [5, 6].

In this work, we performed electrochemical investigation on the interaction of MB with DNA. The recognition interface consisted of mixed monolayer of thiolated ss-DNA probes and a diluent component of 6-mercapto-1-hexanol on a gold electrode. The recognition interface was incubated in an MB solution before and after hybridization and transferred to a MB free solution for electrochemical measurement. Under the selected experimental conditions a greater signal was observed after hybridization, indicating that the combination of the intercalator MB and a modified electrode interface allows the electrochemical detection of DNA hybridization via long-range electron transfer. This approach allowed the detection of the single base pair mismatches with high sensitivity.

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~ F6 ~

CHARACTERISATION OF PATTERNED COPPER SULPHIDE THIN FILMS BY SECM AND PROFILOMETRY

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Patterned semi-conducting copper sulphide thin films can be characterised by their electron transfer ability and conductivity using direct current (DC) and alternating current (AC) scanning electrochemical microscopy (SECM), and step height and surface roughness using profilometry. Characterisation is important when using these films as substrates in experimental investigation. Copper sulphide thin films have interesting optical and electrical properties, which can be exploited. Patterned copper sulphide thin films were synthesised by chemical bath deposition. SECM distinguished conductive copper sulphide bands from insulative silica bands from their higher current. Profilometry showed the coppers sulphide bands had clear vertical definition and that the horizontal surface was very rough. These techniques were also applied to assess the ability of different pH and redox potential conditions to extract copper from the copper sulphide substrate.

~ F7 ~

PRECONCENTRATION OF MERCURIC IONS FROM WASTE WATERS USING POLYMER INCLUSION MEMBRANES

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The presence of toxic metal ions in environment can cause lethal threat to all the living beings[1]. In recent years, considerable efforts have been devoted to the detection and determination of Hg(II) in waste waters. This is due to the wide use of highly toxic mercuric salts in industries. Also, mercury has bioaccumulative property due to its strong affinity for sulfydryl groups present generally in proteins, enzymes and biomembranes. Because of its hazardous effects to human and environment, there is a strong need to establish a simple method to remove and preconcentrate Hg(II) with high selectivity and sensitivity from aqueous media. The present work describes the use of polymer inclusion membranes(PIMs) to separate and preconcentrate Hg(II) from aqueous medium. Polymer inclusion membranes with 20% (w/w) Aliquat 336, 10% (w/w) 1-dodecanol and 70% poly(vinyl chloride) were synthesized as reported in our earlier publication[2]. Gold nanoparticles (Au nps) were synthesized on the membrane surface as reported previously[3]. Hg(II) uptake studies with these membranes revealed 80% uptake from 10 μg/L $HgCl_2$ solution. An attempt was made to increase the extraction capacity of these membranes by functionalizing the Au nps of these membranes with molecules containing thiols at one end (supposed to bind with the Au nps) and the other end containing other thiol or carboxylic acid group (proposed to bind with Hg(II) in solution) such as 1,4-dithioerythritiol,1,8-octanedithiol, 1,4-butanedithiol, N-(2-mercaptopropionyl)glycine and 2,2'-(ethylenedioxy)diethanthiol (EDT). Hg(II) uptake studies with these functionalized membranes showed that while the former four molecules, decrease Hg(II) sensitivity, the last one removes 100% Hg(II) from the solution. In the former case, this may be due to unavailability of the other functional group for Hg(II) due to ring formation between the two functional groups and Au nps on membrane surface while in the latter case, the other thiol group is available for Hg(II). The EDT functionalized membranes were then checked for their reproducibility, sensitivity, Hg(II) capacity and pH dependence.

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~ F8 ~

MOLECULAR TUNING OF GRAPHENE OXIDE- INCITING CONDUCTIVITY

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Graphene and graphene oxide are the major field of research in current scenario as they possess many unique properties such as electrical, mechanical, thermal and electrochemical which are difficult to obtain in a single material, if available they are of high production cost like gold nanoparticles. Graphene oxide are nonconductive [1] and due to large amount of functional groups present on surface of these nanoparticles they could be bound with metals like Mg^{2+}, Ca^{2+} [2] to increase the mechanical property, Fe^{2+} [3] to increase the magnetic properties, silver nanoparticles [4] to make substrates for surface enhanced raman spectroscopy. Herein, we reported a new hybrid material consisting of copper ions complexed with graphene oxide (GO) films on a flexible substrate to induce conductivity. The method of formation is based on cross-linking GO using Cu^{2+} followed by filtration onto nanoporous supports. The binding can be rationalized due to the chemical interaction between the functional groups on GO and the metal ion. Binding of Cu^{2+} to GO is characterised using scanning electron microscopy, UV-Visible spectroscopy, fourier transform infrared spectroscopy (FT-IR) and cyclic voltammetry (CV). Electrochemical impedance spectroscopy (EIS) was performed to calculate the charge transfer resistance upon binding of Cu^{2+} and CV is used to calculate surface coverage of Cu^{2+} on the electrodes. Furthermore, we also investigated flash reduction to increase the conductivity of both GO and GO+Cu^{2+} samples. These hybrid graphene films could be used as transparent conductors [5], chemical/biological sensors [6] and thin film transistors [7].

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~ F9 ~

MOLECULARLY IMPRINTED POLYMER IN TIPS FOR THE EXTRACTION OF FLAVONOIDS, WITH HIGH RESOLUTION GC ANALYSIS

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The use of offline molecularly imprinted polymers (MIP) in micropipette tips as solid phases for extraction of catechin from chocolate is reported. MIP construction used quercetin, methacrylic acid (MA) and ethylene glycol dimethyl methacrylate (EGDMA) as the template, functional monomer and cross linker respectively. Surface morphologies of MIP and non-imprinted polymer (NIP) in tips were characterized using scanning electron microscopy (SEM). Loading the standard solution of catechin, morin and quercetin prepared in methanol, allowed sorption of analyte into the prepared MIP in the micropipette tips. Recovery of catechin was conducted by elution using 10% acetic acid in methanol. The collected fractions from the tips were confirmed and quantified using GC–qMS. Extraction of a series of flavonoid standards was also performed in order to test the selectivity of prepared MIP, which was compared to the corresponding NIP. Adequate extraction performance of the quercetin-imprinted MIP was demonstrated for all tested flavonoids, but was insignificant for the other compounds in dark chocolate. The study confirms the simplicity of the MIP solid phase extraction technology using micropipette tips, with the use of gas chromatography as a tool for high resolution analysis of flavonoids.

~ F10 ~

VOC EXPOSURE IN A RESEARCH AND TEACHING FACILITY

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Volatile Organic Compounds [VOC's] exposure can be an on-going component work within a Chemistry area's activities at a tertiary education campus. Although considerable emphasis is placed upon the efficient use of Engineering controls, via fume cupboards, Administrative Controls, via Hazard and Risk Assessment, the bulk of exposure prevention centers upon Personal Protective Equipment [PPE] usage. To ensure complete exposure control, a personal exposure monitoring program was completed upon two discrete exposure groups.

This study measured the levels of six [6] selected VOC's in personal air samples obtained from monitoring Post Graduate [PG] students (n=4) and laboratory technicians (n=2) in the School Applied Sciences' chemistry laboratories, during their daily activities.

The source of PG personal exposure was mainly from using a variety of organic solvents during research work, and, for the laboratory technicians' exposure came from preparing solutions for student practical.

Personal air samples were collected on SKC activated charcoal tubes with pocket pumps (active sampling) and SKC diffusion badges (diffusive sampling), and analyzed by Gas Chromatography - Flame Ionization Detector (GC-FID). Gas Chromatography - Mass Spectrometry (GC-MS) was used as a qualification tool to search for any other VOC's that may be present, in their working area.

Overall, all VOC levels detected were at least an order of magnitude below the exposure standard. Personal exposure to VOC's was much higher for PG students than for laboratory technicians.

Acetone was found to be the dominant VOC exposure. The exposure levels for n-hexane and n-heptane were found to be reasonable high when compared to the results reported in other indoor air quality [IAQ] studies (Srivastava et al. 2000).

Comparison results between two [2] sampling methods showed that for low levels of VOC's diffusive samples were ineffective. For high levels of VOC's there is a correlation between the results for the two [2] sampling methods.

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~ F11 ~

QUANTITATIVE ANALYSIS OF RENAISSANCE PAINTS AND PIGMENTS BY PORTABLE X-RAY FLUORESCENCE (PXRF)

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PXRF has gained popularity archaeological and art analyses[1] due to its portability, relatively low cost, low detection limits, simple sample preparation, rapid data acquisition and non-destructive nature of analysis. These characteristics make PXRF optimal for analysing priceless artworks. While the majority of studies use PXRF for qualitative assessments, quantitative analysis can provide further information on pigment analysis however the validity and accuracy of the quantitative data obtained has not been investigated. Researching these aspects of PXRF and producing standardisation techniques for data acquisition and interpretation is highly beneficial as PXRF analysis is used for validating cultural heritage materials[1b, 2]. As such it is essential that the analysis technique produces accurate results.

PXRF is a spectroscopic technique that involves the interaction of instrument-generated X-rays with the inner shell electrons of an atom. The electron is ejected from an inner shell and an electron from a higher energy shell fills this vacancy, producing a fluorescent photon characteristic of the energy difference between the two shells. These photons are specific to certain elements and are measured in real-time by a built in detector within the PXRF instrument. The data is then used in conjunction with software on a computer directly connected to the instrument to determine the elemental composition based on energy of the fluorescent X-rays.

Parameters that influence data acquisition include acquisition time, concentration, and thickness. A series of experiments were conducted to investigate these parameters on three pigments common to the Renaissance era: orpiment (yellow, As_2S_3), azurite (blue, $Cu_3(CO_3)_2(OH)_2$) and vermillion (red, HgS) as well as titanium dioxide (TiO_2). The quantitative data obtained underwent statistical analysis using linear least squares regression analysis to assess the accuracy and validity of the data obtained through varying different parameters and develop protocols and standardisations for the quantitative analysis of paint by PXRF.

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~ F12 ~

POSSIBLE NEW CO-REACTANTS FOR TRIS(2,2'-BIPYRIDINE)RUTHENIUM (II) ELECTROGENERATED CHEMILUMINESCENCE

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Electrogenerated chemiluminescence (also known as electrochemiluminescence or ECL) is the emission of light from an electrochemically initiated reaction, which has been used as a highly sensitive detection system for a wide range of laboratory and commercial analytical instrumentation. Currently available commercial systems use tripropylamine as the co-reactant, however this compound it is very toxic, volatile and it is usually required in relatively high concentrations (100 µM). Possible new co-reactants such as the far less toxic 2-(dibutylamino)ethanol (DBAE) have been proposed previously as alternative safer co-reactants. In this project it was found that tertiary amines similar in structure to DBAE (containing at least one hydroxyethyl group) generated greater ECL intensities from tris(2,2'-bipyridine)ruthenium (II)than amines that were similar in structure to tripropylamine at gold electrodes and at concentrations below 5 mM at glassy carbon electrodes. Tertiary amines similar in structure to tripropylamine meanwhile performed better at higher concentrations using glassy carbon electrodes.

Recent advances in ECL detection include the combination of multiple ECL active species that emit different colours of light and/or can be excited at different electrode potentials, which has created new possibilities for rapid, multiplexed detection. However, very little is understood about the mechanisms of these multi-emitter systems. These systems have only been performed previously using tripropylamine as the co-reactant and interestingly intensities emitted from one of the ECL active species are quenched at high electrode potentials. Substituting tripropylamine with alternative co-reactants has provided new insight into the mechanism of these multi-emitter systems.

~ F13 ~

METHOD DEVELOPMENT AND ANALYSIS OF NEUTRACEUTICAL COMPOUNDS IN VICTORIAN STRAWBERRY VARIETIES

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Strawberries (*Fragaria*x *ananassa*Dutch) are a growing industry in Australia, with Victoria the second largest strawberry producer in Australia. Imported and local strawberry varieties are grown in Victoria and much research has been carried out with a focus on flavour and quality improvement of these varieties. To date, no research has been published on nutrient value and nutraceutical compounds present in domestically grown crops. Strawberries are high in vitamin C and bioactive compounds however; the availability of these compounds is variety dependant. Cross breeding of different varieties to boost nutrient values such as vitamin C and bioactive compounds is one of the main focuses of this research. To achieve this, an analytical method using LC-MS/MS is required. Furthermore, identifying the genes responsible for vitamin C and bioactive compounds is predicted to potentially link molecular plant breeding and increase nutrient value. The first step for this major research is to develop an analytical method for phenotype profiling. An optimised analytical method has been developed for bioactive compounds using LC-MS/MS for improved sensitivity and selectivity. Results will used to classify varieties with high and low levels of vitamin C and bioactive compounds. As a part of this research a microarray chip specifically designed for strawberry genome will be utilised for vitamin C and bioactive compound gene identification. The results of this study can be used to inbreed the varieties for better nutrient value and also in the development of new varieties for the market with improved flavour, aroma, colour and nutrients.

~ F14 ~

THE USE OF A POLYMER INCLUSION MEMBRANE IN THE DEVELOPMENT OF A PAPER-BASED MICROFLUIDIC SENSOR FOR THE SELECTIVE DETERMINATION OF CU (II)

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A polymer inclusion membrane (PIM)[1,2] consistingof 40% (m/m) di(2-ethlyhexyl) phosphoric acid (D2EHPA) as the carrier, 10% (m/m) dioctyl phthalate (DOP) as a plasticizer, 49.5% (m/m) poly(vinyl chloride) (PVC) as the base polymer, and 0.5% (m/m) 1-(2'-pyridylazo)-2-naphthol (PAN) as the colour reagent has shown high selectivity under mildly acidic conditions for Cu(II) in the presence of frequently encountered in natural waters and tap water base metal ions such as Fe(III), Al(III), Zn(II), Cd(II), Ca(II), and Mg(II). The laminated paper-based device consists of a PIM disc (2 mm in diameter) attached to the centre of the circular hydrophilic zone (7 mm in diameter) of the paper-based device. The pretreated with 0.01% HCl zone separates the sample port (a circular hole in the plastic cover) from the PIM sensing disc. After introducing 20 mL sample/standard solution to the sample port Cu(II) diffuses across the hydrophilic paper zone and is extracted into the PIM disc as the Cu(II)-D2EHPA complex which subsequently reacts with PAN to produce the red-purple coloured Cu(II)-PAN complex[3]. The colour intensity of the PIM disc 15 min after sample/standard introduction is determined by Image J software (National Institutes of Health, USA, http://imagej.nih.gov./ij) after scanning the paper-based device with a flatbed scanner. The acidic environment in the paper hydrophilic zone prevents the other common base metal ions listed above to be extracted into the PIM disc. Under optimal conditions the device is characterised by an LOD and LOQ of 0.06 and 0.1 mg Cu(II) L^{-1}, respectively, and a working linear range of 0.1 to 10 mg Cu(II) L^{-1}. The paper-based device was successfully applied to the determination of Cu(II) in tapwater.

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~ F15 ~

MOLONGLO RIVER SEDIMENT METAL CONTAMINANTS AND THEIR EFFECTS ON BIVALVE HEALTH BY LINKING ORGANISM METAL EXPOSURE-DOSE-RESPONSE

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Metals are mined in many countries worldwide resulting in significant amounts of metal contaminants entering aquatic systems. There is growing awareness of the toxicological effects of metal contaminants to aquatic organisms, however, the effects of metal contaminants in aquatic systems are diverse, complex and often unpredictable. In this context, integrated monitoring of aquatic ecosystems is important to identify their present status for future management and sustainable development. Integrated monitoring involves measuring chemicals in the environment-exposure, accumulated metals in cellular and sub-cellular compartments of the body- internal dose and associated biological responses at different levels of biological organization using effect biomarkers.

Historically the Molonglo River, NSW was contaminated lead, zinc and copper from mining activities at Captains Flat, NSW. Existing metal loads in the riverbed and surrounding floodplain may still be having significant adverse effects on the fauna that inhabit the River. In this study, effects of Molonglo River sediment metal contaminants on freshwater bivalves will be determined using exposure-dose-response relationship of transplanted caged bivalves in the Molonglo River sediments. Initially, the usefulness of the freshwater mussel Hyridelladepressa as biomonitors of metal contamination will be assessed using 28 daymicrocosms exposures with two different concentrations of Pb spiked sediments. Dose will be measured by total Pb content in gill, mantle, kidney, hepatopancreas and muscle tissues at day 0, 7, 14, 21 and 28. Sub-cellular distribution of Pb will be examined in gill and hepatopancreas tissues at day 28 to evaluate the biologically active metal fraction. After 28 days exposure mussel total antioxidant capacity, lipid peroxidation and lysosomal membrane stability will be measured as biomarkers of Pb toxicity.

~ F16 ~

INTEGRATED MULTIDIMENSIONAL AND COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY ANALYSIS OF FATTY ACID METHYL ESTERS

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Characterisation of fatty acid compounds in complex samples such as milk fat and animal oils requires analytical methods that are capable of providing superior separation power for the analysis[1,2]. Recently, the advanced analytical methods of multidimensional gas chromatography (MDGC) and comprehensive two-dimensional gas chromatography (GC×GC) have proven to offer greater resolving power and enhanced peak capacity over conventional 1D GC, and are being applied to studies in a wide range of fields[3]. In present study, an integrated GC×GC and MDGC was demonstrated for fatty acid methyl ester (FAME) profiling in complex fish oil and milk fat samples. By the use of GC×GC, FAME compounds - *cis* and *trans* positional isomers, and essential fatty acid isomers - ranging from C18 to C22 in fish oil and C18 in milk fat were clearly displayed in contour plot format according to structural properties and patterns, further identified based on authentic standards. Incompletely resolved regions were subjected to MDGC, with Cn (n = 18, 20) zones transferred to a second dimension column. Elution behaviour of C18 FAME on various ^{2}D column phases (ionic liquids IL111, IL100, IL76, and modified polyethylene glycol) were evaluated by using heart-cut MDGC approach. Individual isolated Cn zones demonstrated about 4-fold increased peak capacities. The IL100 provided superior separation, good peak shape and utilization of elution space. For milk fat-derived FAME, the ^{2}D chromatogram revealed at least 3 peaks corresponding to C18:1, more than 6 peaks for cis/trans C18:2 isomers, and 2 peaks for C18:3. More than 17 peaks were obtained for the C20 region of fish-derived FAMEs using MDGC, compared with 10 using GC×GC. The tentative identification based on GC×GC position, with improved isomer separation using MDGC, is a useful strategy for FAME confirmation.

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~ F17 ~

APPLICATION OF MULTIPLE HEADSPACE SOLID PHASE MICROEXTRACTION (MHS-SPME) TECHNIQUE TO THE QUANTITATIVE ANALYSIS OF FRAGRANCE AND FLAVOUR COMPOUNDS

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Solid phase microextraction is a simple and rapid extraction technique based on the partition of an analyte between its matrix and the coating of a fused-silica fiber, introduced for the first time by Arthur and Pawliszyn [1]. This technique is very powerful for the determination of volatiles and semi-volatiles in a wide variety of samples. Since it is a non-exhaustive technique, only a small portion of the analyte is removed from the sample. However, for standard solutions, there is a linear correlation between the amount extracted by the fiber and the real amount present in the sample matrix, thus calibration curves can be built up for quantitative purpose. Totally different is the case of absolute quantitation of analytes in complex-matrix samples because the distribution constants depend on the composition and the polarity of the sample. To avoid the matrix effect, multiple extractions can be performed and the peak area of few successive analyses used to calculate the total amount of the analytes in the sample [2]. This technique is called Multiple Headspace Extraction (MHS) and its theory has been described by Ezquerro et al. [3]

In this work, multiple headspace solid-phase microextraction, coupled with GC-MS and GC-FID, have been applied to the qualitative and quantitative analyses of standard compounds typical of fragrances and flavours. Vaseline oil has been used as matrix and the fiber chosen was 65µm polydimethylsiloxane/divinylbenzene (PDMS/DVB). Different amounts of samples and dilutions were tested in order to optimize the MHS-SPME extraction and the calibration curves for the quantification of each analyte were built-up.

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~ F18 ~

THE PREPARATION OF A MONOLAYER SILVER NANOPARTICLES ON THE SURFACE OF A POLYMER INCLUSION MEMBRANE

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Polymer inclusion membrane (PIM) consisting of 45% (m/m) di-(2-ethylhexyl)phosphoric acid (D2EHPA) and 55% (m/m) poly(vinyl chloride) (PVC) was used as a template for the preparation of silver nanoparticles (AgNPs. The Ag(I) ion was firstly extracted into the membrane via cation-exchange and then subsequently reduced with $NaBH_4$, trisodium citrate, citric acid, or L-ascorbic acid to form AgNPs. The most effective reducing agent was found to be L-ascorbic acid which at pH 2.0 formed a uniform monolayer of AgNPs of an average size of 360 nm on the surface of the PIM. Citric acid also produced AgNPs but these were embedded in the bulk of the membrane and did not provide a good surface coverage. $NaBH_4$ and trisodium citrate, on the other hand, gave rise to the formation of black silver oxide on the membrane surface.

Factors such as the membrane loading with Ag(I), PIM composition, reduction time, temperature and shaking time were found to have a significant influence on the surface coverage and size of the AgNPs.

~ F19 ~

BIOAVAILABILITY OF ARSENIC FROM SOILS TO EARTHWORMS AND LETTUCE

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100 million people worldwide are affected by chronic arsenic poisoning through the use of contaminated groundwater for drinking and watering crops.[1] This groundwater arsenic is mostly of natural origin (geogenic) and is present in two forms – arsenate $[As^VO_4^{3-}]$ and arsenite $[As^{III}O_3^{3-}]$. While both forms are toxic, reduced arsenic (As^{III}) is much more toxic. Elevated and mobile As^V tends to occur in arid or semi-arid regions with poor drainage and high evaporation rates, producing groundwaters with high salinity and pH.[3] Elevated As^{III} occurs in poorly drained soils with high organic matter, where microbial activity depletes oxygen and reducing conditions develop.[2] Interaction with iron(III) and sulfide are also critical.[3] Such reducing conditions also occur in coastal and freshwater sediments.

The biological availability and toxicity of arsenic released from contaminated soils (following water inundation) will be investigated. This will be achieved by characterising the soil chemistry, and measuring the soils' toxicity to earthworms (*Eiseniafetida*) and iceberg lettuce (*Latucasativa*an agricultural product). We will compare the toxicity of the soils before and after inundation with either fresh (e.g. storm event) or marine waters (e.g. high tides).

Soils (control and contaminated) will be collected and characterised, e.g., metal concentrations, particle sizes, and binding properties (exchange capacity, organic matter, pH, sulfide levels, DGT). The soils will be tested at four arsenic concentrations, obtained by diluting the control soils with arsenic contaminated soils at 0% (100% control soil), 0.1%, 10%, and 50% (mixtures of arsenic and control soils) and 100% (arsenic contaminated soil). These soils will be seeded with lettuce or worms for several weeks, submerged with (i) freshwater or (ii) seawater for several days (simulating sea-level rise or flooding events) and allowed to drain. Soil toxicity to the lettuce and worms will be assessed using 'standard' toxicity bioassays (as per Scott-Fordsmand et al.[8]).

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~ F20 ~

A COMPARISON OF ENHANCEMENT TECHNIQUES FOR PERMANGANATE CHEMILUMINESCENCE

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Potassium permanganate chemiluminescence has been widely used as a sensitive mode of detection for pharmaceuticals and drugs. Many compounds have been used as enhancers of permanganate chemiluminescence. These include sulphites, fluorescent compounds and metal ions, though the most commonly used are formaldehyde or polyphosphates. The use of formaldehyde as an enhancer is problematic due to its carcinogenic nature and toxicity. It was found that ethanol also gave a substantial enhancement of the chemiluminescence reaction of permanganate (containing polyphosphates) Considering the toxic effects of formaldehyde, a comparison of ethanol and formaldehyde as enhancers of permanganate chemiluminescence could offer a new and safer method for the detection of dihydroxybenzenes and related analytes. This study compares the effect of ethanol and formaldehyde on the chemiluminescence signal for a range of analytes.

~ F21 ~

STUDY OF COPPER (II) COMPLEXES OF TRIPEPTIDES CONTAINING GLU, GLY AND HIS USING POTENTIOMETRY, UV-VIS SPECTROSCOPY AND GENERALIZED MULTIPLICATIVE ANALYSIS OF VARIANCE

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The presence of metals in the environment is a widespread concern due to their potential health effects. Peptides proved to be very efficient in metal ions removal. This project aims to systematically study the effects of the types and positions of amino acid components within tri-peptides on the copper (II) ion binding process for the purpose of environmental remediation and in order to build up the optimum biosensor for copper detection.

Copper (II) complexes of tripeptide ligands containing glutamic acid (Glu, E), glycine (Gly, G) and histidine (His, H) were investigated using potentiometry and UV-Vis spectroscopy. Formation constants ($log\beta$) were calculated for each ligand's copper species from the titration curves, and the UV-Vis spectra were used to investigate copper binding modes, looking at the predominant species and the type and number of donor atoms involved in metal complexation. Generalized multiplicative analysis of variance (GEMANOVA) was used to model the multiway interactions between Cu^{2+} and the amino acid residue based on the ($log\beta$) values. The best model found comprised one multiplicative term describing the interactive influence of the first-, second - and third amino acids on ($log\beta$).

The copper coordination mode and the structure/colour of the predominant species were found to be related. Three major coordination modes were found for Cu^{2+} associated with three predominant ligand structures. With non-coordinating side chains {(CuH$_{-2}$L, 3N), purple} predominates; {(CuH$_{-1}$L, 3N), blue} predominates when histidine is at the second position and {(CuH$_{-2}$L, 4N), pink} predominates when histidine is at carboxy-terminal. The coexistence of histidine at second and carboxy-terminal positions allows two copper coordination modes to occur cooperatively producing two major species, (CuH$_{-1}$L,3N) at pH 5 then (CuH$_{-2}$L,4N) at basic pH. Glu and Gly were found to have no significant effect on Cu^{2+} coordination mode, but the presence of Glu increases the formation constant of Cu^{2+} complexes.

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~ F22 ~

SYNERGISTIC EFFECT OF FIELD ENHANCED SAMPLE INJECTION ON MICELLE TO SOLVENT STACKING IN CAPILLARY ELECTROPHORESIS

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Several stacking mechanisms have been used to overcome the poor concentration sensitivity in capillary electrophoresis techniques employing UV detection. The combining of stacking mechanisms, in particular, has been found interesting due to the additional gain in sensitivity.

In this study, the combination of field enhanced sample injection (FESI) and micelle to solvent stacking (MSS) (FESI-MSS) is presented. FESI or electrokinetic injection of sample prepared in a low conductivity matrix increased the amount of sample ions introduced into the capillary while analyte focusing was by MSS only. MSS was achieved by preparing the samples devoid of micelle but contained the organic solvent (acetonitrile). The organic solvent induced the effective electrophoretic mobility reversal, characteristic of MSS. A micellar plug (sodium dodecyl sulphate) injected prior to the sample acted as transient micellar phase concentrator of the analytes. The synergistic effect of FESI-MSS was applied to the analysis of cationic antipsychotic drugs.

The experimental conditions such as electrolyte concentration in the sample and injections of micellar and sample solutions were investigated. The strategy afforded thousands-fold improvements in peak height and LODs (S/N=3) of as low as 1.1 ng/mL. The results were repeatable and linear. Adaptability to real sample analysis was evaluated using spiked urine sample after a simple extraction procedure.

~ F23 ~

THE USE OF EIGEN SYSTEM PEAKS FOR IMPROVEMENT OF CHIRAL RESOLUTION IN SEPARATIONS WITH POROUS LAYER OPEN TUBULAR CAPILLARY COLUMNS

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In this study, various polymerization methods for the preparation of chiral molecular imprinted polymer porous layer open tubular (MIP-PLOT) capillaries were developed and compared, as well as their corresponding non imprinted polymer (NIP-PLOT) capillaries, for the use in capillary electrochromatography (CEC). As an exemplar, different Z-L-ASP-OH imprinted MIP-PLOT capillaries were prepared to separate Z-L-ASP-OH from its corresponding D-enantiomer. The morphology of the polymer layer on the inner capillary wall of the modified capillaries was characterized using scanning electron microscopy (SEM). One of the prepared capillaries gave poor separation resolution. A novel displacement mechanism using eigen system peaks was then developed in order to achieve the resolution of the Z-ASP-OH racemate under overloading conditions. In addition, this mechanism can even result in peak splitting of a single analyte separated using fused-silica capillaries. Ones should thus be more considerate with chiral separations in CEC mode.

~ F24 ~

MECHANICAL MIXING TECHNIQUES FOR CHEMILUMINESCENCE DETECTION

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Optimal detection of chemiluminescent reactions in flow injection systems relies on the optimised mixing of reagents and samples. In conventional flow injection analysis (FIA) systems, constant flow rates and suboptimal fluid dynamics limit homogeneous mixing and high reaction yields. As a result, reactions can occur past the detection zone, thus limiting sensitivity. The flow rates normally used in conventional FIA do not actively promote efficient or turbulent mixing due to the lower energy input of the laminar fluid flow. The high flow conditions required to create turbulent mixing in conventional systems impose limitations on residence time and volume. Alternatively, turbulence can be increased by external mechanical input. We have evaluated the efficiency of turbulent mixing in a series of mechanically agitated reaction/detection cells. Mixing efficiency was measured as a function of the chemiluminescent signal produced by the reaction between tris(2,2'-bipyridine)ruthenium(III) and proline in pH 9.0 buffer within mechanically agitated and non-mechanically agitated cells. The results showed a positive correlation between mechanical agitation and increased sensitivity. The lowest limits of detection (nM – μM) for mechanically agitated cells were on average ten times lower than those for non-agitated cells. Detection of the chemiluminescent signal was measured using a photomultiplier tube and the system was controlled by a virtual instrument designed using the software LabView.

~ F25 ~

TRANSPORTOF THIOCYANATE USING A POLYMER INCLUSION MEMBRANE BASED ON INTERPENETRATING POLYMER NETWORK OF PVDF-CO-HFP AND PEG-DMA

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There has been an increasing interest in polymer inclusion membranes (PIMs) as an alternative to liquid extraction. PIMs typically consist of an extractant immobilised in polymer chains. A plasticiser/modifier may be added to lower the glass transition temperature and/or to improve the solubility of the extractant in the polymer. Poly(vinylidene fluoride) (PVDF) is an attractive alternative to conventional base polymers such as poly(vinyl chloride) (PVC) and cellulose triacetate (CTA), because of its properties such as low glass transition temperature and high chemical resistance. Previously we showed that PIMs containing the commercial extractant Aliquat 336 and poly(vinylidene fluoride-co-hexafluoropropene)(PVDF-*co*-HFP) as the base polymer could be prepared by casting and these PIMs provided higher extraction rates than a PVC-based PIM.

One of the limitations of PVDF-*co*-HFP-based PIMs is the slow leaching of Aliquat 336 during their exposure to an aqueous phase which leads to a gradual decrease in their extraction capacity. To minimise this problem a crosslinking oligomer poly(ethyleneglycoldimethacrylate) (PEG-DMA) was introduced into the PVDF-*co*-HFP-based PIMs. PEG-DMA (21%) was successfully incorporated into a PIM with Aliquat 336 (30%) and PVDF-*co*-HFP (49 %) and UV-crosslinked to form an interpenetrating polymer network with PVDF-*co*-HFP. These membranes were studied for their ability to transport thiocyanate. The crosslinking was found to minimise membrane performance loss over repeated use. It was also found that the presence of PEG-DMA in the membrane significantly improved the transport rate of thiocyanate compared to a control without PEG-DMA.

~ F26 ~

STUDIES OF BRISBANE MUNICIPAL WATER QUALITY USING INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY AND CHEMOMETRICS

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Water is one of the most basic and essential constituents of the global environment [1] and is an especially precious commodity in Australia due to the extremes of drought and flood. Some elements appear naturally in the environment and are vital to human health; whereas other heavy metals are the result of urban run-off or atmospheric emission. Levels of potentially harmful heavy metals require regulation. However, limited study has been undertaken on heavy metal and trace element concentrations in potable water, especially locally. This research analyses various potable water samples from the greater Brisbane area through the combined use of ICP-MS and Chemometrics. This study focuses specifically on the elemental composition of water (including heavy metal content), an integral aspect of water quality. Points of investigation include water sources, source contaminants and the effect of changing climatic conditions on the water quality of these samples, namely potable water sources of tap, tank, filtered and desalinated water. General source contaminants to be considered are lithogenic and anthropogenic contaminants.

The hypothesis established is that a model or models using ICP-MS and Chemometrics will identify heavy metal content in potable Brisbane water for factors including water sources, source contaminants and changing climatic conditions.

The significance of this research is to determine whether all potable Brisbane water tested from the sources mentioned conform to the 2004 Australian Drinking Water Guidelines [2]. The contributors of source contamination will be identified and it will be determined if heavy metal content in these waters varies under changing climatic conditions. This research will provide a more comprehensive understanding of Brisbane water quality, as well as a Chemometric predictive model that can be used to better manage wider water issues regarding source identification and changing climatic conditions.

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~ F27 ~

EVALUATION OF SELECTED PLATINUM GROUP METAL COMPLEXES AS CHEMILUMINESCENCE REAGENTS

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This poster will encompass the chemiluminescence of selected platinum group metal complexes.

Firstly, an investigation into the chiral nature of tris(2,2'-bipyridyl)ruthenium(II) (Ru(bipy)$_3^{2+}$) will be described. The enantiomers of Ru(bipy)$_3^{2+}$ were isolated and characterised. The intriguing possibility of using these enantiomers as chirally selective reagents was then evaluated.

Secondly, the diverse spectral and electrochemical properties of iridium(III) and osmium(II) complexes have been exploited in the development of a dual emission system. Various combinations of iridium(III), osmium(II) and ruthenium(II) complexes were detected by electrochemiluminescence, and the emission of each complex successfully resolved. The control afforded by electrochemical oxidation allowed the selective oxidation of one of the chemiluminophores in the mixture; in this way, the colour of the emission could be either the unadulterated emission from one chemiluminophore, or a combination of the two.

Oral Abstracts

Wednesday 12th December

~ LLOYD SMYTHE MEDALLIST ~

MASS SPECTROMETRY IN THE AUSTRALIAN LANDSCAPE

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In association with gas and liquid chromatography, mass spectrometry has been essential to our understanding of the complex chemical ecology of the Australian bush and plantation forests. This includes the chemical defences of eucalypts against herbivory and fungal decay, and pheromones used for communication between individuals of the same species. Organic chemical classes encountered in this broad chemical ecology network include:

- relatively simple (but often novel) aliphatic compounds
- terpenes
- hydrolysable tannins
- condensed tannins
- flavonoids
- formylated phloroglucinol compounds (FPCs), which have strong antifeedant properties towards marsupials
- highly oxidized terpenes formed by metabolic processes in marsupials to detoxify their essential oil rich diet

Mass spectrometry has enabled the determination of the structures or partial structures of many new compounds in these classes, as well as being fundamental to the assignment of known compounds. Specific examples, all using negative ion electrospray MS and MS/MS, will relate to eucalypt phenolic chemistry. These include the discovery and assignment of new types of FPCs in eucalypt leaves and wood, the discovery of the mechanism of feeding deterrence to marsupial herbivores conferred by the presence of high levels of FPCs in eucalypt leaves, and detailed investigations into eucalypt tannin chemistry.

UNUSUAL PH DEPENDENT PHOTOPHYSICAL AND ELECTROCHEMICAL BEHAVIOUR OF 1,2,4-TRIAZOLE BASED IRIDIUM COMPLEXES

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Luminescent octahedral iridium complexes have a number of possible uses across a wide variety of applications. From cellular tagging to OLED design, the unique photophysical and electrochemical properties exhibited by these complexes make them a fascinating area of study. 1,2,4-triazoles also have a number of impressive features including high electron density, strong sigma donation and the ability to act as powerful oxidants; which makes them an interesting class of compound in their own right.

The concept of using triazole based iridium complexes was intended to help overcome some common limitations of using iridium complexes in electrochemical sensing applications such as electrochemiluminescence (ECL). Significantly, it has been found by many researchers that taking advantage of the amazing emission tunability of iridium complexes often results in a detrimental effect upon the electrochemical properties of the complexes. A decrease in the oxidative power of the complex or a significant loss of electrochemical reversibility are the most common issues faced when attempting to design an efficient blue shifted ECL luminophore.

Using 1,2,4-traizoles as a class of ancillary ligand has been quite successful in working around this issue, however, combining the somewhat unique features of these ligands with those exhibited by iridium complexes has also led to a number of unexpected and rather surprising properties in the resulting complexes. This has made the study of these complexes a far wider investigation than simply looking at ECL responsivities.

Some of these more unexpected features are presented with special focus on the somewhat unique ability to respond to differences in pH.

APPLICATION OF MULTI-DIMENSIONAL CHROMATOGRAPHY TO THE SEPARATION AND IDENTIFICATION OF THE COMPONENTS OF DISSOLVED ORGANIC MATTER (DOM)

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Dissolved organic matter (DOM) in sea and freshwater represents a carbon reservoir comparable to atmospheric CO_2 (respectively 624 and 750 Gigatonnes). CO_2 is a primary product of DOM mineralisation, therefore an intimate link exists between this dissolved pool of carbon and the atmosphere. However, the complexity of DOM inhibits conventional chromatographic analysis (LC and GC) with common detectors and little structural information can be obtained due to extensive co-elution. The chemical composition of DOM is in fact extremely complex, containing various classes of compounds. These are polyfunctional, heterogeneous (amino acids, organic acids, lipids, phosphonates, carboxyl-rich alicyclic molecules (CRAM) and carbohydrate like precursors), polyelectrolytic, polydisperse in molecular weight (typically between 300 and 7000 Da) and in concentrations ranging from picomolar to micromolar.

To achieve the separation and identification of DOM, two multi-dimensional approaches were used: size exclusion chromatography (SEC) and high performance counter current chromatography (HPCCC) as the first chromatographic dimensions and reversed-phase tandem mass spectrometry (RP-MS/MS) as the second. In SECxRP-MS/MS, an isolation and group classification of 150 to 250 compounds, according to the sample, was performed and critical DOM components separated. With the second multi-dimensional approach, HPCCC was used to isolate the main fractions from DOM according to their partition coefficient towards the binary solvent system. This technique proved to be an excellent new alternative approach to DOM fractionation, and is shown here for the first time. The off-line collection of the eluted compounds from this first chromatographic dimension was followed by further characterisation by RP-LC coupled with high resolution mass spectrometry.

For the first time materials derived from linear terpenoids (MDLT) and CRAM were isolated using SECxRP-MS/MS and identified from the DOM mixture. Furthermore, on other separated peaks, the mass patterns show the main molecular features of characteristic DOM constituents, demonstrating their alkylic, phenolic and benzoic nature.

GLUTATHIONE REDOX RATIOS: THE DETECTION OF COPPER INDUCED STRESS IN MARINE MICROALGAE

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Glutathione, a low-molecular-weight thiol found in most prokaryotic and eukaryotic, occurs in two forms, reduced glutathione (GSH) and an oxidised form known as glutathione disulfide (GSSG). Intracellular ratios of these two forms (GSH:GSSG) have been shown to be sensitive indicators of metal-induced stress in some freshwater and marine algal species, however the relationship between GSH:GSSG and the ability to tolerate copper exposure is not yet well understood. This study investigated the optimisation of a commercial GSH:GSSG detection method, an enzymatic recycling assay, for one green (*D. tertiolecta*) and two brown (*N. closterium* and *P. tricornutum*) marine microalgae, to identify changes associated with exposure to copper.

72-h growth inhibition bioassays were conducted at two copper exposures for each species, achieving inhibitory concentration (IC) values of: *P. tricornutum* IC60 and IC80; *N. closterium* IC55 and IC70; and *D. tertiolecta* IC25 and IC45. Although there was no correlation between TGSH and Cu-tolerance, each species exhibited an overall increase in response to copper exposure. GSSG concentrations also increased with copper exposure and, as such, GSH:GSSG ratios tended to decrease. The GSH:GSSG responses observed between the species, however, were dramatically different and, as such, there was no relationship between Cu-tolerance and changes in GSH:GSSG ratios.

The results of this study suggest that the differing ability of these three species to tolerate copper toxicity may be derived from distinct differences in the efficiency of their ascorbate-glutathione redox cycling, phytochelatin production and GSH biosynthesis mechanisms as a response to different rates of copper internalisation.

DETERMINATION OF SMALL BIOMOLECULES IN COMPLEX BIOLOGICAL MATRICES USING PERMANGANATE CHEMILUMINESCENCE

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This presentation describes the selective simultaneous determination of a number of low molecular weight biomolecules in complex biological sample matrices using acidic potassium permanganate chemiluminescence (CL) coupled to high performance liquid chromatography.

The selectivity and sensitivity of the potassium permanganate can be tuned by the addition of thiosulfate to the reagent for the analysis of key cannabinoids found in hemp. The developed method has been applied to the comparison of cannabinoid content between regions of the hemp plant[1] and coupled to two-dimensional high performance liquid chromatography to offer a high separation capacity for the characterisation of hemp samples. The limit of detection for cannabidiol was 1×10^{-6} M.

The simultaneous analysis of 5-hydroxytryptamine (5-HT) and selected catecholamine neurotransmitters in three regions of the rat brain, and their metabolites in urine, is also demonstrated using permanganate chemiluminescence detection. The detection was optimised in the presence of an enhancer merged with the analyte immediately prior to detection to gain the sensitivity required for the identification of the neurotransmitters in key regions of the brain. Limits of detection were in the range of 5×10^{-8} M to 5×10^{-7} M for 5-HT, nor-epinephrine, dopamine, epinephrine, 3,4-dihydroxyphenylacetic acid and homovanillic acid.

Acidic permanganate chemiluminescence detection provides an alternative, relatively inexpensive and simple system to overcome the limitations associated with common detection systems used for the analysis of low molecular weight biomolecules in biological samples. These include the lack of selectivity and sensitivity with UV absorbance detection, the time consuming sample derivatisation required for GC-MS and fluorescence detection, and interferences using electrochemical detection[2]. Acidic permanganate chemiluminescence also allows the use of ion pairing reagents without interference to improve the retention and separation of the relatively polar neurotransmitters under reverse phase conditions.

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2   Tsunoda, M., Recent advances in methods for the analysis of catecholamines and their metabolites. Anal. Bioanal. Chem. 2006, 386 (3), 506-514.

CHARACTERISATION OF ORGANIC POLLUTANTS IN CONTAMINATED SEDIMENTS OF A DYNAMIC ESTUARINE ENVIRONMENT: AN ASSESSMENT APPROACH APPLIED TO THE BRISBANE RIVER

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Organic pollutants such as Polycyclic Aromatic Hydrocarbons (PAH) have resulted from increased level of urbanisation and economic development and act as anthropogenic indicators in marine and aquatic ecosystems. They are a main focus of environmental studies due to their toxicity, persistence and bioaccumulative capabilities. The current assessment study examined the spatial distribution and characterisation of PAH in sediment deposits of the Brisbane River as a result of urban pollution. Sediment PAH profile were characterised to determine the sources of PAH within the lower catchment of the Brisbane River.

The concentrations of the Environmental Protection Agency's priority PAH congeners varied widely along the catchment area under study from residential and light commercial area to the heavily industrialised area. Highest concentrations were found along the creek inlets and most parts of the industrial zone of the catchment. Results from the diagnostic and thermodynamic isomeric ratios showed that the distribution of the higher molecular weight, (4-6 rings) PAH in each monitored station corresponded to mixture profiles typical of high temperature combustion processes and a predominantly pyrogenic source. Multivariate analysis will be used to compare the relative pollutant loads in sediment. The results of this study will aid in the evaluation of the effectiveness of plans undertaken for abatement of pollution in this area.

Au@Fe$_3$O$_4$ NANO-ELECTRODES: THEIR ELECTROANALYTICAL PERFORMANCE AS 'DISPERSIBLE ELECTRODES' AND THEIR USE AS SENSORS

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Au@Fe$_3$O$_4$ nano-electrodes, which we refer to as 'dispersible electrodes', involves using modified gold-coated magnetic nanoparticles as the active elements in scavenging and then detecting ultra-trace amounts of analytes in solution. The fact that the dispersible electrodes are magnetic provides a means by which the analyte can be captured and brought back to the sensing surface for detection. [1] In conventional electrochemical analysis with a single monolithic electrode the analyte takes a long time to reach the sensing surface resulting, in long response times for low concentrations of analyte. Nano-sized dispersible electrodes solve this problem as they are released in high number concentration in the test solution to capture the analytes of interest in a reasonable time frame and then brought to an electrode surface using a magnet. Previous research in our group has demonstrated that 50-180 nm peptide-modified gold coated magnetite nanoparticles with 3-mercaptopropionic acid as the thiol have been used for the capture and detection of Cu^{2+}.[2]

This current research focuses on analysis of other metals such as Pb^{2+} and Cd^{2+} as single analytes leading to the development of a multiple analyte sensor. Multiple-array sensors involve functionalizing the nano-sized dispersible electrodes with different analyte seeking molecules. We report the method of peptide modification of the dispersible electrodes using thioctic acid and detection of metal Pb^{2+} and Cd^{2+}. XPS results obtained showed successful attachment of the thiol by the emergence of peaks in the C 1s spectra. Peptide modification of angiotensin and hexapeptide was confirmed by emergence of peaks in the N 1s spectra. SWV results showed a reduction potential of Pb^{2+} and Cd^{2+} at -0.37 V and 0.40 V. Current studies involve use of a primary analytical method to detect the single analytes leading to multiple element analysis and detection of non electroactive analytes such as protein.

BETTER SNIFFING – A STORY OF HIGH-RESOLUTION WINE AROMA ANALYSIS

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Analysis of odour-active compounds in complex samples requires effective molecular separation from a multitude of other matrix components. Single dimensional gas chromatography-olfactometry (GC-O) - a common screening method - exhibits incomplete resolving capability.[1,2] integrated system having the combined capability to perform GC, comprehensive two-dimensional GC (GC×GC) and target heart-cut multidimensional GC (MDGC) using olfactometry (O), flame ionisation (FID) and/or mass spectrometry (MS) detection is described. This combines contemporary GC methods in a single instrument to provide very high resolution profiling. Initial assessment of volatile compound composition is achieved by GC×GC-FID analysis, correlated with GC-O. Subsequent microfluidic switching selects regions (heart-cuts) from the first dimension column for further resolution on a long secondary column for parallel detection using O and MS. Various operational conditions are compared; the favoured MDGC mode involves cryotrapping of heart-cuts, cooling the oven, reducing carrier flow then re-commencing the analysis. An analytical strategy incorporating the above analyses with cumulative solid phase microextraction sampling for volatile enrichment is presented. Excellent qualitative and quantitative performance was demonstrated for a Shiraz wine, with tentative identification of acetic acid, octen-3-ol, ethyl octanoate, β-damascenone, ethyl phenylpropanoate as aroma contributors. The integrated system allows direct comparison among multiple GC techniques, simplifying analytical implementation, and improving the method accuracy, for efficient identification of unknown odorants.

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CHANGES IN METAL BIOAVAILABILITY DURING DISCHARGE OF ACIDIC DRAINAGE WATERS IN THE RIVER MURRAY

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The Lower Murray Reclaimed Irrigation Area (LMRIA) represents approximately 5,200 hectares of flood irrigated agriculture protected by a levee bank system on the former floodplain of the River Murray in South Australia. During the drought of 2007 to 2009, an increase in the ingress of oxygen into soils resulted in the oxidation of previously waterlogged anaerobic acid sulfate soils. The persistence and severity of the acid drainage in the LMRIA creates a possible risk to water quality in the River Murray. To address these risks, research on acid and metal behaviour following dilution and neutralisation of the drainage water with river water and neutralising agents was performed.

Acidic drainage waters from the LMRIA had low pH, and Al, Co, Mn, Ni and Zn concentrations (major metals) were greatly higher than the water quality guidelines for 95% species protection, indicating very few aquatic organisms could live in the drainage waters. To assess the effect on water quality upon discharge of the drainage waters into the River Murray, dilution and neutralisation were performed and changes in pH and metal concentrations and speciation (labile and colloidal were measured over time. The metal concentrations and speciation changed rapidly when acidic drainage waters are diluted with River Murray water, with metal concentrations at some time points exceeding the water quality guidelines and were considered high risk. However, overall the results indicated that, for most LMRIA waters, dilutions to 10% should result in concentrations acceptable for 95% protecting aquatic life within the mixing zone, and toxicity bioassays using the water flea *Ceriodaphniadubia* indicated that dilutions to ≤20% should be acceptable for 95% protecting aquatic life. For high risk LMRIA waters, treatment or remediation may be necessary to reduce any immediate impact the samples may have on the environment when they are first returned to the River Murray.

Keywords: Murray River, drainage channels, discharges, metals, acid

TOWARDS AT SCENE FORENSIC STR ANALYSIS ON A MICROFLUIDIC PLATFORM

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DNA analysis based on polymerase chain reaction (PCR) amplification of short tandem repeats (STR) within the DNA sequence is a powerful forensic tool for the identification of individuals and wildlife. Currently performed using capillary electrophoresis, this technique is lab-based and not amenable to at scene analysis. Microfluidic devices have the potential to provide a portable platform for rapid DNA analysis. Several microfluidic systems have been developed for this purpose, however these are limited by poor resolution of DNA base pairs and their coupling to conventional large scale detection systems.

This presentation details our recent work into the development of a novel microfluidic STR analysis device with incorporated on-chip detection. Specific details and results relating to our system for the capture of forensically relevant STR's inside polymer microfluidic channels followed by their subsequent release will be presented. In conjunction we will also present results obtained from preliminary work into the development and optimisation of a novel capacitively coupled contactless conductivity detection (C_4D) system. This is aimed at use for the detection of the released STR's within the microfluidic platform resulting in an overall portable analysis system.

ISOTACHOPHORESIS OF CELLS

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The rapid and robust detection of pathogenic microorganisms is important for quality and safety control in food supply, medical industries and water treatment. These pathogens can cause severe diseases in society upon introduced internally via food or medical products at low concentration. The most common reference method for enumeration of bacteria is the plate count method using either specific or general agar for bacterial growth identification to detect culturable bacteria under specific conditions. While the advantage of plate count is the low detection limit, it suffers from long assay time. Hence, there is still a significant focus on developing and improving methods for detecting and quantifying bacterial cells. Capillary electrophoresis (CE) has been explored as an alternative method for separation and identification of microorganisms due to its robust nature include fast analyses, easily automated and low detection limit. The major problem of CE is to detect a single cell from a larger sample volume. By using laser induced fluorescence (LIF) it is possible to detect a single cells but the challenge is to inject a large sample volume instead of nanolitre into a capillary.

In this study, we explored the potential of ITP under FASI condition for concentration of cells using fluorescence detection. The cells are stained with SYTO 9 in a lower concentration of trailing electrolyte (TE) and using electrokinetic injection to inject and concentrate the cells into a single peak prior to LIF detection. With this approach, we were successful to detect 39 cells in 100 μL (398 cells/mL), with a detection limit of 14 cells per 100 μL (135 cells/mL). This result coincides with the river waters collected from local streams with conventional optical density and cells plating methods was obtained to validate this approach as a simple approach for quantitative.

THE DETERMINATION OF PHTHALATE MIGRATION IN FOOD CONTACT MATERIALS COMPARING GRAVIMETRIC AND GC-MS/MS TECHNIQUES

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Background: Phthalate migration into foods poses a health risk given that these compounds are present in most plastic materials. The main purpose of which is to act as plasticizers. Due to these health concerns, regulations have been put in place to restrict the content of phthalates within plastic materials.

Aim: The aim of this project is to develop a GC-MS/MS method in which comparisons can be made to the present method involving gravimetric techniques.

Implementation: Six regulated phthalates (Dibutylphthalate (DBP); Di(2-ethylhexyl)phthalate (DEHP); Di(noctyl)phthalate(DnOP); Dimethylphthalate(DMP); Benzylbutylphthalate(BBP); Diisononylphthalate (DINP)) shall be determined both qualitatively and quantitatively using GC-MS/MS methodology. This shall be implemented after a testing period according to EU Regulation in which simulations shall be utilized in lieu of food matrices. The various food contact materials (flat sheet plastics, biodegradables and recyclables) shall then be subject to a simulation period at pre-determined temperatures to reflect "worse case scenario" conditions. Overall migration levels of phthalates shall then be quantitated using gravimetry. Specific migration levels will then be attained using GC-MS/MS instrumentation. Comparison between the two techniques shall then be made and correlations determined. This shall have implications due to old and emerging EU Regulations regarding overall and specific migration levels of phthalates. Addressed shall be whether current plastics, biodegradables and recyclables meet the compliance demands of emerging, more stringent EU Regulations which focus upon specific migration limits.

Method optimisation led to a GC-MS/MS technique which enabled the determination of specific phthalate qualification and quantitation for the levels of migration which have occurred from food contact materials into food simulations over a simulation period.

Conclusion: A rapid and sensitive GC-MS/MS method shall be developed for identification and quantitation of phthalates. A comparison shall be made to current techniques involving gravimetry. This pertains to overall and specific migration limits and how these limits relate to emerging EU Regulations.

Oral Abstracts

Thursday 13th December

~ ROBERT CATTRALL EARLY CAREER MEDALLIST ~

ELECTROCHEMICAL BIOSENSORS

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The development of ultrasensitive electrochemical DNA/protein biosensors is of great interest. In order to achieve high sensitivity, a signal amplification step is usually required. Nanoparticle labels have been widely used for this purpose, since nanoparticles can be (1) used to increase the loading of an electroactive species, (2) employed as microelectrode arrays for the electrolysis of a large concentration of substrate or (3) applied as seeds to mediate the deposition of an electroactive species or electrocatalyst. A wide variety of DNA/protein biosensors have been successfully developed based on these principles and show some promising performance. However, these DNA/protein biosensors also suffer from some common drawbacks, such as (1) the complexity of the detection method, and (2) the lack of characteristic features in the signal that can be easily distinguished from the background. In this talk, I will present a simple signal amplification strategy that utilizes a highly characteristic solid-state Ag/AgCl process associated with Ag nanoparticle labels for the development of ultrasensitive DNA/protein. The key advantage of using this solid-state process, instead of the commonly used stripping process, is that the signal obtained is much sharper and hence can be easily distinguished from the background. This eliminates much of the uncertainty in differentiating the actual signal from the background. Theoretical assessments of binding and mass transport effects in this type of biosensors are presented to identify the current challenges of this field and to provide some guidance for the design of new biosensors. In this talk, I will also briefly present a new family of voltammetric ion selective electrodes which has been developed in collaboration with Prof Bob Cattrall to honour him for his contributions to this important field.

HIGH THROUGH-PUT AND HIGH SENSITIVITY LC-MS ANALYSIS OF AMINO ACIDS USING SEGMENTED FLOW CHROMATOGRAPHY COLUMNS

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There are generally three primary factors that determine the overall 'efficiency' of an analysis undertaken by HPLC. The first is sample through-put: The increasing demand for chemical characterization has meant that the modern laboratory is faced with greater time-management challenges. The second factor is sensitivity. Often more information is required from less, placing demand on the LOD and LOQ. The third factor is column performance. Resolution is related to the N, samples are often complex, and hence they require high column performance.

Perhaps the most widely used tool for chemical characterization is HPLC-MS. However, it is in this application of separation science where perhaps the greatest challenge exists in the optimization of these three factors. In HPLC-MS there is significant conflict between obtaining high-speed, high column performance and high sensitivity.

A serious limitation in HPLC-MS lies in the volumetric through-put of the detector. Hence, practitioners of HPLC-MS commonly employ columns with 2 or 1 mm internal i.d., but at the sacrifice of column performance and sample loading. Recently we reported a new design concept in HPLC columns, referred to as 'parallel segmented flow' whereby, special end-fittings separate the flow from the central region of the column from that at the wall. These columns yield higher N values, higher sample concentration for sample extracted from the central section of the column, and a reduced peak volume. A significant benefit therefore is that 4.6 mm i.d. parallel segmented flow columns can be utilized and operated at high flow rates: solute can be transported directly to the MS without the need for post column splitting.

In this study, we show how parallel segmented flow chromatography columns can be employed in the analysis of amino acid samples with improved performance compared to conventional columns.

EXPLORATION OF THE POTENTIAL ELECTROANALYTICAL APPLICATIONS OF NEAR-INFRARED EMITTING QUANTUM DOTS

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Quantum dots (QDs) are semiconductor nanocrsytals, sought after for their interesting properties: tuneable emission, broad absorption and good photostability. Nanoparticles, due to their size, have large surface areas, thus the interacting environment also influences their behaviour. Over the last decade the amount of research into quantum dots has steadily increased and with it their usefulness in sensors and other electronic and photonic devices. We set out to investigate near infrared red quantum dots using electrochemistry, to observe their energy states as well as their potential usefulness for electrochemilumescence and energy transfer based detection. A major hurdle of this is synthesising stable and highly fluorescent particles that do not aggregate in electrolytic solutions. $CuInS_2$ were initially chosen due to their simpler synthesis, low toxicity and prospective tunability in the near-infrared. Due to the ternary nature of these particles the emission was typically broader then binary QDs. Another disadvantage involved a substantial blue-shift of the emission when the $CuInS_2$ cores were coated with a ZnS shell. This may be due to the fact that zinc can migrate into the core and replace copper, resulting in a decrease of the core size and thus an increase in the QD's band-gap and decrease in emission wavelength. To overcome these problems PbS or InAs QDs are also considered.

ASSESSING THE PERFORMANCE OF DIFFUSIVE GRADIENTS IN THIN FILMS FOR PREDICTING TRACE METAL BIOAVAILABILITY IN ESTUARINE SEDIMENTS

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Evaluating contaminants bioavailability has become a well-established procedure included in most of environment quality assessment programs. Trace metal speciation in sediments is regulated by both biological and geochemical processes which determine whether metals are present in forms available for uptake by benthic organisms. The assessment of trace metal bioavailability usually relies on measurements of porewater concentrations, acid-extractable metals (AEM) and acid-volatile sulfides (AVS), which in some cases have provided a poor prediction of toxicity to organisms.

The technique known as *diffusive gradients in thin films* (DGT) employs a simple *in situ* device which contains a diffusive gel (polyacrylamide) overlapping a second gel embedded with a chelating resin (e.g. Chelex). Once deployed in the sediment, the DGT resin accumulates metals present in pore waters and labile-weakly bound metals released from the sediment. DGT provides a time-integrated metal flux measurement making it ideal for *in situ* testing. In this study, the toxicity of a range of naturally contaminated estuarine sediments collected from the Sydney harbour area was assessed by looking at both lethal and sublethal effects occurring to the amphipod *Melitaplumulosa* during a 10-day laboratory-based bioassay. Adverse effects (mainly due to Zn) observed on amphipod survival and reproduction were well predicted by DGT metal fluxes. These results indicate that the sediment labile fraction measured by DGT is representative of toxicity occurring to *M. plumulosa*, supporting the applicability of this technique as a rapid monitoring tool for sediments quality assessments.

HOW TO USE A MOBILE PHONE AS A POTENTIOSTAT

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Driven by the recent development of paper as an alternative material for microfluidics, there has been significant interest from researchers in producing low-cost sensors for applications in the developing world. Apart from using cheaper materials and fabrication techniques, another approach to keeping costs down, is to use an extant ubiquitous device such as a mobile phones as the detector. Most such work reported to date has focused on exploiting the built-in camera for colorimetric detection; while we recently reported paper microfluidic based electrogenerated chemiluminescence (ECL) detection using the camera as a luminescence detector. [1]

Detection with a mobile phone is attractive not only because of the reduction in cost, but also because of the opportunities for telemedicine it affords. Colorimetric detection with a cell phone however suffers from dependence on ambient light, which adversely affect reproducibility, especially for field use. ECL is advantageous over colorimetric detection because it is completely independent of ambient light. Other methods of detection include electrochemical, however electrochemical detection requires extra instrumentation. As we will show, not only can ECL be captured and analysed with a mobile phone, but the electrochemical excitation necessary to initiate the ECL emission can also be provided by such a device.

In this presentation we will illustrate an approach to sensing suitable for resource-limited environments based on ECL, paper microfluidics and a mobile phone. We will also demonstrate the process on which we initiate the ECL reaction using voltage applied by the mobile phone itself via the audio jack. With the use of this technique an ECL paper-based sensor has the potential to be a solution for diagnostics and other sensing applications in resource-limited environments.

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DIFFERENTIATION OF BINDERS IN ABORIGINAL AND EUROPEAN PAINTED WORKS USING PYROLYSIS GAS CHROMATOGRAPHY MASS SPECTROMETRY

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Binders are macromolecular organic compounds added to paints to adhere pigments together and to the support [1], with the materials used varying between cultures [2]. It is known that after European settlement in Australia, Indigenous Australians began using European-style binders rather those obtained from native flora and fauna, however when and how this transition occurred is unclear [3]. European binders have been extensively investigated, however very little chemical characterisation of Australian Aboriginal media has been conducted [4]. Such characterisation would identify whether binders from each culture could be distinguished from each other, which could provide a basis for conservation, restoration, authentication, and dating of indigenous artefacts, as well as provide insight into Australian history.

Pyrolysis Gas Chromatography Mass Spectrometry (Py-GCMS) has been commonly used to analyse binders due to the small sample sizes (0.5-100 mg) [5], minimal sample preparation, and ability to characterise a wide range of complex, non-volatile organic compounds that make it advantageous for use in analysing artefacts [6-8]. A heated platinum filament in the pyrolyser heats the sample to cause predictable fragmentation into smaller, volatile molecules [9, 10]. These pyrolysis products then enter the gas chromatograph (GC), in which their difference in adsorption to a polar stationary phase and a non-polar carrier gas is used to separate them by their polarity [11]. The products then enter the mass spectrometer (MS), where an electron beam causes fragmentation of the molecules. These fragments are then separated by their mass to charge ratios to produce a spectral pattern characteristic of each compound, allowing each separated pyrolysis product to be identified [12].

During this research a Py-GCMS method capable of distinguishing between binders from European and Aboriginal cultures has been developed, and a library of typical binders has been compiled for comparison to Indigenous objects for identification.

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HEAVY METALS IN THE SEDIMENTS OF DECEPTION BAY, QUEENSLAND AUSTRALIA

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Deception Bay in Queensland is one of four small bays encapsulated in Moreton Bay. The Caboolture River is a major source for sediments in Deception Bay and the Caboolture River extends from the D'Aguilar Range, through agricultural land and the urban centre of Caboolture, which has a growing population.

In addition to the environmental strain from the increased urbanisation of the Caboolture area, there is a significant industrial estate in the area, along with a sewage treatment plant and ship building businesses in the mouth of the Caboolture River, all of which contribute to the heavy metals loading of Deception Bay.

Sediment samples from the Caboolture River and Deception Bay were analysed for heavy metals content using X-ray Fluorescence and the enrichment factors and modified contamination indices were calculated, allowing qualification of the degree of pollution within the sediments at the sites. Chemometric analysis of the sediment samples was also conducted to identify heavy metal signatures for Deception Bay and the Caboolture River.

Oral Abstracts

Friday 14th December

CO-REACTANT ELECTROGENERATED CHEMILUMINESCECE (ECL) FROM CARBON DIOXIDE IN IONIC LIQUIDS

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Ionic liquids allow access to a variety of different electrochemical mechanisms that are not seen in traditional molecular solvents. When used as a thin layer on a screen printed electrode, ionic liquids allow rapid and responsive detection of carbon dioxide gas via electrogenerated chemiluminescence (ECL). While in traditional solvents, reduction of carbon dioxide typically produces oxalate, in ionic liquids, the carbon dioxide radical anion is sufficiently stabilised to allow it to partake in an ECL reaction with a species such as $Ru(bpy)_3^{3+}$.

SOIL PHOSPHORUS REQUIREMENTS OF DIFFERENT SOILS IN THE SUGARCANE BELT OF FIJI

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Phosphorus (P) is one of the most important nutrients required by plants for healthy growth. Knowledge about the available phosphorus in the soil is fundamental to determine the appropriate required amount of P fertilizers. It is possible to measure the bioavailable forms in the soil and adding fertilizer to attain the level of phosphorus required by the crop; however, phosphorus is easily fixed by the soil. Many factors contribute to P sorptivity of soils therefore; these factors need to be considered in proper estimation of P requirements. The main objective of this research was to ascertain the amount of bioavailable phosphorus in the soils which will be useful in determining the required amount of inorganic fertilizer to be applied to the soil.

In this study, twelve different soils were selected from the sugarcane belt of Fiji on which phosphorus buffer index and phosphorus isotherm experiments were performed. The PBI analysis was carried out using Australasian Soil and Plant Analysis Council method 912- extractions with Murphy and Riley analytical finish. Other basic soil tests were performed for each soil type and Pearson's correlation tests were performed to identify patterns.

It was found that Oxisols had the highest PBI values of 217 mg P/kg while Inceptisols had the lowest at 33 mg P/kg. The use of PBI as an indicator of the phosphorus status of the sugarcane soils in Fiji will reduce the risk of over-fertilization and the loss of phosphorus to waterways, hence protecting the environment. Soils with low PBI have greater potential for P leaching through runoff into waterways. Further research is still required to develop proper fertilizer recommendations based on soil types and also considering other factors affecting P availability.

Keywords: Phosphorus, PBI, sugarcane, fertilizer recommendation, runoff, soil types

DEVELOPING A RAPID LIQUID CHROMATOGRAPHY TANDEM MASS SPECTROMETRY (LC-MS/MS) METHOD FOR THE ANALYSIS OF PARALYTIC SHELLFISH TOXINS (PST)

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Background: Seasonally occurring harmful algal blooms contain dinoflagellates which produce endogenous toxins capable of causing paralysis. These paralytic shellfish toxins are accumulated by filter feeding shellfish such as mussels, oyster, and clams. The current method for testing is the mouse bioassay developed in 1959. There is a strong impetus to move away from this method to instrumental methods due to the animal welfare issues. A need for a rapid and sensitive chromatographic method was identified.

Aim: The aim of this project was to develop a rapid and sensitive method for the detection of hydrophilic shellfish toxins.

Implementation: Purified paralytic shellfish toxin standards were purchased from the National Research Council Canada and multiple reaction monitoring (MRM) transitions were obtained individually for the following PSTs: Saxitoxin, decarbamoylsatxitoxin, neosaxitoxin, decarbamoylneosaxitoxin, gonyautoxins 1, 2, 3, & 4, decarbamoylgonyautoxins 2 & 3, and N-sulfocarbamoyl-gonyautoxin-2 & 3. A toxin mix was prepared and separated using a Tosoh Biosciences TSKgel Amide-80 column (150 × 4.6 mm, 3 μm) and an Agilent Technologies 1260 LC system with a 6460 QqQ. Instrument settings were also optimised to maximise sensitivity. Oyster and mussel tissue was obtained from the local market and spiked with toxin standards. Samples were extracted with 0.1% acetic acid and cooked, followed by centrifuging and filtering. The filtered extracts were cleaned up using a C18 solid phase extraction (SPE) cartridge

Method optimisation led to a method which is capable of quantitatively detecting 8 hydrophilic shellfish toxins within 6 minutes. SPE cleanup reduced matrix interferences but affected retention times and recoveries of some toxins.

Conclusion: A rapid and sensitive LC-MS/MS method was developed for identification and quantitation of paralytic shellfish toxins. Matrix interference is an issue which needs to be resolved by investigating cleanup techniques.

~ RACI Environmental Chemistry Medallist ~

CONSISTENT CHANGES IN MOLECULAR FOSSILS (MICROBES, FLORA, EXTREMOPHILES) AND STABLE ISOTOPES ACROSS SEVERAL OF MAJOR EXTINCTION EVENTS OF OUR PLANET:

A FIGHT FOR SURVIVAL AND RESURGENCE OF LIFE

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The interaction of biological & geological processes has created the Earth & driven the evolution of its biodiversity from Early life. Organisms have continually adapted to changing environments, the evolution of individual species has consequently impacted the chemical & physical properties of Earth. Life's signatures that reveal the evolution of biological forms & their geological consequences are not only restricted to visible remnants (e.g. fossils), but also can encompass molecular fossils (biomarkers), isotopic signals & mineral associated fabrics. Organisms often alter their chemical environment, contributing to the assemblage &/or destruction of minerals, rocks & petroleum in reservoirs &/ our modern environment. Biomarker geochemists have largely focused their interest on organic-matter rich sediments (e.g. shales, deltaic & lake deposits), petroleum & their potential source-rocks. The analyses of biomarkers & their role in the construction of calcified mounds, cherts & clayey horizons have been limited. The significance of these matrices & the development of novel records of environmental change across the largest extinction events in Earth's history will be summarised. In particular the isotopic excursions associated with such events will be presented at a molecular level. The changes in isotopic signals appear to be consistently similar for several events associated with the collapse/ recycling of organic matter from marine & terrestrial ecosystems.

SEPARATION AND CHARACTERISATION OF HUMAN IMMUNOGLOBULIN G VARIANTS UTILISING A POLY(ETHYLENE GLYCOL)-BASED MONOLITHIC COLUMN

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The separation, characterisation and purification of monoclonal antibodies is a fast growing and important area in the use of biopharmaceuticals. Hydrophobic interaction chromatography (HIC) is a common technique utilised in these purification schemes owing to its soft interactions. Human Immunoglobulin G (IgG) consists of four subclasses, IgG1, IgG2, IgG3 and IgG4, and within these subclasses there exist λ and κ variants, signifying differences in the light chain of these proteins. Purification of these subclasses is often done using protein A based affinity chromatography, however this technique is expensive, prone to leakage of the sorbent and under elution the formation of aggregates is sometimes observed. In terms of separation of these proteins and their variants, this is known to be challenging and currently more sophisticated techniques are often employed in the literature, which are also expensive and require complex and/or time consuming sample preparation, which is not practical for a manufacturing plant. The use of monolithic columns is an attractive alternative to many other chromatographic formats, owing to their robustness, high permeability, fast mass transfer kinetics, as well as ease and affordability of synthesis. These properties make the use of monolithic columns in this field a particularly attractive alternative to these other methods.

In this work we explored the potential of a monolithic column prepared from poly(ethylene glycol) diacrylate, as the sole monomer, by thermal polymerisation, for the separation and characterisation of some IgG variants under HIC conditions. The ability and robust nature of this monolith was demonstrated in both a rapid separation, allowing relatively fast separations of some of these antibodies, but also high resolution separations that could potentially differentiate some IgG variants further. Differences in separation selectivity were achieved by varying the salt gradient employed to establish optimum conditions. Using this approach separations were achieved that were superior to previous work in terms of both separation time and resolution.

FLOW ANALYSIS OF ORTHOPHOSPHATE USING POLYMER INCLUSION MEMBRANES FOR ON-LINE SEPARATION AND PRECONCENTRATION

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Sensitive flow-injection analysis (FIA) and continuous flow (CF) systems for the determination of phosphate at trace levels in water have been developed, based on the well-known molybdenum blue reaction. A polymer inclusion membrane (PIM) was utilised for on-line phosphate separation and preconcentration. This is the first application of PIMs for on-line preconcentration in flow analysis. Under optimal conditions, the FIA system was characterised by linear ranges between 0-10 and 10-1000 $\mu g\ L^{-1}$P(V), sampling frequency of 10 h^{-1}, a limit of detection 0.5 $\mu g\ L^{-1}$, and RSD of 1.2%. The CF allowed further improvement in sensitivity (e.g. 0.03 $\mu g\ L^{-1}$ at 3 h^{-1} sampling rate).

Interference studies were conducted with several anions commonly found in water samples. Furthermore, the phosphate transport behaviour of the PIMs was studied via several FIA configurations, showing that the membrane required a degree of pre-conditioning with phosphate before efficient transport could be achieved. The system was successfully applied to the analysis of natural samples containing low $\mu g\ L^{-1}$P(V), with the use of the multipoint standard addition method.

NANOPARTICLE-MEDIATED ELECTROCHEMICAL GATING: APPLICATION TO ELECTROANALYSIS

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It has been shown many times that long chain amino-alkanethiols form a self-assembled monolayer (SAM) on a gold surface, and are able to passivate this surface such that no electrochemistry can be performed. By then attaching gold nanoparticles to the surface of the SAM we achieve a return of the electrochemical signal.[1]

Another concept our group has demonstrated is the use of gold-coated magnetic nanoparticles as dispersible electrodes for detecting extremely low concentrations of analyte within a solution with a reasonable response time. By using a magnetic field to control the location of nanoparticles we are able to direct them within a solution as we desire. Thus we can use these modified gold nanoparticles to isolate specific analytes within a solution using these nanoparticles as nanoelectrode arrays.

With a typical electrode the response time depends on the diffusion of the analyte to the electrode. By dispersing modified gold-coated magnetic nanoparticles within the solution to capture the analyte, and then exposing the particles to a magnetic field to bring the nanoparticles back to a macroelectrode for electrochemical detection, the response time is no longer limited by the rate of diffusion to the surface of the electrode and quantitative isolation of 100% of an analyte can be achieved.[2-4]

By combining the above concepts we will herein describe the use of 'electrochemical gating' for electroanalytical purposes. Magnetic particles will be dispersed to actively seek out the analyte. A magnetic field will be used to control the location of the particles, and therefore switch on or off the electrochemistry at a passivated electrode surface. This passivating monolayer will prevent interference from the matrix, allowing ultra-sensitive, highly selective detection, on demand.

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ANALYSIS OF ANTARCTIC PETROLEUM SPILL SITES BY RESISTIVELY HEATED GAS CHROMATOGRAPHY

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Petroleum spills are some of the most pervasive and persistent causes of pollution in the Antarctic and sub-Antarctic regions. The consequences of such environmental contamination are far reaching in that petroleum spills are notably resistant towards natural degradation, while still being potent toxicants towards the flora and fauna of these ecosystems. As a result it is essential to instigate active environmental remediation for areas that have been exposed to petroleum spills as well as monitor the progress of such remediation.

Commonly gas chromatography (GC) has been employed in order to analyse the volatile and semi-volatile components of petroleum products. Unfortunately the application of GC towards fuel spills is complicated by the petroleum attenuation process, which is utilised to clean up such spills. Often chromatograms reveal an unresolved complex mixture despite GC separation, due to the degradation of petroleum in the sample. As such the characterization and quantification of petroleum spills necessitates the application more effective separations or data deconvolution following analysis.

A front-end solution to improving the separation of such complex mixtures is provided by two dimensional comprehensive gas chromatography (GC×GC). GC×GC offers increased peak capacities, and provides the opportunity for group based separations to characterize different compound classes. An alternative to improving the separation is to utilize a detector which is able to better discriminate and deconvolve co-eluting analytes within a single chromatographic peak such as a time of flight mass spectrometer (TOF-MS).

Normally such GC×GC analyses and TOF-MS analyses are restricted to large immobile instrumentation. In this work the portability of such instrumentation is explored by the utilization of a transportable resistively heated GC. Resistive heating represents a paradigm shift in GC analysis, and offers the advantages of low power consumption, rapid and reproducible temperature programmability as well as minimizing instrumental size to facilitate fast and effective GC analysis in the field, thus making it particularly amenable towards analysis of fuel spill sites.

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AEROSOL MASS SPECTROMETRIC ANALYSIS OF ORGANIC AEROSOL IN BRISBANE SCHOOLS

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Aerosol mass spectrometry is a technique that can determine the size resolved chemical composition of non refractory airborne particulate matter with a diameter that is less than 1 micron (NR-PM$_1$). The ambient concentration of organic aerosols (OA) in an urban environment is highly dynamic and the use of an aerosol mass spectrometer can achieve the necessary temporal resolution to capture the hourly variation in OA concentration. In an urban environment a major source of OA are vehicle emissions. Currently there is a limited understanding of effects of long term exposure to traffic emissions on children's health. In the present study, we used an aerosol mass spectrometer at five schools within Brisbane to monitor OA and determine children's potential exposure to traffic emissions in school environment. The study is a part of a larger project aimed at gaining a holistic picture of the exposure of children to traffic related pollutants, known as UPTECH (www.ilaqh.qut.edu.au/Misc/ UPTECH%20Home.htm).

At each school the NR-PM$_1$ was found to have a different overall chemical composition and in particular the OA was found to have distinct characteristics. Thus, the source and age of the OA was determined from the level of oxidation of OA. Primary emissions of OA were not found to be a main source, rather OA that has been oxidised by secondary processes to varying degrees were implicated as significant sources. Analysis of the diurnal cycle of OA components found that the concentration of OA was at a minimum during school hours, with secondary OA the main component that school children were exposed to. The school that was near the busiest road was found to have the highest levels of hydrocarbon like organic aerosols (HOA), which can be considered a surrogate for vehicle emissions. The maximum exposure for children to vehicle emissions at each school occurred during drop-off times, with the concentration decreasing to a minimum in the afternoon.

CHIRAL GOLD NANOPARTICLES FOR METAL ION DETECTION

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The metal ions mediated nano-assembly reveals a new direction to detect and determine the concentration of metal ions. Here we report use of core-satellite structured chiral gold nanoparticle linked by L-Cysteine to determine the concentration of Cu^{2+}. The plasmonic properties of core-satellite nanoassemblies were studied. Our results demonstrated a new red shifted absorbance peak from about 600 to 800nm depending on ratios with assembly of large and small GNPs. In addition, a linear relationship between concentration of Cu^{2+} and UV-Vis absorbance was found which may lead to applications of metal ions detection.
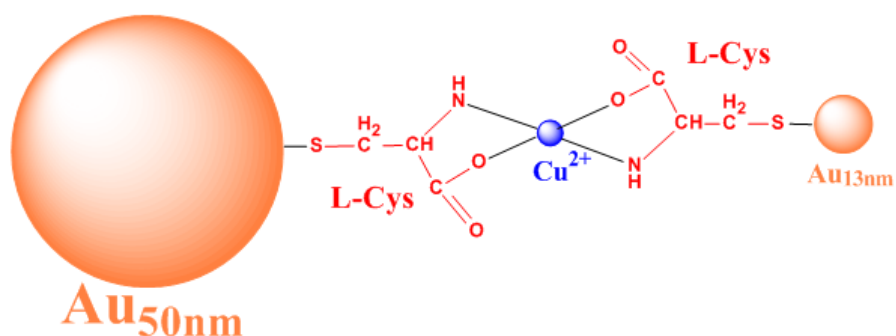
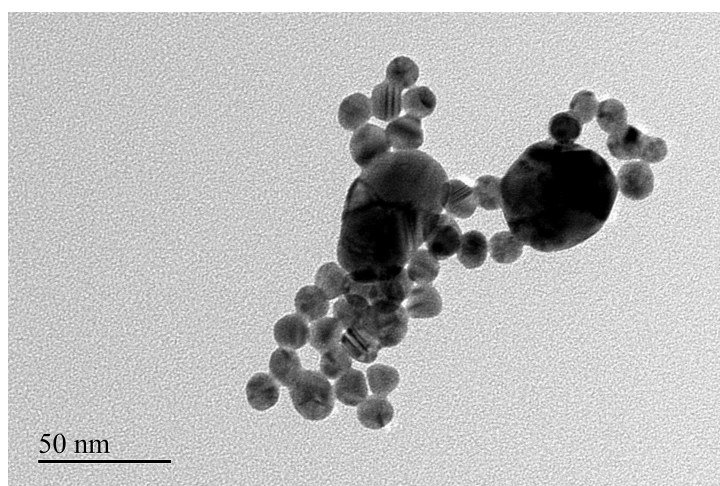Fig 1a Illustration of Cu^{2+} mediated chiral GNP self-assembly which modified by coated with L-Cysteine

Fig 1b TEM image of Cu^{2+} meadiated core-satellite nanoassembly of GNP_{13nm} and GNP_{50nm} linked by L-Cysteine

SWITCHING ON THE LIGHTS IN DIATOM CELL WALLS: USING PDMPO TO INVESTIGATE SILICON UPTAKE IN DIATOMS

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Diatoms are the oceans dominant siliceous organisms and are significant exporters of organic carbon to the deep ocean. They have a unique ability to utilise dissolved silicon (DSi) in the formation of their cell walls (frustules) and consequently, play a central role in the marine biogeochemical cycling of silicon and carbon. Iron is essential to the metabolism and growth of diatoms and often limits diatom production in parts of the ocean where iron supply is low, particularly in high nutrient-low chlorophyll (HNLC) regions such as the Southern Ocean. The kinetics of silicon uptake by diatoms is already well constrained by several studies, however little is known on the extent by which iron influences silicon uptake/depostion and frustule morphology. We investigate the effects of iron limitation on the coastal diatom *Thalassiosirapseudonana* using the fluorescent tracer, PDMPO [2-(4-pyridyl)-5{[4-dimethylaminoethylamino-carbamoyl)-methoxy]phenyl}oxazole]. PDMPO selectively binds to polymerizing silica and emits an intense fluorescence under UV excitation where newly formed biogenic silica has been deposited. Using this technique, we can delineate the new formation of biogenic silica, and monitor the formation of diatom frustules. It is hoped that results from this work will provide a better understanding of silicon uptake in diatoms, and subsequently allow researchers to better determine the level of silicon utilization by diatoms in the Southern Ocean.

HIGH SPEED SCREENING OF NATURAL PRODUCTS USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY WITH MULTIPLEXED DETECTION

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Natural products, such as plant extracts, contain a vast variety of different compounds with different properties. This significantly complicates the analysis of natural products using high performance liquid chromatography as there is no single detector capable of detecting all compounds. It follows that multiple detection methods are used to screen natural products post HPLC analysis. Multi-detection with HPLC can be accomplished using one of two formats: either the detectors can be arranged in series, or the flow post-column can be split to allow simultaneous multi-detection. However, there are drawbacks to both multi-detection formats. Both formats suffer from band broadening, which reduces chromatographic resolution. In addition to band broadening, post-column stream splitting suffers from a loss of sensitivity. Analysis with HPLC using one detector can reduce band broadening, however the cost is either a reduction in information with regards to the sample composition or multiple analyses using different detectors; one detector per analysis. Multiple analyses are not a favourable as it requires more time and sample to be used.

We introduce a new format of multi-detection, known as multiplexed detection, which has the benefits of conventional detection without the additional band broadening. Multiplexed detection is performed using Parallel Segmented Flow chromatography columns. These columns have multiple ports in the column end fitting which can be connected to various detectors to allow simultaneous multi-detection. In this study, we utilised multiplexed detection to screen wine, green tea and espresso coffee for antioxidants using the 2,2-diphenyl-1-picrylhydrazyl radical assay, fluorescence and UV spectrometry. Chromatographic resolution and peak shape was comparable to single detector-HPLC, however, the time taken for analysis with multiplexed detection was reduced by a factor of 4 as multiple detectors were used simultaneously.

A RATIONAL APPROACH TO QUANTITATIVE PREPARATIVE GAS CHROMATOGRAPHY WITH NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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Caffeine as a test solute was employed in combination with an internal standard (IS), 1,4-dimethoxybenzene in an on-line preparative-gas chromatography (prep-GC) and off-line nuclear magnetic resonance (NMR) experiment. The use of an IS served several purposes: (i) to quantify the trapping efficiency of an external tapping assembly (xTA), which consists of cryotrap and capillary column at the end of the column; (ii) when added to the sample for NMR analysis, it allowed quantification of the solute in the different NMR samples; and (iii) it permitted correlation of the expected level of response of a compound in the NMR experiment, based on the relative responses of the IS and the solute in the GC result. In order to accumulate sufficient analyte for NMR analysis, repeat injections/collections were conducted. The caffeine recovery rate from the sample (1x, 2x, 5x and 10x injections) was 69.6 ± 1.3%, which correlated well (R = 0.999) with the number of collections and the quantity of target compound trapped. Recovery can be estimated from either GC-MS or NMR on the final eluate. This was deemed satisfactory trapping efficiency for the xTA. A ^{1}H NMR spectrum contained sufficient detail to enable structural characterisation of the reference compound (i.e. caffeine) was achieved with recovery of small amounts (≤ 10 µg) from a single aliquot. About 400 µg of caffeine, achieved by injecting 40 aliquots of the compound, provided structural characterisation by ^{13}C NMR spectral analysis. On the basis of this result, it is possible to estimate the total amount of solute that should be collected for target analytes, using high resolution separation, taking into account relative sensitivities expected for the NMR structural interpretation.

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