

28th Annual RACI R&D Topics 2022

Analytical and Environmental Chemistry Student conference



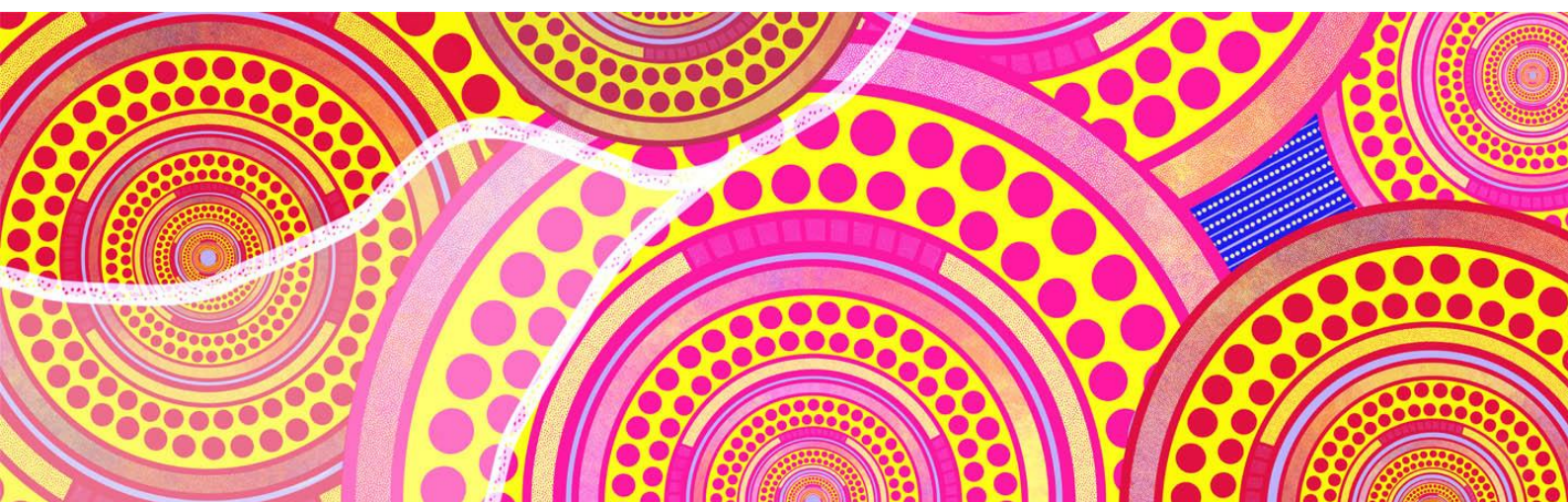
4th - 7th December 2022

RMIT University, Melbourne, Australia.

#RnDTopics2022

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“We would like to acknowledge Wurundjeri people of the Kulin Nations as the Traditional Owners of the land on which the University stands. We respectfully recognise Elders past, present and future.”



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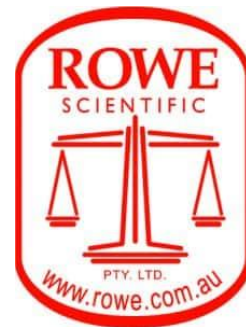


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STUDENT AWARDS

Enabling Capability Platform

RMIT University

4 December 2022

Time	Program Outline
4.00 – 6.00 PM	Registration and Pre-mixer at the Garden Building Terrace

5 December 2022

Time	Program Outline
8.00 – 9.00 AM	Registration Open
9.00 – 9.15 AM	Welcome and Conference Opening Prof Charles Brennan - Dean of School of Science RMIT University
9.15 – 9.25 AM	Message from Prof Bronwyn Fox Chief Scientist – CSIRO Australia
9.25 – 10.10 AM	Plenary Talk Prof Oliver Jones – RMIT University 'Environmental Chemistry' Medallist RACI Analytical and Environmental Chemistry Division
10.10 – 10.45 AM	Morning Tea
	Trade Display
10.45 – 12.05 PM	Oral Presentation Session 1
12.05 – 1.00 PM	Lunch
	Trade Display
1.00 – 2.20 PM	Oral Presentation Session 2
2.20 – 2.30 PM	Break
2.30 – 3.30 PM	Oral Presentation Session 3
3.30 – 4.45 PM	Poster Presentation Session Day 1
	Afternoon Tea
	Trade Display
5.00 – 6.30 PM	Student Networking Session at the Garden Building

6 December 2022

Time	Program Outline
8.30 – 9.00 AM	Registration
9.00 – 9.45 AM	Plenary Talk Prof Conor Hogan – La Trobe University 'Graeme Batley' Medallist RACI Analytical and Environmental Chemistry Division
9.45 – 10.45 AM	Oral Presentation Session 4
10.45 – 11.15 AM	Morning Tea
	Trade Display
11.15 – 12.45 PM	Oral Presentation Session 5
12.45 – 1.45 PM	Lunch
	Trade Display
1.45 – 2.45 PM	Oral Presentation Session 6
2.45 – 3.15 PM	Mr Dinesh Kumar Market Manager – Anton Paar Australia
3.15 – 4.45 PM	Poster Presentation Session Day 2
	Afternoon Tea
	Trade Display

7 December 2022

Time	Program Outline
8.30 – 9.00 AM	Registration
9.00 – 9.45 AM	Plenary Talk Prof Xavier Mullet Enabling Capability Platform Director- RMIT University
9.45 – 10.45 AM	Oral Presentation Session 7
10.45 – 11.15 PM	Morning Tea
	Trade Display
11.15 – 12.45 PM	Oral Presentation Session 8
12.45 – 1.45 PM	Lunch
	Trade Display
1.45 – 2.45 PM	Oral Presentation Session 9
2.45 – 3.15 PM	Afternoon Tea
	Trade Display
3.15 – 3.45 PM	Awarding Ceremony
3.45 – 4.00 PM	Thank You Speech
4.00 – 4.30 PM	RACI Analytical and Environmental Chemistry Division AGM
6.00 – 10.00 PM	Conference Dinner at The Oxford Scholar Hotel

Oral Presentations

Session 1	5 December 2022
	Chair Daksh Shah, RMIT University
10.45– 11.05 AM	Samridhi Bajaj, La Trobe University. New sensing concepts based on bipolar annihilation electrochemiluminescence.
11.05 – 11.25 AM	Ashakiran Maibam, RMIT University. Sustainable ammonia production on single site catalyst anchored 2D materials.
11.25 – 11.45 AM	Steven J. Blom, Deakin University. Cathodic Co-reactant Electrochemiluminescence of Water-soluble Heteroleptic Iridium(III) Complexes Containing N methyl(pyridyl)pyridinium Cyclometalating Ligands.
11.45 – 12.05 PM	Raymond Fernando Yu, University of Tasmania. Pseudophase microextraction: a novel sample concentration method in capillary electrophoresis.
Session 2	5 December 2022
	Chair Jolene Anthony, Flinders University
1.00 – 1.20 AM	Neil Byrnes, Monash University. The Puzzling Presentation of Pyrethrins: Exploring Isomerization in Comprehensive Two-Dimensional Gas Chromatography.
1.20 – 1.40 AM	Kaiwen Zhang, RMIT University. Temporal analysis of human mesenchymal stem cells under electrical stimulation with AFM.
1.40 – 2.00 PM	Lisa E. Hua, University of New South Wales. Metal organic frameworks for improving the analysis of perfluoroalkyl substances from water.

2.00 – 2.20 PM	Navneet Singh, RMIT University. Understanding the Fate and Behaviour of PFAS in Port Philip Bay.
Session 3	5 December 2022
	Chair Wan Sin Heng, Deakin University
2.30 – 2.45 PM	Monalisha Ghosh Dastidar, The Australian National University. Highly tuneable and ultrasensitive platform for diabetes management.
2.45 – 3.05 PM	Oshadie De Silva, RMIT University. The synergistic and antagonistic roles of CoOOH phase in β -Co(OH) ₂ electrocatalyst for driving oxygen evolution reaction.
3.05 – 3.25 PM	Helmini Jayarathne, La Trobe University. Unexpected dependence on choice of electrochemical technique of reproducibility with screen-printed carbon electrodes.
Session 4	6 December 2022
	Chair Steven Blom, Deakin University
9.45 – 10.05 AM	Wan Sin Heng, Deakin University. Rapid detection of bacteria in milk using static headspace-comprehensive two-dimensional gas chromatography.
10.05 – 10.25 AM	Michelle S.S. Amaral, Monash University. Application of biotechnology to aroma sustainable synthesis: taking nature's perfection to another level.
10.25 – 10.45 AM	Adam Kolobaric, RMIT University. Remote sensing of marine plastics and their chemical additives using Near-Infrared (NIR) and Hyperspectral imaging and applied chemometrics.

Session 5	6 December 2022
	Chair Monalisha Dastidar, The Australian National University
11.15 – 11.35 AM	Alishba T. John, The Australian National University. Tuneable Metal Organic Framework Encapsulated Metal Oxide Network for Enhanced Chemiresistive Sensing.
11.35 – 11.55 AM	Piyumi D. Liyanage, RMIT University. Understanding the transient interactions between nanozymes and aptamers in nano-aptasensors.
11.55 – 12.15 PM	Ivan Lozada Lawag, University of Western Australia. Antioxidant Activity and Phenolic Compound Determination and Quantification in Western Australian Honeys.
12.15 – 12.35 PM	Tharani T. Dissanayake, Deakin University. Investigating Derivatisation Methods in Fatty Acid Profiling.
Session 6	6 December 2022
	Chair Adam Kolobaric, RMIT University
1.45 – 2.05 PM	David Tambaru, The University of Melbourne. Development of a sequential injection analysis method for the automatic speciation of selenium.
2.05 – 2.25 PM	Sunil Luhar, RMIT University. Waste to wealth- Fabrication of Low-Cost Working Electrode from waste (Thermocol) for electrochemical Applications.
2.25 -2.45 PM	Abdullah OS Bawazeer, RMIT University. Characterise the contribution of nanoparticles to Multidrug-Resistant Organisms (MDROs) by comparing the Examine responses of disrupting the membrane of (Gram-negative and positive bacteria).

Session 7	7 December 2022
	Chair Ashakiran Maibam, RMIT University
9.45 – 10.05 AM	Gayatri Bagree, RMIT University. Aptasensors for the detection of neuro-pathological protein conformers.
10.05 – 10.25 AM	Muhandiramge Ranasinghe, University of Tasmania. Micellar Chromatographic Methods for Ethyl Carbamate Determination in Alcoholic Beverages.
10.25 – 10.45 AM	David S. Macedo, CSIRO/La Trobe University. Improved measurement of return peak current in cyclic voltammetry using diffusional fitting.
Session 8	7 December 2022
	Chair Oshadie De Silva, RMIT University
11.15 – 11.35 AM	James N. Smith, The University of Melbourne. Polymer inclusion membranes as green alternatives to solvent extraction for lithium separation.
11.35 – 11.55 AM	Ian A. Wittman, Monash University. Boiling down the finer points of separation in gas chromatography.
11.55 – 12.15 PM	Ruvini Jayawardena, Swinburne University of Technology. High methylene blue adsorption capacity of graphene oxide-biopolymer foams.
12.15 – 12.35 PM	Sanjana Naveen Prasad, RMIT University. Single-step colorimetric detection of acid phosphatase in human urine using an oxidase-mimic platinum nanozyme.

Session 9	7 December 2022
	Chair Daksh Shah, RMIT University
1.45 – 2.05 PM	Charles F. Croft, The University of Melbourne. Detection of lanthanum using Arsenazo III-based polymer inclusion membranes.
2.05 – 2.25 PM	Glaucimar A.P. Resende, Monash University. Effect of Se, Mo and Cr on the physical-chemical profile of beers.
2.25 – 2.45 PM	Piumie Rajapaksha, RMIT University. Polyvinyl alcohol-graphene oxide membranes for removing microbial and chemical contaminants from wastewater.

Poster Presentations

01	Batool A.M. Aljubran, Flinders University. Influence of titanium dioxide pigment on the photodegradation of tattoo pigments.
02	Mihiravi P Wickrama Arachchige, Deakin University. Isolation and analysis of bioactive lipids from commercially valuable seafood.
03	Ashis Chhetri, RMIT University. Programmable Melamine-based Organic Materials as Efficient Electrocatalysts for Water Oxidation.
04	Satnam Kaur, RMIT University. Superparamagnetic iron oxide nanoparticles for Magnetic particle imaging.
05	Sanje Mahasivam, RMIT University. Spatial controlled chemical reaction in plasmonic nanoparticle using external stimuli.
06	Natasha Adamson, Deakin University. Enhancing the Electrochemiluminescence of Tris(2,2'-bipyridine)ruthenium(II) and Tri n propylamine.
07	Benjamin Boyle, Flinders University. Phthalocyanine tattoo pigments: The effect of ageing and laser removal.
08	Felicity Draper, Deakin University. Extending photocatalyst activity through choice of electron donor.
09	Krishmali N. Ekanayake, Deakin University. Development of aquaculture feed using food waste residues from an unconventional approach.
10	M.F.R. Mohd Fauzi, The University of Melbourne. Microfluidic Fabrication and Characterization of core-shell Micro Polymer Inclusion Beads (μ PIBs) for Thiocyanate Extraction.

11	Samantha Harriage, Federation University Australia. Quantification of pharmaceuticals in water and flora along an Australian river system.
12	Ashakiran Maibam, RMIT University. PFAS capture using MOFs with functionalised biphenyl linkers.
13	Ovini Jayawardana, Deakin University. Synthesis and characterization of luminescent heteroleptic cyclometalated iridium(III) complexes.
14	Asavari Joshi, Deakin University. Squid waste (viscera) oil processing: Enzymatic treatment to produce high quality omega-3 rich oil.
15	Gabriel Machado Silva, RMIT University. Characterisation of layered double hydroxides aided by simple ab initio and crystallographic simulations.
16	Serena Nihal, Queensland University of Technology. Label-free detection of viral disease agents through their cell surface proteins: Rapid screening SARS-CoV-2 in biological specimens.
17	Damien Nzabanita, RMIT University. Heavy metal concentrations in three species of ducks from south-eastern mainland Australia.
18	Oi Man Sherlly Tsui, The University of Melbourne. Development of a novel microfluidic paper-based ethanol sensor.
19	Pravinda Pandigamage, University of Tasmania. Metal-Organic Framework/Polymer Coatings on Solid-Phase Extraction Frits for the Preconcentration of Phenols.
20	Gerson Dewantier, RMIT University. Classifying Cheddar cheese based on maturity level and manufacturer using vibrational spectroscopy and chemometrics.

21	Daksh Shah, RMIT University. TiO ₂ /CoAl-LDH nanocomposites for CO ₂ photoreduction.
22	Yang Liu, RMIT University. Zirconia solid acid catalysts for sustainable chemical manufacturing.
23	Jolene Anthony, Flinders University. Understanding the effects of ochre pigment processing on the physicochemical 'fingerprint'.
24	Raymond Fernando Yu, University of Tasmania. Cyclodextrins as chiral phase mobile additives in open-tubular liquid chromatography with a pseudophase coating.
25	Rajagopal Venkatachalam, RMIT University. Gold Nanoparticle Decorated Covalent Organic Polymers; Electrocatalysts for Water Splitting in Alkaline Medium.

Oral Presentations Abstracts

New sensing concepts based on bipolar annihilation electrochemiluminescence.

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Bipolar electrochemistry, where faradic reactions are promoted at the extremities of a conductor by an electric field in the absence of direct ohmic contact.

In electrochemiluminescence (ECL), anodic/cathodic reactions take place at the surface of an electrode which results in the production of excited species in the diffusion layer, that emit light.^{1,2} The combination of bipolar electrochemistry with electrochemiluminescence is very interesting for its possible analytical applications³ and ease of miniaturisation.^{4,5} Bipolar electrochemiluminescence (BP-ECL), has been demonstrated to be useful for quantitative analysis of analytes with high sensitivity.

All the work reported in this area so far uses coreactant ECL in combination with bipolar electrodes to correlate analyte concentration with coreactant ECL intensity. This approach has some limitations, however. Firstly, most coreactant ECL reactions take place in aqueous media, and there are relatively few luminophores that can be used in aqueous medium. Also, as most useful coreactant aqueous ECL reactions are anodic, this restricts the type of analytes that can be quantified using coreactant BP-ECL.

In this work we use a closed annihilation BP-ECL system, that has its ECL reporting site immersed in organic solvent and its sensing site in aqueous medium. This enables us to use many organic luminophores which have never been used for analysis due to their insolubility in water. Allowing us to explore the many possibilities that these organic luminophores have to offer.

Keywords: Closed bipolar electrochemistry, Annihilation electrochemiluminescence, Bipolar electrochemiluminescence

References:

- (1) Bard, A. J. *Electrogenerated Chemiluminescence*; CRC Press, 2004.
- (2) Richter, M. M. Electrochemiluminescence (ECL). *Chem. Rev.* **2004**, *104* (6), 3003–3036. <https://doi.org/10.1021/cr020373d>.
- (3) Renault, C.; Scida, K.; Knust, K. N.; Fosdick, S. E.; Crooks, R. M. Based Bipolar Electrochemistry. *J. Electrochem. Sci. Technol.* **2013**, *4* (4), 146–152.
- (4) Bouffier, L.; Manojlovic, D.; Kuhn, A.; Sojic, N. Advances in Bipolar Electrochemiluminescence for the Detection of Biorelevant Molecular Targets. *Curr. Opin. Electrochem.* **2019**, *16*, 28–34. <https://doi.org/10.1016/j.coelec.2019.04.004>.
- (5) Moghaddam, M. R.; Carrara, S.; Hogan, C. F. Multi-Colour Bipolar Electrochemiluminescence for Heavy Metal Ion Detection. *Chem. Commun.* **2019**, *55* (8), 1024–1027. <https://doi.org/10.1039/C8CC08472F>.

Sustainable ammonia production on single site catalyst anchored 2D materials

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Sustainable large scale ammonia production from N₂ under mild conditions has been explored through catalyst design with computational tools. The chemical insights from molecular orbitals of N₂ molecule has been adopted to design N-N bond activation by introducing electrons into the empty anti-bonding orbitals. Here, two-dimensional (2D) materials can be exploited as electron reservoirs and its electrons can be tapped and directed to the anti-bonding orbital of N₂ through metallic or non-metallic single atom catalyst (SAC) or catalytic centres introduced as surface modifications. Density Functional Theory (DFT) study implemented with N-N bond activation and N₂ chemisorption as two crucial factors [1] showed metal SAC anchored graphene to be a recyclable heterocatalyst capable of ammonia fixation under mild temperature and pressure with an energy barrier of 1.2 eV.[2] Another environment friendly approach to ammonia fixation is the electrocatalytic nitrogen reduction reaction (eNRR), and investigations on electrically conducting 2D materials (Mo₂C and VX₂) coupled with non-metal catalytic centers or dopants has led to efficient nitrogen reduction. These materials brought about ammonia fixation through an augmented electron transfer (i.e., donation) from the non-metal@2D material, which is then followed by back-donation from N₂. Boron anchored Mo₂C (MXenes) showed high NRR performance with a lower limiting potential of 0.57 eV [3], while boron doped VX₂ demonstrated higher performance with a record low overpotential of 0.06 eV and selectivity from reported vanadium dichalcogenides.[4] This research highlights the aspect of implementing earth abundant metals and non-metals on several 2D materials to develop an active, low cost, stable and efficient electrocatalyst for NRR via an exhaustive DFT study.

References:

1. Ashakiran Maibam, Thillai Govindaraja, Kaliaperumal Selvaraj and Sailaja Krishnamurty, *J. Phys. Chem. C*, **2019**, 123, 27492–27500.
2. Ashakiran Maibam and Sailaja Krishnamurty, *Journal of Colloid and Interface Science*, **2021**, 600, 480-491.
3. Ashakiran Maibam, Sailaja Krishnamurty and Manzoor Ahmad Dar, *Mater. Adv.*, **2022**, 3, 592-598.
4. Ashakiran Maibam, Ravichandar Babarao and Sailaja Krishnamurty, *Applied Surface Science*, **2022**, 602, 154401.

Cathodic Co-reactant Electrochemiluminescence of Water-soluble Heteroleptic Iridium(III) Complexes Containing *N*-methyl(pyridyl)pyridinium Cyclometalating Ligands

Steven J. Blom,^a Timothy U. Connell,^a Egan H. Doeven,^a David J. Hayne,^b Emily Kerr,^b Luke C. Henderson,^b Paul S. Francis^{a*}

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Electrochemiluminescent systems have enjoyed analytical application in, *inter alia*, forensically important detection systems, biosecurity, and clinical diagnostics. However, most of these analyses rely upon the conventional tris(2,2'-bipyridine)ruthenium(II) ([Ru(bpy)₃]²⁺)/tri-*n*-propylamine (TPrA) co-reactant anodic system, where the sacrificial TPrA is first oxidised, undergoes hydrogen atom abstraction, and forms strongly reducing TPrA[•].¹ This radical species then reduces [Ru(bpy)₃]²⁺ which is subsequently oxidised by TPrA^{•+} in the abovementioned assay systems to catalyse formation of electronically excited [Ru(bpy)₃]^{2+*}.

In this work, we focus on the development of a cathodic ECL system using peroxydisulfate (S₂O₈²⁻) as the sacrificial co-reactant. The inverse to TPrA, this species is very easily reduced upon application of a negative potential, and this results in the formation of a correspondingly powerful oxidant, SO₄^{•-}.²

Whilst previous research has shown that [Ru(bpy)₃]²⁺ typically does not produce intense ECL in this system without the assistance of non-conventional electrode materials,³ the closely related bipyrazine analogue, [Ru(bpz)₃]²⁺, does. It is thought that this is due to the relatively low-magnitude reduction potentials of this complex compared to [Ru(bpy)₃]²⁺, thereby limiting quenching of the excited state and stabilising the reduced intermediate.⁴ We found that iridium(III) chelates decorated with *N*-methyl(pyridyl)pyridinium cyclometalating ligands described by Coe *et al.*^{5, 6} offered similarly shifted reduction potentials, and so produced comparative ECL intensities as the [Ru(bpz)₃]²⁺ complex, whilst further enabling access to green/blue shifted emission. Moreover, holding the concentration of S₂O₈²⁻ at 10 mM, it was found that these iridium(III) complexes offered excellent limits of detection, with the best species giving an LOD of *ca.* 7 × 10⁻⁹ M in purely aqueous media. It is thought that these species may, therefore, find use as potential bioconjugates for sensitive cathodic ECL analysis.

References:

1. W. Miao, *Chemical Reviews*, 2008, **108**, 2506-2553.
2. H. S. White and A. J. Bard, *Journal of the American Chemical Society*, 1982, **104**, 6891-6895.
3. J. Zhang, E. Kerr, K. A. S. Usman, E. H. Doeven, P. S. Francis, L. C. Henderson and J. M. Razal, *Chemical Communications*, 2020, **56**, 10022-10025.
4. K. Yamashita, S. Yamazaki-Nishida, Y. Harima and A. Segawa, *Analytical Chemistry*, 1991, **63**, 872-876.
5. B. J. Coe, M. Helliwell, J. Raftery, S. Sánchez, M. K. Peers and N. S. Scrutton, *Dalton Transactions*, 2015, **44**, 20392-20405.
6. B. J. Coe, M. Helliwell, S. Sánchez, M. K. Peers and N. S. Scrutton, *Dalton Transactions*, 2015, **44**, 15420-15423.

Pseudophase microextraction: a novel sample concentration method in capillary electrophoresis

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A main drawback in capillary electrophoretic (CE) analyses is poor detection sensitivity due to low sample loading and short detection path length of the capillary. Several approaches have been developed to improve detection sensitivity in CE such as microextraction and in-line sample concentration. In this study, we introduce pseudophase microextraction (PPME) as a new in-line sample concentration method in CE. PPME is similar to solid-phase extraction, except that the chromatographic phase is a pseudophase consisting of cetyltrimethylammonium bromide (CTAB) micelles formed *in situ* at the capillary surface. CTAB micelles have demonstrated the ability to retain analytes in open-tubular separations [1], which we harnessed for in-capillary analyte enrichment. In PPME, a very large volume of dilute solution of analytes prepared in a CTAB solution at the critical micellar concentration was injected in the capillary, trapping the analytes in the CTAB pseudophase. The capillary was then flushed with a background solution that allowed the release of analytes from the CTAB pseudophase and focused the analytes at the inlet tip of the capillary. This method was applied to the different CE modes for the analyses of various analytes [2, 3, 4]. Improvements in detection sensitivity in the order of 10^2 - 10^3 were observed. PPME has the potential of being applied in the detection of analytes in real samples.

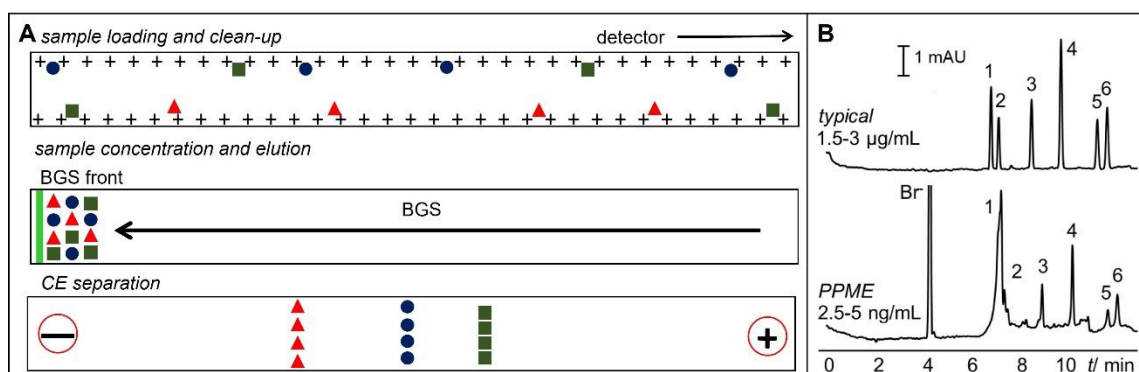


Fig 1: (A) General mechanism of pseudophase microextraction. (B) Typical injection MEKC vs PPME-MEKC of model analytes

Keywords: capillary electrophoresis, pseudophase, microextraction, in-line sample concentration

References:

- [1] Quirino, J.P. and F.M. Tarongoy, *Liquid chromatography with micelles in open-tube capillaries*. Green Chem., 2018. **20**(11):2489-2943.
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- [3] Yu, R.B. and J.P. Quirino, *Pseudophase-to-solvent microextraction for in-line sample concentration of anionic analytes in capillary zone electrophoresis*. J. Chromatogr. A, 2022. **1679**: 463383.
- [4] Vaas, A.P.J.P., R.B. Yu and J.P. Quirino, *In-line sample concentration in capillary electrophoresis by cyclodextrin to admicelle microextraction*. Anal. Bioanal. Chem., 2022. **414**(22):6671-6680.

The Puzzling Presentation of Pyrethrins: Exploring Isomerization in Comprehensive Two-Dimensional Gas Chromatography

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Comprehensive two-dimensional gas chromatography (GC×GC) imparts an additional degree of separation and enhanced resolution when compared to traditional one-dimensional gas chromatography (1DGC). The visual presentation of results in the form of a contour plot aids in analyte identification but can also yield interesting patterns which provide insight into chemical processes, not immediately apparent by 1DGC. Chemical isomerization has been reported in GC×GC literature, yet the influence of heat on this process and its visual presentation has not been fully explored. The six natural pyrethrin pesticides are produced by pyrethrum daisies (*Chrysanthemum cinerariifolium*); two of them, pyrethrin I and pyrethrin II, are susceptible to irreversible thermal isomerization.^[1,2] These pyrethrins convert to isopyrethrin I and II, respectively, when exposed to temperatures above 200 °C.^[3] Using natural pyrethrins as a case study, this work aims to investigate how GC×GC method parameters affect thermal isomerization occurring during GC×GC analysis, and how these changes are visually represented in the 2D plot. The utility of GC×GC will be highlighted through comparison to the 1DGC results. The effect of inlet temperature, oven temperature, and oven temperature program (isothermal vs. gradient) will be examined with a focus on the qualitative interpretation of results. Through the unconventional approach of using GC×GC columns comprising the same stationary phase in both dimensions, the thermal isomerization of pyrethrins will be presented.

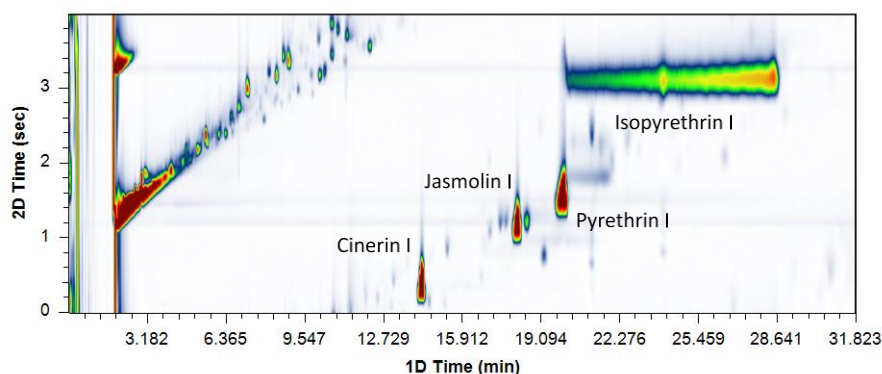


Figure 1: GC×GC contour plot of pyrethrin extract. The 'peak bridge' of isopyrethrin I is formed by irreversible isomerization of pyrethrin I within the GC system, during 210 °C isothermal analysis.

Keywords: isomerization, peak bridging, pyrethrin, isopyrethrin, GC×GC

References:

- [1] Goldberg AA, Head S, Johnston P. Action of heat on pyrethrum extract: the isomerisation of pyrethrins to isopyrethrins. *J Sci Food Agric*. 1965;16(1):43-51.
- [2] Wenclawiak BW, Krappé M, Otterbach A. In situ transesterification of the natural pyrethrins to methyl esters by heterogeneous catalysis using a supercritical fluid extraction system and detection by gas chromatography-mass spectrometry. *J Chromatogr A*. 1997;785(1-2):263-7.
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Temporal analysis of human mesenchymal stem cells under electrical stimulation with AFM

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Human mesenchymal stem cells (hMSCs) have great potential for tissue engineering application due to their multipotent differentiation ability, but with limitation of time-consuming using current method. Electrical stimulation can induce stem cell to differentiate into many pathways (bone, muscle, etc) efficiently, without exogenous growth factors,¹ but the mechanism by which this occurs is unclear. We hypothesise that electrical stimulation may influence cytoskeletal structure, which is a known factor for differentiation. Hence, we used Atomic Force Microscopy (AFM) in this project to monitor the structural and mechanical properties of these cells throughout the period of stimulation.² This will provide information on the mechano-transduction pathway of the cells which will further enhance stem cells application in tissue engineering.

After 1h electrical stimulation (0.3V, 1Hz, 100ms), the cytoskeleton realigned. (**Fig.1**) The “little hand” of the cells gradually disappeared, meaning the adhesion of cells edge decreased. Post stimulation, less cells can be observed may due to detachments (decreased adhesion). Stimulated cells presented more elongated structure. (**Fig.2**).

In conclusion, this project applied electrical stimulation with various parameter on stem cells to affect their fate. The change of cytoskeleton structure, mechanical properties as well as the focal adhesion were clearly observed, which will further affect the differentiation of stem cell.

(This project is supported by Australian Research Council through Discovery Project DP20010612)

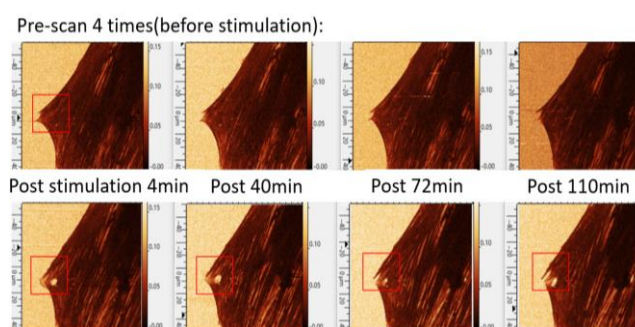


Figure 1: AFM images of cell stiffness before (top row) and after (bottom row) stimulation.

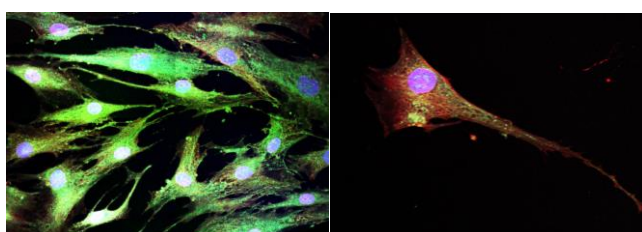


Figure 2: Confocal microscopy images of cell without (left) and with (right) stimulation. Blue, green, red represents nuclei, actin, vinculin respectively.

Keywords: Atomic Force Microscopy, differentiation, mechano-transduction, tissue engineering

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Metal organic frameworks for improving the analysis of perfluoroalkyl substances from water

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Per and polyfluorinated alkyl substances (PFAS) are a group of substances that resist heat, oil, stains and water.^[1] Of note, PFAS are exceptionally effective at fighting liquid fuel fires, leading to its use in fire-fighting foams and subsequent groundwater contamination near airports and military bases where fire-fighting training often occurs. This is of great concern as PFAS are persistent organic pollutants, characterized by the many strong C-F bonds throughout their structures. There are thousands of distinct PFAS compounds that have been detected in the environment where the characterisation and monitoring of PFAS particularly challenging from an analytical perspective.

To improve PFAS analysis at lower concentrations, metal organic frameworks (MOFs) are highly promising for the pre-concentration of PFAS prior to detection by mass spectrometry. MOFs are permanently porous materials that have been used for gas separation, sensing and catalysis. MOFs have been used to detect PFAS, including MIL-101,^[3] UiO-66,^[4] and ZIF-8.^[5] These studies have been limited to a few of the most common PFAS, in which the use of MOF powders as dispersive adsorbents does not readily enable the direct integration of MOFs into a standard EPA method that is required by commercial labs for widescale adoption.

In this project, we find that ZIF-8A has the highest adsorption capacity for perfluorooctanoic acid (PFOA) out of the tested MOF samples. To make ZIF-8A compatible with solid phase extraction and improve extraction efficiencies, we synthesised a new hybrid material consisting of ZIF-8A, an amine functionalised ZIF-8 framework, immobilised on silica particles. Solid phase extraction (SPE) cartridges containing this hybrid material were evaluated for use in the EPA PFAS analysis method and compared to commercially available polymer extraction materials against 24 PFAS compounds that are regularly tested by industry. The use of the hybrid material could be used to lower detection limits by over 30% on average across all 24 analytes. Additionally, ZIF-8A on silica particles as a SPE adsorbent was validated by quantifying PFAS in water samples collected in vicinity of Sydney airport and RAAF base Williamstown with concentrations ranging from 0.016 mg/L to 42 mg/L and 0.019 mg/L to 0.21 mg/L respectively. Metal organic frameworks are promising for significantly improving the performance of solid phase extraction materials for the analysis of persistent organic pollutants.

Keywords: Perfluoroalkyl substances, Metal organic frameworks, Limit of detection

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Understanding the Fate and Behaviour of PFAS in Port Philip Bay

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Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) are a diverse group of >5000 synthetic organofluorine chemicals. They have been in use since the 1940s to make products resistant to heat, stains, grease, and water. Often labelled “forever chemicals” due to their stability and resistant to degradation PFAS are found in throughout the world. They were originally thought to be safe and little thought was given to their environmental fate and effects. This turned out to be a mistake, and today there are high concerns over their potential impacts on human and environmental health. In humans, exposure to high levels PFAS has been associated with increased cholesterol levels, decreased vaccine response, change in liver enzymes, increased risk of high blood pressure and increased risk of kidney or testicular cancer.

Port Philip Bay has an approximate area of 1950 square kilometres. The Bay’s catchment covers 9790 square kilometres encompassing 21 natural drainage basins. It supports ~300 species of fishes as well as over 200 species of sea weeds, jelly fishes, corals and sponges and has significant environmental, economic, and social significance to Victoria. The greatest risk to Port Philip Bay is from catchment-based pollution (such as PFAS) and marine pests. Inputs of PFAS to Post Philip Bay mainly come from industry but the type and temporal variation in PFAS entering the bay is not well understood and this hinders their effective management.

The aim of this study is to understand the sources fate and behaviour of PFAS in Post Philip Bay and surrounding catchments. We will create a detailed mass balance of major PFAS in the bay which will include storm water, rivers and creeks, sediments, rainwater, biota and the bay itself. Understanding the major sources of PFAS, how they move through the environment as well as their ultimate fate over time will enable us to better target control and remediation efforts to improve environmental safety.

Samples from creeks that lead into the bay from the western and eastern side of the bay were sampled in triplicates and analysed for 16 PFAS compounds using LCMS/MS in March 2022. 0.2 ng/L detection limits were reached using solid phase extraction and blowing down the sample volumes from 200 ml to 0.5 ml reaching 400 times concentration. Six sediment core samples were sampled and analysed for 44 PFAS compounds using LCMS/MS including short and long chain with functional groups carboxylic acids and sulphonic acids. The sediment samples were taken from Werribee, Sandringham, Mt. Eliza, Central, Rosebud and Indented Head areas providing a bit of an overview of the PFAS concentration in the sediments.

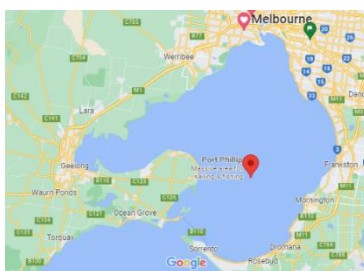


Figure: Port Philip Bay map

Highly tuneable and ultrasensitive platform for diabetes management

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Nanotextured electrodes exhibit better sensitivity and selectivity towards biomarker detection. Herein, we report a tuneable and scalable strategy for nanotexturing carbon substrates using gas phase aerosol technology for advanced electrochemical bio-sensing applications. Briefly, different surface coverages of gold nanoislands (AuNIs) are deposited on screen-printed carbon electrodes (SPCEs) by regulating the deposition parameters. This provides flexibility to fine tune the sensitivity of the platform towards detection of clinically relevant biomarkers. An extensive comparison with other gold deposition techniques and commercially procured gold electrodes reveal superior sensitivity and selectivity of our material platform. This platform is utilized to develop an ultrasensitive and extremely selective label-free electrochemical aptasensor for the detection of glycated albumin (GA), a biomarker for diabetes (**Figure 1a**). Using different surface coverages of AuNIs, different sensitivity regimes between 1 aM to 1 mM was achieved with a LOD down to 1 aM (**Figure 1b**). Together with the lowest detection limit ever reported for GA, we also showcased the ability to detect GA in a clinically relevant range.^[1] The performance of this platform in serum samples further validated its clinical utility.

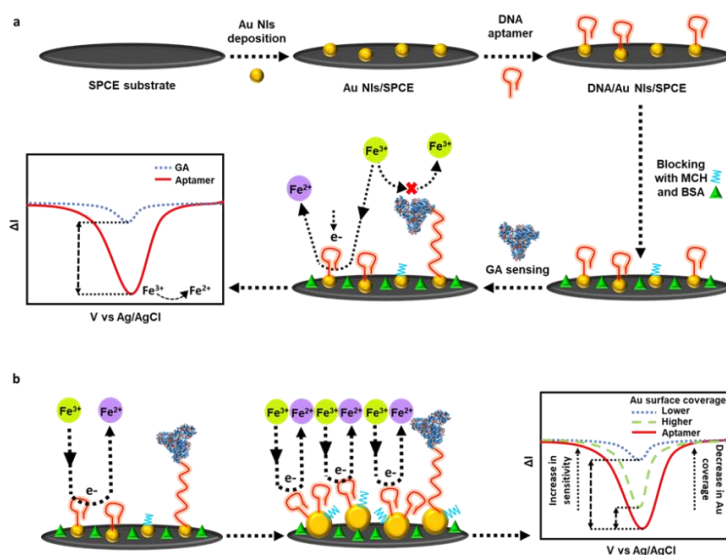


Figure 1: Schematic representation of our biosensor for miniaturised selective attomolar sensing.

Keywords: attomolar biosensing, gold nano-islands, electrochemical biosensor, glycated albumin, diabetes

References:

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The synergistic and antagonistic roles of CoOOH phase in β -Co(OH)₂ electrocatalyst for driving oxygen evolution reaction

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Electrochemical water splitting is considered as an efficient, sustainable, and eco-friendly approach to produce hydrogen gas as an alternate fuel. This involves an oxidation reaction in which the oxygen evolution reaction (OER) occurs on the anode surface and a reduction reaction in which the hydrogen evolution reaction (HER) occurs on the cathode surface. However, the OER reaction has a higher activation energy barrier compared to HER. Therefore, developing efficient OER electrocatalysts is vitally important to achieve the commercially viable production of hydrogen gas. In a catalyst, the minority impurity phases typically present alongside the main catalytic phase, can play either synergistic or antagonistic roles during catalytic activity. During the synthesis of β -Co(OH)₂, which is commonly known as a promising layered electrocatalysts for OER, the material can transform into CoOOH phase. This study revealed that the presence of CoOOH impurity on Co(OH)₂ can reduce the thermodynamic barrier of OER while adversely impacting upon the kinetics of the reaction. The reduction of the thermodynamic barrier could be attributed to the presence of both Co²⁺ and Co³⁺ with the co-existence of CoOOH in β -Co(OH)₂. Conversely, the significantly improved kinetics in pure β -Co(OH)₂ could be attributed to better accessibility of electrochemically active sites compared to the material containing CoOOH impurity phase^[1]. This study emphasizes upon the importance of controlling reaction conditions while synthesising electrocatalysts to minimize the antagonistic effect on catalytic activity.

Keywords: β -Co(OH)₂, CoOOH, 2D nanosheets, oxygen evolution reaction (OER), phase purity

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Unexpected dependence on choice of electrochemical technique of reproducibility with screen-printed carbon electrodes

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Screen-printed carbon electrodes (SPCEs) have been emerging as an alternative to conventional carbon electrode materials such as glassy carbon (GC) for several decades.¹ SPCEs offer several advantages for real-world sensing applications. In particular, the individual cost per SPCE can be sufficiently low such that single-use disposable sensors can be developed, which circumvents many issues such as electrode fouling. Electrode printing methods are now sufficiently well-developed that the geometric area of the active electrode can be reproduced with high precision.

While engaged in a sensor development project using SPCEs, we realised that the reproducibility of the electrochemical response with such electrodes is often governed by factors other than the tolerance of the conductive geometric area. Surprisingly, we have found that the reproducibility varies strongly depending on the electrochemical technique used to interrogate the sensor. We have investigated this phenomenon by evaluating the relative standard deviation (%RSD) for the voltammetric responses of GC and various brands of SPCE with the electrochemical probe, ferrocene carboxylic acid (FcCOOH). We compared the %RSD among 1st Harmonic Fourier Transform Alternating Current voltammetry (1H FTACV), 2nd Harmonic FTACV, square-wave voltammetry (SWV) and cyclic voltammetry (CV). Our results show that the RSD increases in the order CV < SWV < 1H FTACV < 2HFTACV; and that the RSD with GC is generally lower than that with SPCEs. We suspect that the occurrence of this phenomena is due to variability in capacitance between SPCEs, as the available microscopic area of each working electrode of SPCE may differ from one to another.^{2,3}

Keywords: Screen printed electrodes, reproducibility, voltammetry

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Rapid detection of bacteria in milk using static headspace-comprehensive two-dimensional gas chromatography

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Foodborne microbial contamination is a serious threat to public health and a major hindrance to safe food production. Early detection of pathogenic microbes can minimise the spread of contaminated food, but current reliance on conventional culture-based methods is time-consuming and laborious. A new approach is introduced for rapid and reliable bacteria detection in food. Namely, static headspace comprehensive two-dimensional gas-chromatography (HS-GC×GC) with backflushing. We proposed that detection of volatile organic compounds emanating from food samples (dairy milk) spiked with *Escherichia coli* (*E. coli*) might serve as putative markers to indicate *E. coli* presence. Quasi-stop-flow modulation was employed as part of the workflow to measure volatile organic compounds emanating from enriched milk samples spiked with *E. coli* and our investigation suggests that ethanol, 1-propanol, and acetaldehyde may be used as such markers.

Different incubation times (5, 10, 15, and 20 h) were investigated to determine the minimum enrichment time required to detect *E. coli*. Results showed that enrichment as low as 15 h reveals *E. coli* presence at an initial load of 1 cfu/mL. Incorporation of the backflushing step had greatly maximised the sample throughput and permits the time-to-response to be reduced by more than one full day. Timely detection of pathogenic microbes is crucial for a secure food supply. The described approach has great potential to complement the conventional workflow) and be utilised for rapid microbial screening of foodstuff.

Keywords: *Escherichia coli*, GC×GC, headspace, food safety, MVOC

Application of biotechnology to aroma sustainable synthesis: taking nature's perfection to another level

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Nature does a fabulous job of providing us with a fascinating range of products with special properties that can be used as flavours, fragrances, medicines and foods. These are often complex mixtures of secondary metabolites derived from plants, such as essential oils; or arising from plant-microorganism interactions, as in the case of 'oud', a precious and distinctive aromatic oil resin derived from Agarwood's defensive response to the presence of a fungus. [1]

In order to explore other biosynthetic approaches for the sustainable production of high-valued aromas, this research seeks to apply and evaluate the performance of different lipase enzymes to promote chemical changes in aroma samples (standards and essential oils). Qualitative and quantitative gas chromatography methods (GC-FID, GC-MS and GC×GC-MS) were applied to assess the reactions' yield and enantioselectivity and help selecting the best experimental conditions (e.g. concentration, temperature). CALA was the best performing enzyme, achieving >95% and 74% conversion of primary and secondary alcohols, respectively, in the optimised conditions (37-40 °C, 3-4 mg/mL of enzyme and 58-60% vinyl acetate). [2]

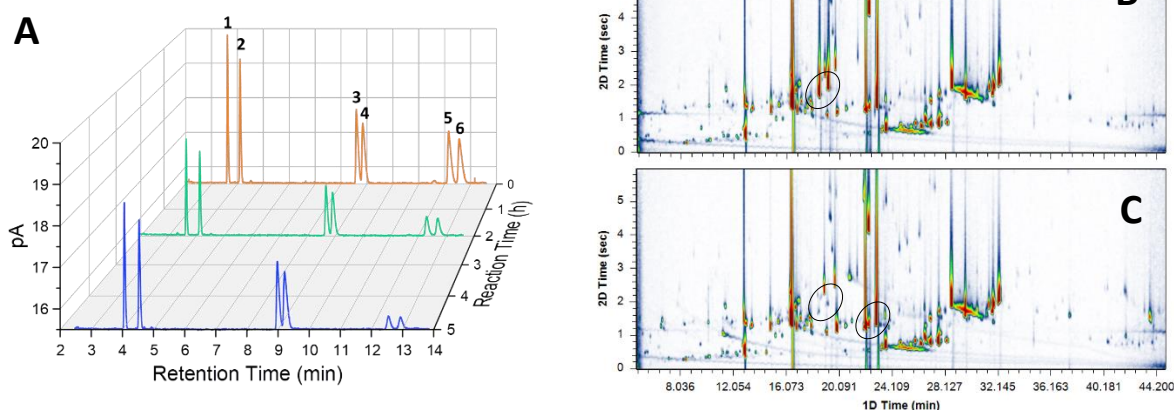


Figure 1. The eGC-FID chromatograms (A) illustrate the chiral assessment of the lipase CALA, using a mixture containing the aroma standards (-/+)-linalool (1, 2), (-/+)-menthol (3, 4), and (+/-)-citronellol (5, 6). The results indicate that citronellol enantiomers (peaks 5 and 6) were converted in equal ratios, demonstrating this enzyme is not enantioselective. The GC×GC-MS chromatograms (B and C) demonstrate the changes in the chemical profile of citronella oil before (B) and after the enzymatic reaction (C), highlighting the complete conversion of the major alcohols citronellol and geraniol into their respective ethyl esters.

Keywords: gas chromatography, aromas, essential oil, biocatalysis, enzymes.

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Remote sensing of marine plastics and their chemical additives using Near-Infrared (NIR) and Hyperspectral imaging and applied chemometrics

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Plastic pollution is ubiquitous in our oceans. 8 million tonnes of plastic enter our oceans every year [1, 2] negatively affecting hundreds of marine species. Plastic is slow to degrade and typically breaks down into smaller and smaller particle sizes (Macro>micro>nano- plastics). To top it off, these plastics leach out chemical additives such as brominated flame retardants (BFRs), perfluoroalkyl substances (PFASs), BPA (Bis-phenol-A) and phthalate plasticizers, which accumulate in tissues and have been demonstrated to disrupt endocrine, thyroid and estrogenic receptors respectively. There are more than 10,000 chemical additives in the plastic industry's chemical cabinet [3], and they can make up 10-70% of plastic by weight [4]. The estimated 1 million + tonnes of these chemical additives entering our oceans are almost completely unaccounted for. The scope of marine plastic pollution requires a new way to 'visualise' the plastic pollution issue [5-7]. The power for hyperspectral imaging to monitor the vast area of our oceans will provide insights in a way the fragmented point sampling tendencies of analytical chemistry would never be able to achieve with classical approaches. Advancements in this area will be a vital tool when humanity's hand is forced to intervene and finally clean up our plastic mess. This study aims to demonstrate potential for near-Infrared (NIR) and hyperspectral imaging (HSI) analysis to rapidly, and non-destructively, detect plastic debris and plastic chemical additives via remote sensing of the marine environment. Chemometric pre-processing of NIR spectra will be utilised as unique signatures of target polymers and additives. Machine learning approaches will be explored to data-mine high resolution hyperspectral images revolutionising the way we 'visualise' the plastic pollution issue. The power for hyperspectral imaging to monitor the vast area of our oceans will provide insights in a way the fragmented point sampling tendencies of analytical chemistry would never be able to achieve with classical approaches. Advancements in this area will be a vital tool when humanity's hand is forced to intervene and finally clean up our plastic mess.

Keywords: Remote sensing, Marine plastic, plasticisers, chemometrics, spectroscopy

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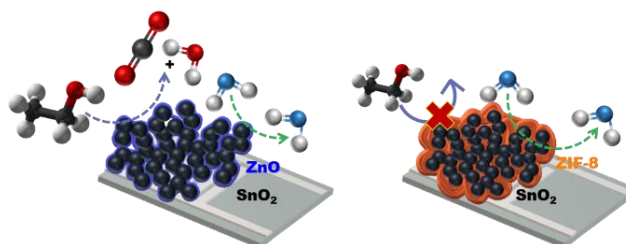
Tuneable Metal Organic Framework Encapsulated Metal Oxide Network for Enhanced Chemiresistive Sensing

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Detection of toxic gases is of great importance for environmental monitoring and non-invasive health diagnosis [1]. In this work, we present a novel approach in fabricating a metal organic framework (MOF) encapsulated metal oxide nanoparticle network for selective chemiresistive gas sensing. Fabrication of the sensing structure was carried out using flame spray pyrolysis (FSP), atomic layer deposition (ALD) and chemical vapour conversion (CVC). FSP [2] and ALD were applied to deposit thin films of the sensing and filtering metal oxide layer, while CVC was employed to convert the filtering metal oxide layer to MOF using appropriate organic linkers [3]. The sensing interface utilizes the combined synergistic property of the highly sensitive metal oxide layer and filtering capacities of the porous MOF to selectively detect NO₂. The developed sensor demonstrates a wide linear range, a detection limit of 0.1 ppm and good selectivity against common interfering gases [4].



Selective chemiresistive gas sensing using MOF encapsulated metal oxide nanoparticle network

Keywords: chemiresistive, metal organic frameworks, fractal network, sensor array, selectivity

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Understanding the transient interactions between nanozymes and aptamers in nano-aptasensors

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Transient non-covalent interactions play an important role in biological systems. Such interactions also play a critical role in the working of sensing platforms. An example is the non-covalent interaction between enzyme mimic nanoparticles (nanozymes) and ssDNA aptamers resulting in colorimetric sensors for the detection of small molecules to whole cells. To rationally design such aptasensing platforms, understanding the nature and the thermodynamics of such interactions is the key. The current work provides fundamental knowledge on how to control the dynamic nature of interaction between nanozymes and aptamers. As an initial testbed, 4 nanozymes with different metals (same capping agent) were chosen along with an aptamer sequence for ampicillin. Using steady state fluorescence quenching principles, in depth understanding of the interaction between the ampicillin aptamer and citrate capped metal nanozymes was studied. The fundamental knowledge allowed us to control the affinity between the aptamer-nanozyme such that the strength of binding of the aptamer to its target was several orders of magnitude higher than the aptamer to the nanozyme. This allowed efficient desorption of the aptamers from the surface of the nanozyme allowing us to develop a sensor to detect ampicillin in the attomolar concentration. Further, the fine control over the interactions allowed the sensor to detect ampicillin in diluted milk samples outlining the robustness of the newly developed nanozyme aptasensor.

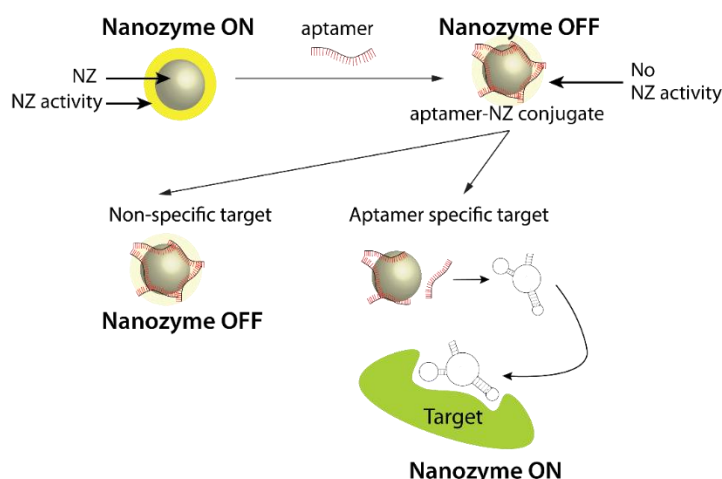


Figure: Schematic representation of the working concept of a transient interactions-driven NZ-aptasensor platform.

Keywords: Nanozymes, aptamers, sensors, non-covalent interactions, steady-state fluorescence quenching

Antioxidant Activity and Phenolic Compound Determination and Quantification in Western Australian Honey

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This study reports on the total phenolic content and antioxidant activity as well as the phenolic compounds that are present in Red Bell (*Calothamnus* spp), Coastal Peppermint (*Agonis flexuosa*), Marri (*Corymbia calophylla*) and Jarrah (*Eucalyptus marginata*) honey from Western Australia. The total phenolic content of the honeys was determined using a modified Folin-Ciocalteu assay, while their total antioxidant activity was determined using FRAP and DPPH assays. Phenolic constituents were identified using a High Performance Thin-Layer Chromatography (HPTLC)-derived phenolic database[1, 2], and the so identified phenolic compounds were quantified using HPTLC. Finally, constituents that contribute to the honeys' antioxidant activity were identified using a DPPH-HPTLC bioautography assay. Among the honeys tested, Red Bell was found to have the highest TPC, as well as FRAP and DPPH antioxidant activity, followed by Jarrah, Coastal Peppermint and Marri honey. Kojic acid and epigallocatechin gallate were found in all honeys, other constituents (e.g. m-coumaric acid, lumichrome, gallic acid, taxifolin, luteolin, epicatechin, hesperitin, eudesmic acid, syringic acid, protocatechuic acid, t-cinnamic acid, o-anisic acid) were only identified in some of the samples. DPPH-HPTLC bioautography demonstrated that most of the identified compounds possess antioxidant activity, except for t-cinnamic acid, eudesmic acid, o-anisic acid, and lumichrome.

Keywords: HPTLC, HPTLC-DPPH, HPTLC-derived database, phenolics, flavonoids

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Investigating Derivatisation Methods in Fatty Acid Profiling

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Fatty acids; a vital structural unit of lipids and membranes, account for a major class of biomolecules and their evaluation is significant to numerous industries. They are a major substrate of lipid oxidation, and their study has been important to many industries and research. The level of saturation and isomeric conformation of fatty acids has been vital in interpreting the extent of oxidation [1]. The most conventional method for profiling fatty acids is to convert them into volatile derivatives known as fatty acid methyl esters (FAMES) and analyse them by gas chromatography paired with flame ionisation detection (GC-FID) (figure 1) [2]. However, this area of lipid analysis has a shortcoming with most existing derivatisation methods often being procedurally complex or outdated; using toxic catalysts and high concentrations, harsh temperature conditions, vague durations, and tedious extraction protocols. In addition to this, literature lacks an acceptable comparison between these methods.

This study focuses on comparing five such derivatisation methods and their efficacy in profiling the fatty acid content in a range of oils and samples. These methods were carried out on three different oil samples and a mixture of known standards containing different lipid classes and their ability to derivatise the fatty acids were compared in terms of the absolute and relative amounts of fatty acids derivatised.

This comparison provides a better understanding of enabling and limiting aspects of the respective methods and their applicability, particularly in industry. It also discusses the feasibility of optimising one well-performing method to be simple, effective and chemically green.

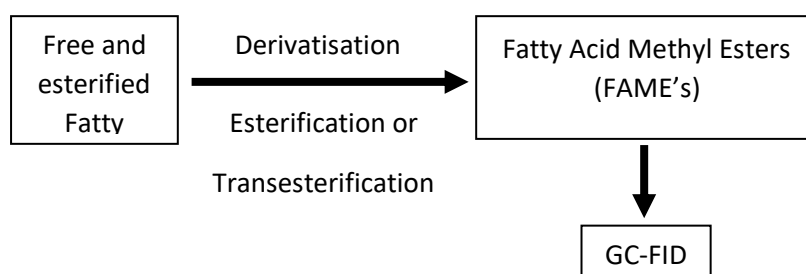


Figure 1: The process of profiling fatty acids.

Keywords: fatty acids, lipid oxidation, gas chromatography, derivatisation

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Development of a sequential injection analysis technique for the automatic speciation of selenium

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Selenium is considered an essential element for human health but is toxic when present in excessive amounts. Selenium deficiency can cause heart disease and other metabolic system disorders, whilst excessive amounts in the human body can cause selenosis [1]. Among other essential elements, selenium has the narrowest concentration window between dietary deficiency and toxicity, from 40 to 400 $\mu\text{g d}^{-1}$ [2] and therefore, a prudent control and monitoring of this element in both the human body and in the environment is essential.

Several methods have been used for the determination of selenium, such as hydride generation-atomic absorption, fluorescence or inductively coupled plasma optical emission spectrophotometry [2], but they involve expensive and bulky instruments which are often expensive to run and may require off-line treatment steps [3].

Here, we present the development of an automatic method for speciation of Se(IV) and Se(VI) using a sequential injection analysis (SIA) technique based on the oxidation of iodide by Se(IV) to iodine which subsequently changes the colour of the non-toxic and inexpensive indicator starch to blue. Total selenium is determined after the complete on-line reduction to Se(IV), while Se(IV) is determined by bypassing this reduction step. The absorbance of the intense-blue-coloured product of the reaction between starch and iodine is correlated to the selenium concentration. The concentration of Se(VI) is determined by the difference of the total (Se(IV)+Se(VI)) and Se(IV) concentrations.

Keywords: Selenium speciation, sequential injection analysis, automation

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Waste to wealth- Fabrication of Low-Cost Working Electrode from waste (Thermocol) for electrochemical Applications

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The feasibility of a graphite-thermocol (waste material) composite electrode for electrocatalytic as well as methylene blue degradation applications have been investigated. The plastic chip electrode (PCE) was fabricated by using graphite as a filler and thermocol waste as a polymer matrix in a fixed ratio. The fabricated chip electrode was thoroughly characterized by various analytical techniques such as FE-SEM, XRD, TGA, AFM, SRI etc. DC conductance of the electrode was measured by I-V measurements. This electrode was also used as a working electrode for water splitting, in which a reported MOF based electro catalyst was load over the PCE and water splitting experiment was done. The obtained results of OER are found comparable with the reported work. Utilization of waste material, low cost and electrochemical properties are the major advantage of the fabricated this plastic chip electrode

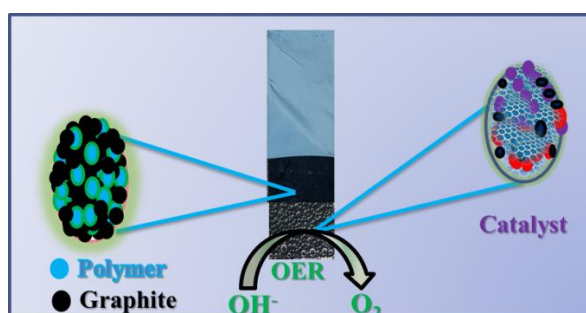


Figure: Graphical representation of the catalyst modified thermocol Plastic chip electrode

Keywords: Thermocol, Electrode, OER. Catalyst. PCE.

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Aptasensors for the detection of neuro-pathological protein conformers

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Gold nanoparticles (AuNPs) have been utilized in the development of molecular beacons based on their remarkable ability to act as quenchers of fluorescence [1] In addition, owing to their ability to form efficient and stable complexes with oligonucleotides [2], they have been a popular choice for aptasensor development [3,4,5]. The current study explores the applicability of AuNPs in sensing of proteins related to neurodegenerative disorders. This approach uses fluorophore labelled DNA aptamers specific for alpha-synuclein (a-syn) protein adsorbed onto the surface of AuNPs. This leads to the quenching of fluorescence. Target recognition is achieved through recovery of fluorescence by aptamer desorption from AuNPs surface due to extremely high affinity and selectivity of the aptamers for a-syn. We demonstrate the importance of a fine-balance of binding forces between AuNP-aptamer versus aptamer-target for the working of the sensor. Further, we show that quenching is sensitive to temperature and ratio of AuNP to aptamer concentration; with almost 80% of fluorescence being quenched at temperature below the melting point of the aptamers. In the presence of a-syn target protein, these aptamers desorb from the AuNP surface in a concentration dependent manner, detected by a simultaneous regain in fluorescence. Our approach provides a simple model for stable and selective sensing for pathological proteins, that can be expanded into a multiplexing system to include a battery of disease specific target molecules.

Keywords: gold nanoparticles, fluorescence quenching, aptamers, alpha-synuclein, protein aggregation

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Micellar Chromatographic Methods for Ethyl Carbamate Determination in Alcoholic Beverages

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Ethyl carbamate can be found in alcoholic beverages such as wine, beer, stone-fruit brandies, and spirits^[1,2]. According to the World Health Organization's International Agency for Research on Cancer in 2007, ethyl carbamate was classified under 'Group 2A' as it is a probable carcinogen to humans^[3]. The aim of this work is to develop and compare the analytical performance of sweeping-micellar electrokinetic chromatography (MEKC) and micellar liquid chromatography (MLC) methods for the determination of ethyl carbamate in complex wine sample matrices.

Prior to chromatographic analysis, ethyl carbamate was derivatized with xanthydrol in acid medium with simultaneous ultrasound-assisted emulsification-microextraction. In the case of MEKC determination, the collected organic layer was evaporated to dryness and reconstituted with 10 mM phosphate buffer at pH 7 (1:2 ratio) to enhance the electric field for sweeping to occur. Zero Electroosmotic Flow capillary with 75µm id × 50.0 cm total (41.5 cm effective) length was used with the background solution of 25 mM sodium dodecyl sulphate, 25 mM phosphate at pH 7 and 20% acetonitrile. For MLC study, reconstituting was done using Milli-Q water (1:1) and the mobile phase used was 50 mM sodium dodecyl sulphate, 25 mM phosphate buffer at pH 7 and 10% acetonitrile.

Current efforts are focused to decrease the limit of detection for both MEKC and MLC methods down to 0.02 µg/mL.

Keywords: Ethyl carbamate, micellar electrokinetic chromatography, micellar liquid chromatography, wine.

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Improved measurement of return peak current in cyclic voltammetry using diffusional fitting

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The problem of how to accurately measure the height of the back peak, (i_{pb}) in cyclic voltammetry (CV) has plagued electrochemists for years. Most commonly, i_{pb} is measured by extrapolating a linear fit from a selected region after the switching potential. However, unless there is a substantial distance between the peak and the switching potential, this approach results in considerable subjectivity in determination of the baseline and consequently poor accuracy. Moreover, experimental conditions can present challenges for this method, as an appropriate region for linear fitting can be lacking due to neighbouring peaks or solvent current.

Here, we present a new method for finding the baseline current for the back peak in CV experiments. By unfolding the CV and examining the current as a function of time rather than potential, it is possible to fit a generalised Cottrell or Shoup-Szabo equation to the current decay of the forward peak and extrapolate this function as a baseline for the return peak. A program has been written in Python to automatically find an appropriate fitting range for this analysis and measure peak currents. The approach was tested using simulated and real data under a variety of conditions. We found that the method allows for more accurate determination of back peak currents, especially when linear fits are complicated by a small electrochemical window.

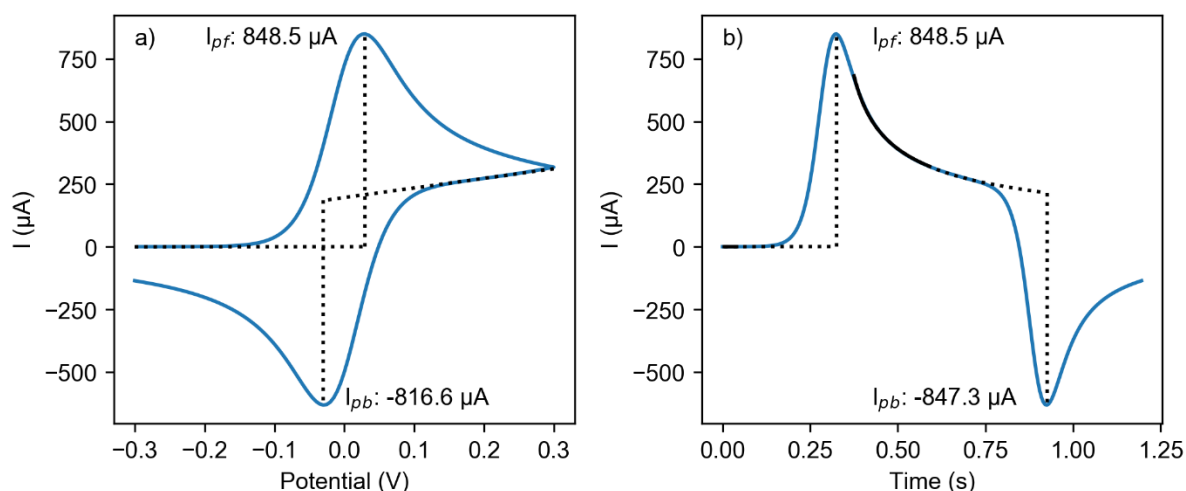


Figure: Simulated CV data demonstrating two peak picking methods. (a) Linear baselines for forward and back peak, and (b) the same CV 'unfolded' using a diffusional fitted baseline for the back peak.

Keywords: cyclic voltammetry, fitting, baseline, Python

Polymer inclusion membranes as green alternatives to solvent extraction for lithium separation

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Polymer inclusion membranes (PIMs) are a green alternative to solvent extraction (SX) which can be used in the extraction of lithium from lithium-ion battery waste or salt-lake brine. PIMs provide many advantages over SX such as lower costs, use of green solvents, no phase separation complications, immunity to biofouling and high versatility. PIMs containing 17 % (m/m) 4,4,4-trifluoro-1-phenyl-1,3-butanedione (BTA) as the extractant, 30 % (m/m) tri-octyl phosphine oxide (TOPO) as the co-extractant, 1 % (m/m) 1-tetradecanol (TD) as a modifier and 52 % (m/m) poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) as the polymer showed promising results for lithium extraction and recovery. Likewise, PIMs containing 17 % (m/m) 4,4,4-Trifluoro-1-(2-naphthyl)-1,3-butanedione (NTA) as the extractant, 30 % (m/m) TOPO, 1 % (m/m) TD and 52 % (m/m) PVDF-HFP showed excellent results for lithium extraction. These systems were studied and compared previously during this work in solvent extraction due to their high performance for lithium extraction. The solid reagents were also successfully modified with TD to create room temperature liquids called eutectic solvents that have great applicability in synthesis and metal processing applications.

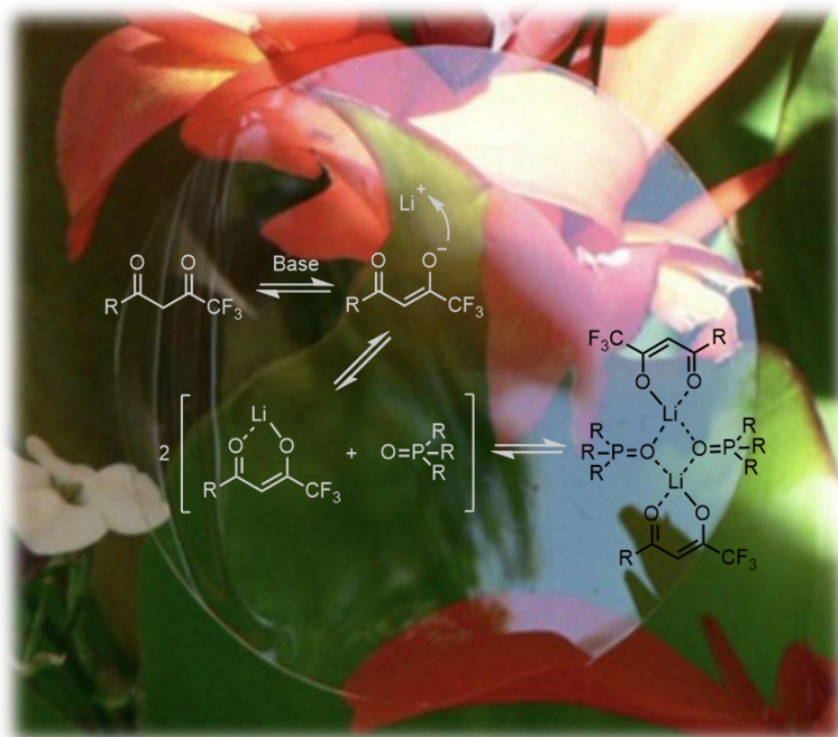


Figure: Photographic image of a polymer inclusion membrane with the extraction mechanism of lithium using β -diketone extractants with phosphine oxides.

Keywords: Polymer Inclusion Membrane. Green Chemistry. Eutectic Solvents. Lithium. Solvent Extraction.

Boiling down the finer points of separation in gas chromatography

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The nomenclature around separation in gas chromatography (GC) may be a topic which receives insufficient attention from users, it is important to establish a basic language for the technology. While nomenclature may not always be a popular topic it is, nevertheless, important as it informs how we conceptualise a process in our mind and how we communicate our research to others. A chemist's initial experience with GC is often in late high school or early university and this often shapes their understanding of the technique for years to come. If GC is not a focus of further study to a teacher or scientist their understanding may be informed partially by what they have learned as an undergraduate. As a result misconceptions can be perpetuated to the next generation.

This research draws common descriptions from literature, both research papers and undergraduate learning materials (e.g. textbooks, online resources, etc.), to gather the terminology is being used and to assess how accurately it can be applied to a GC separation. It draws on linear solvation energy relationship (LSER) research, which can be used to accurately predict the retention time of a compound using molecular descriptors^[1], and the work of prominent figures in the field such as Giddings, who created equations to describe many properties in GC^[2], to suggest new terminology which may be used to more accurately describe these separations and make our language more flexible and accurate. Finally it discusses the field of multidimensional GC (MDGC) and comprehensive two-dimensional GC (GC×GC), and for the latter explains why accurate and descriptive terminology is so helpful to researchers wanting to harness its full potential. This allows us to more clearly enunciate global retention mechanisms in the first and second dimensions (¹D and ²D) of the GC×GC experiment, and correct some poor uses of terminology that have persisted.

Keywords: MDGC; GC×GC; Nomenclature; Separation mechanism;

References:

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High methylene blue adsorption capacity of graphene oxide-biopolymer foams

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Graphene oxide (GO) has attracted great attention for potential applications in water treatment. However, one major drawback for large-scale implementation is the difficulty to separate and collect the adsorbent-contaminant complex for regeneration. In this study, 3 types of 3D GO-based foam materials have been synthesized via a uni-directional freeze-drying method. GO/water, GO/carboxymethyl cellulose (GO/CMC), and GO/Chitosan (GO/CHI) suspensions blended with poly (vinyl alcohol) (PVA) and formaldehyde (FA) were treated, resulting in foams with excellent structural integrity. The adsorbents were characterized by FTIR, XRD, Raman, SEM, and nitrogen gas adsorption. The impact of the physico-chemical modifications on methylene blue (MB) adsorption was determined through adsorption experiments performed as a function of pH, initial MB dye concentration, and contact time. Binding to the surface followed pseudo-second-order kinetics and displayed a good fit to the Langmuir adsorption model. The maximum adsorption capacities for GO/PVA/FA, GO/CMC/PVA/FA, GO/CHI/PVA/FA calculated from the Langmuir models for MB were 1026 mg/g, 970 mg/g, and 700 mg/g at pH 7 respectively. Moreover, the absorbed MB can be effectively recovered through simple squeezing in ethanol, and also the composite materials exhibited high recycling efficiency. The GO/water/PVA/FA and GO/CMC/PVA/FA foams can be used repeatedly while maintaining high adsorption capacities of 96% and 80 % respectively, even after 10 cycles. These 3D GO-based porous structures show great promise as adsorbents for wastewater purification.

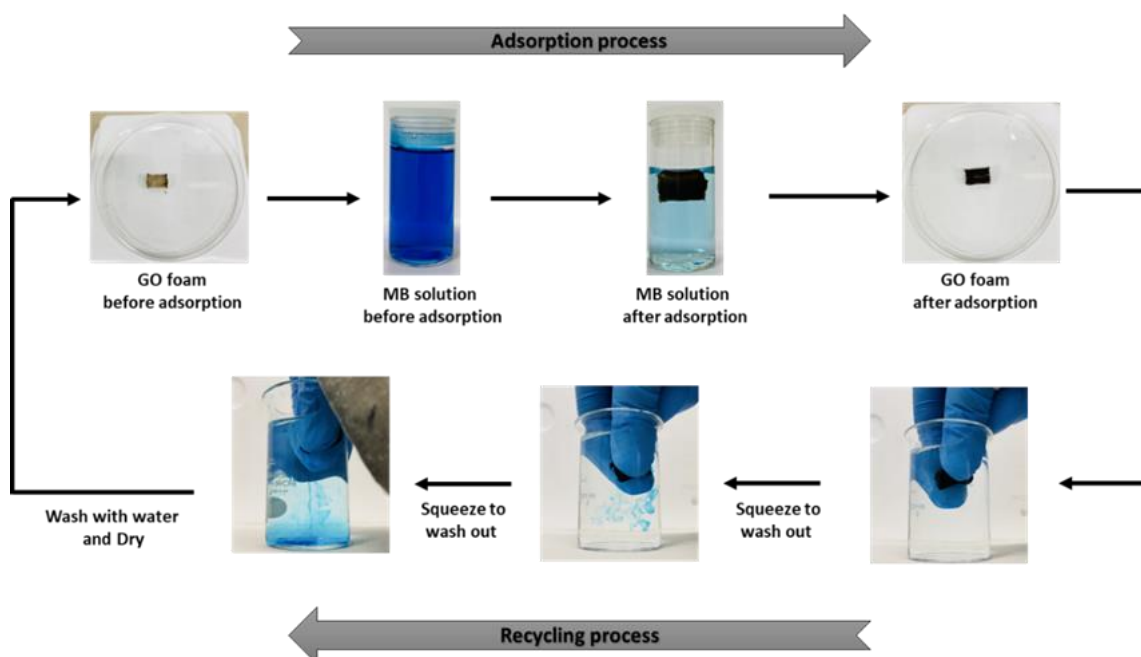


Figure: Flow diagram of GO foam for methylene blue adsorption, and the subsequent recycling process for the upcoming adsorption cycle

Keywords: 3D Graphene oxide, methylene blue, adsorption, Recycling, wastewater purification,

Single-step colorimetric detection of acid phosphatase in human urine using an oxidase-mimic platinum nanozyme

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Acid phosphatase (ACP) is a biologically active enzyme that is regarded as a potential biomarker for the prognosis of several diseases, especially those of the prostate and kidney. Detection of ACP by employing enzyme-mimicking nanoparticles (nanozymes) that can generate a colorimetric response has practical applicability due to the simplicity of detection with an unaided eye. While human serum has been the analyte matrix of choice, serum ACP cannot differentiate between prostatic and renal ACP levels. In this study, the potential applicability of oxidase-mimicking Pt nanoparticles for the detection of ACP in human urine is shown. The sensing strategy is based on the inhibition of the nanozyme-mediated oxidation of the chromogenic substrate by ascorbic acid that is produced *in situ* by the enzymatic activity of ACP. The wider pH activity of the Pt nanozyme allowed the conversion of a typical two-step assay to a single-step assay, thereby reducing the assay time by over 50%. The potential deployment of the Pt nanozyme ACP sensor in complex biological fluids is also demonstrated by estimating ACP in human urine samples in the 0.5-20 mU/mL range where it is possible to differentiate between healthy and diseased scenarios.

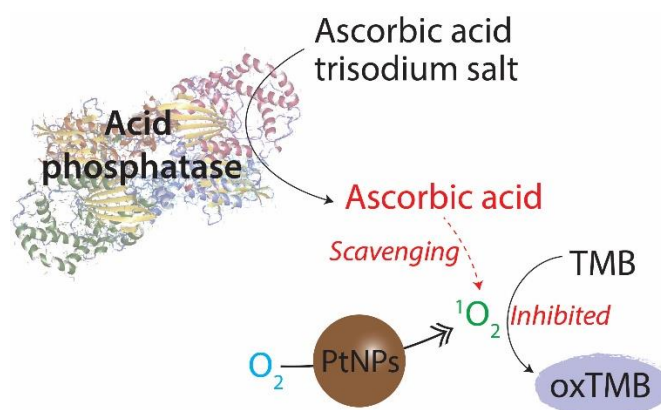


Figure: Sensing strategy used for ACP detection using Pt nanozyme

Keywords: Acid phosphatase; nanozyme; oxidase-mimic; sensor; colorimetric, Pt nanoparticles

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Detection of lanthanum using Arsenazo III-based polymer inclusion membranes

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With increasing global reliance on rare earth elements (REEs), namely for the manufacturing of electric vehicles, wind turbines, and battery technologies, there is a growing concern regarding the accumulation of REEs in the environment [1]. A number of REEs, including La³⁺, have been demonstrated to impact plant and invertebrate growth, and are also associated with humans developing health problems [1]. Despite this, methods for quick and easy in-field REE detection are lacking [2]. Arsenazo III (Az) is a well-known and effective spectrophotometric dye for the determination of REEs, including La³⁺ [3]. However, the application of Az for in-field measurements generally poses significant risks due to the environmental toxicity of Az. Thus, the encapsulation of the Az inside a polymer inclusion membrane (PIM), referred to here as an Az-PIM, could allow for safe, sensitive, and simple in-field La³⁺ detection.

The fabrication of uniform and stable Az-PIMs was found to be possible with the addition of Aliquat 336 (A336), which when mixed with Az produced a purple hydrophobic oil compatible with PVC-based PIMs. However, the addition of the extractant di-(2-ethylhexyl) phosphoric acid (D2EHPA) was also required, as this enabled the Az-PIMs to extract La³⁺ allowing the Az dye inside the Az-PIM to chelate with La³⁺.

Although the addition of D2EHPA enabled La³⁺ extraction, complex interactions between the A336 and D2EHPA affected not only the Az-PIMs ability to extract La³⁺ but also the spectral profile of the Az-PIMs. These interactions were investigated, and the optimal Az-PIM compositions were established (i.e., 50 wt% D2EHPA, 5.0 wt% A336, 0.50 wt% Az, 44.5 wt% PVC, and 45 wt% D2EHPA, 10 wt% A336, 0.5 wt% Az, 44.5 wt% PVC). These Az-PIMs were then applied in a flow-through apparatus for the detection of La³⁺, and a concentration range from 0.5 to 5.0 x 10⁻⁵ M La³⁺ was obtained. These results demonstrate the potential of Az-PIMs for the development of an in-field detection system for La³⁺ which could potentially be applied to the determination of other REEs.

Keywords: Lanthanum, rare earth elements (REEs), Arsenazo III, Ionic liquid.

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Effect of Se, Mo and Cr on the physical-chemical profile of beers

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Beer is the fermentable alcoholic beverage with a high worldwide consumption; consequently, it has a great impact on human health [1]. The addition of nutrients to food products results in benefits to human health if the supplementation meets relevant regulations [2]. For the present methodology, ale beers were produced at lab scale, and fermented with addition of 7.5%, 12.5% and 17.5% of the RDI value according to legislation (35 µg for Cr; 45 µg for Mo; 34 µg for Se). Physical-chemical properties of the beers were analysed in accordance with the American Society of Brewing Chemists (ASBC) [3] and 11 parameters were determined: pH, alcohol content (%v/v), colour (EBC), beer bitterness (IBU), total carbohydrates, vicinal diketones (VDK), total acidity, fixed acidity, volatile acidity, yeast content (OD) and free amino nitrogen (FAN). Data were treated with normality test, homoscedasticity test, removal of outliers and use of one-factor ANOVA test followed by Tukey's test. Chemometric analysis employed Pearson correlation, principal component analysis (PCA) and hierarchical cluster analysis (HCA). Results showed physical-chemical differences in the beers, e.g. higher ethanol content for all beers supplemented with the nutrients, the bitterness profile of beers with addition of Se and Cr, and higher production of off flavour VDK in the Cr added beer was observed. PCA analysis separated the samples (Fig 1a), e.g. the Cr group by PC1, and Se by PC2. The loadings of PCA (Fig 1b) shows the effects that differentiate the samples. As a conclusion, even the addition of ppb levels of the nutrients, their effects on yeast growth and changes in physical-chemical properties of beers are apparent.

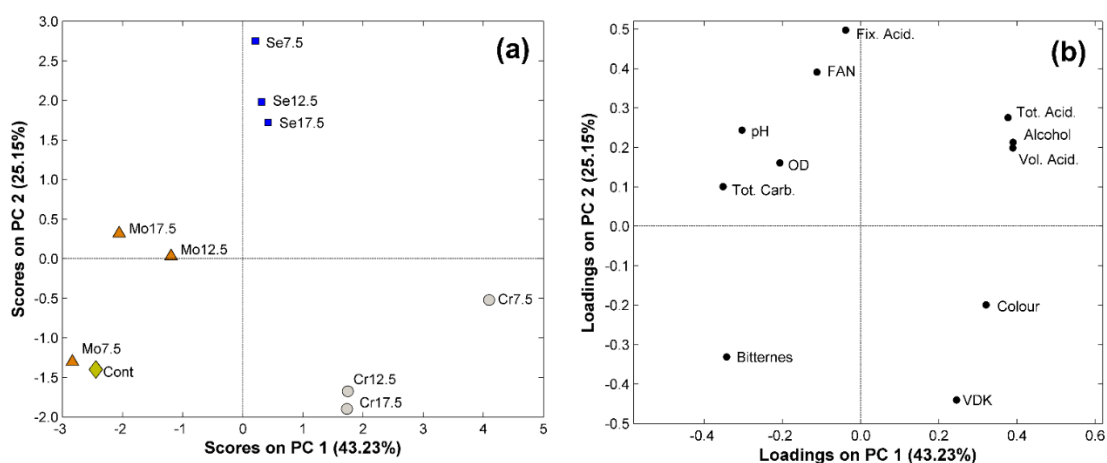


Figure 1: (a) Scores and (b) Loadings of PC1 x PC2 for PCA models for blond ale beers with addition of 7.5%, 12.5% and 17.5% of the recommended daily intake (RDI) of Se, Mo and Cr.

Keywords: Micronutrients; fermentation; Selenium; Molybdenum; Chromium

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Polyvinyl alcohol-graphene oxide membranes for removing microbial and chemical contaminants from wastewater

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A series of electrospun polyvinyl alcohol (PVA) nanofibrous graphene oxide (GO) membranes containing copper and zinc oxide nanoparticles were made as a proof-of-principle filtration device for wastewater depollution. In this work, the membranes were assayed to kill and remove waterborne pathogens and a range of chemical compounds. The nanofibrous membranes were produced using a PVA (10% w/w) with citric acid (30% w/w) as the cross-linker to provide stability in water. Then GO, copper oxide-GO (CuO-GO), and zinc oxide-GO (ZnO-GO) were incorporated into the material synthesis (1% w/w). As indicated by scanning electron micrographs, the membranes were nanofibrous and produced a microporous structure. The GO varieties were successfully attached to the surface of nanofibers making active surface membranes. The PVA control membranes were found to be more hydrophilic than the nanoparticle-GO membranes. These filters were optimised following a series of fundamental studies involving pathogen killing and chemical removal; achieving a multilayered hybrid filtration system. It was found that the best results were achieved by sandwiching the membrane layers in the following order: PVA> GO/PVA> CuO-GO/PVA> GO/PVA>PVA. The optimised filtration system removed >5-log reductions for bacteria, *Escherichia coli* 0157:H7, and fungi, *Candida auris*, from 1×10^6 CFU/mL cell concentrations. Additionally, 99% of the textile dye Rhodamine-6G (R-6G) and 76% of the antibiotic amoxicillin (AMOX) from 10 ppm concentrations were removed as part of a simulated wastewater system. The membrane system was re-used 5 times with consistent performances, with 99% regeneration capacity. The study concludes that this optimised sandwich membrane prototype effectively removes microbes and chemical contaminants as a water depollution application.

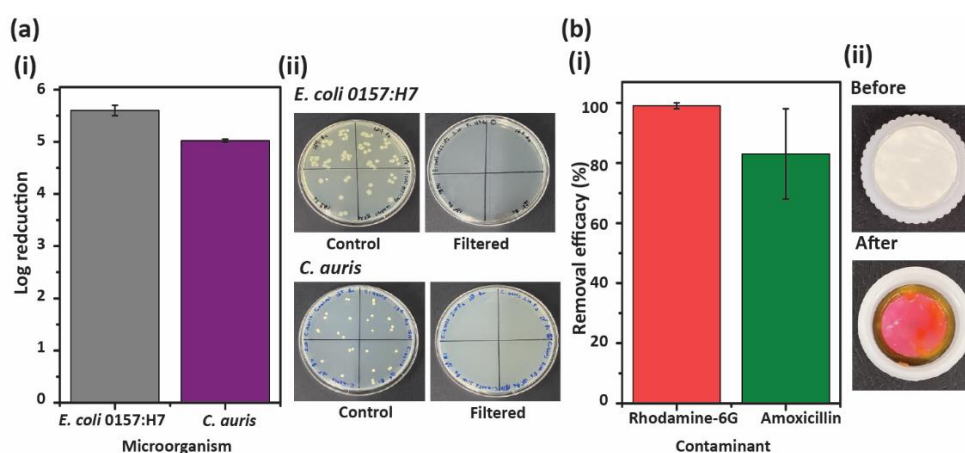


Figure: The waterborne pathogen and chemical removal performance of proposing membrane prototype. (a) (i) *E. coli* 0157:H7 and *C. auris* pathogens removal, (ii) Respective agar plates. (b) (i) R-6G and AMOX chemical removal, (ii) Photographs of membranes before and after use.

Key words: Graphene oxide, polyvinyl alcohol, electrospinning, wastewater treatment

Poster Presentations Abstracts

Influence of titanium dioxide pigment on the photodegradation of tattoo pigments

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Tattoos have long been a feature of human culture. However, as the number of people getting tattoos grows, so does the number of people wanting to remove their tattoos. Laser tattoo removal is the most effective procedure, as it works by breaking down pigments into smaller particle sizes, which are then transported away from the skin.^{1,2} Some of the breakdown products from tattoo pigments have been reported to be hazardous, poisonous, and carcinogenic particles such as benzene, benzonitrile, hydrogen cyanide and aniline. However, there is limited studies and inadequate understanding of laser basic principles and management of its variables which may lead to suboptimal results and an increased risk of side effects. Therefore, this project focuses on studying the effect of the Titanium dioxide (TiO₂) as a white pigment on the degradation products of tattoo pigments by laser. Furthermore, potential risks associated with tattoo laser removal is investigating in the present study. The degradation products are analysed using LC-MS, GC-MS, SEM&EDX, and DLS to determine the fragmentation's composition, shape, and particle size.

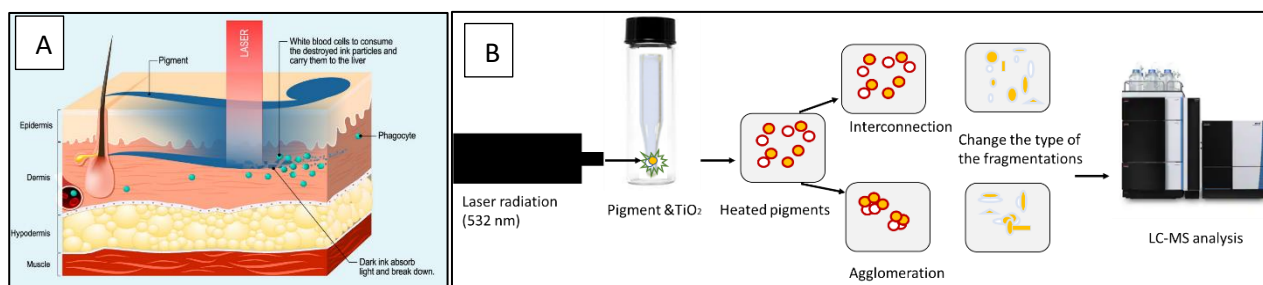


Figure: (A) Selective photothermolysis mechanism of laser tattoo removal, (B) Scheme for investigative the effect of TiO₂ on pigment degradation by laser.

Keywords: Tattoo, Pigment, Degradation, Titanium dioxide and laser.

References:

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Isolation and analysis of bioactive lipids from commercially valuable seafood

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Generally, around 25% (more than 20 million tons) of the total marine fishery catches are discarded as waste globally¹. Most of the marine fishes are sold to customers as fillets and during the filleting process, huge amounts of by-products are discarded as waste during the supply chain due to gutting, beheading, and framing like processing steps². Consequently, environmental pollution and economic loss occur along with the disposal. A considerable cost is incurred when disposing of sea food waste. Hence, identifying the potential value of seafood by-products is a key area of research interest. Briefly, the general aim of the project was to isolate total lipid from several fish species and do a comparative study to determine lipid class compositional data. In the present study, several commercially valuable seafood species and their head and rack waste materials were analysed to isolate total lipid content and determine the lipid profile. While mainly focusing on extracting total lipids and fatty acid analyses, it was also particularly interested in plasmalogen analyses and lipid class analyses such as triacylglycerol, monoacylglycerol, diacylglycerol, wax esters, and phospholipids etc. The lipid profile analysis data revealed that fish head and rack parts show more or similar profiles as the whole fish. Characteristic fatty acid profile of underutilized fish and by-products including EPA and DHA and high plasmalogen content were remarkable findings in the study and will lead to identify potential applications of seafood waste. Ultimately, the findings of the project will be supported for current market and government drivers to demonstrate sustainability and reduction of fish industry related waste and will be a guide for further investigations of identifying waste transformation opportunities into value added products.

Keywords: sea food waste, plasmalogen, fatty acids

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Programmable Melamine-based Organic Materials as Efficient Electrocatalysts for Water Oxidation

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Organic materials including both ionic and covalent materials have garnered interest recently, owing to their potential applications in areas including photovoltaics, fuel cells, catalyst-modifiers and so on. In contrast to the recent reports on the applications of covalent frameworks, organic ionic systems have largely remained unexplored especially as metal-free electrocatalysts. Herein, we have discussed melamine-based ionic and co-crystal systems having the advantages of precisely designed molecular architecture and abundant active sites, for their applicability as electrocatalysts in water oxidation reaction (WOR). The melaminium containing ionic system (BMA) exhibited superior performance achieving a current density of 10 mA cm⁻² at an overpotential of 387 mV. The enhanced activity of BMA, as compared to its neutral co-crystal counterpart could be attributed to the positively charged triazine ring resulting in an ion-pair system, π -conjugated building block, and extensive hydrogen-bonding network that accelerates charge and mass transport processes. The cumulative effects of these factors culminate in a mass activity of 26.8 mA/mg cm⁻² and a high TOF of 0.024 s⁻¹. This work validates the advantages of electron-deficient metal-free organoelectrocatalysts towards WOR, and its potential to supplant carbon-based electrocatalysts.

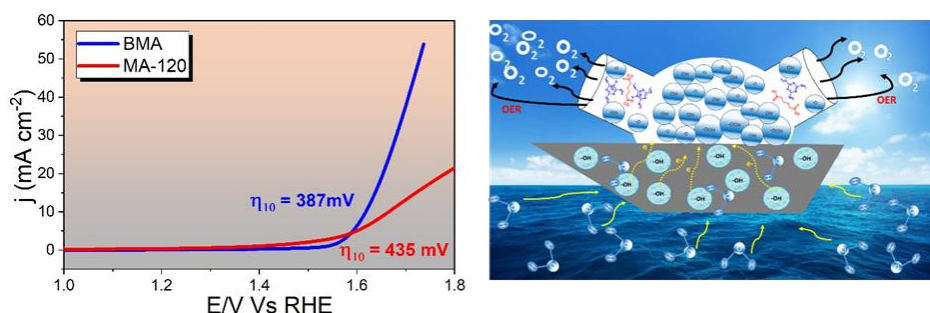


Figure. LSV curve of BMA and MA-120 for OER (left) and graphical representation of overall OER process

Keywords: triazine based, ionic systems, energy crisis, organo-electrocatalyst, water splitting

References:

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Superparamagnetic iron oxide nanoparticles for Magnetic particle imaging

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Magnetic particle imaging (MPI) is a new preclinical imaging modality that offers many advantages, such as fast acquisition times, high resolutions and penetration depth, and has been receiving much attention in the field of biomedical imaging for diagnostic purposes.¹ MPI only sees the tracer, and image contrast is solely produced by the tracer, not tissues, organs, or bones. Superparamagnetic iron oxide nanoparticles (SPIONs) are commonly used in clinics for treating anaemia and for negative contrast-enhanced MRI imaging due to their high biocompatibility, biodegradability and interesting magnetic properties.² MPI also uses SPIONs in the size range of 10 to 30 nm to generate a strong magnetisation response under the effect of static and oscillating magnetic fields.³ This ultimately detect nanoparticle distribution inside the body. Moreover, MRI is different from MPI, to the extent that the electronic magnetisation of iron measured by MPI is 22 million times stronger than MRI. Thus, designing functional tracers and exploring their utility in MPI has a broad scope as this may contribute towards finding better characterisation and treatment techniques for various diseases. I will present how the coating composition and silica shell thickness can be modulated to enhance MPI response of SPIONs. The rational design of nanoparticles and their coatings can also open new avenues for MPI-specific applications.

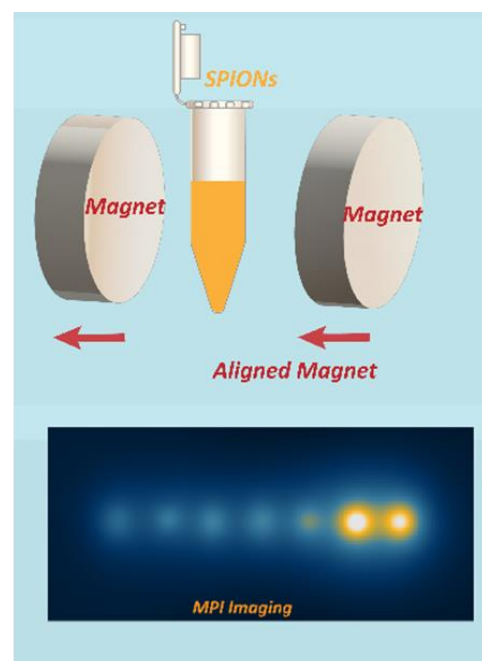


Figure: MPI response of SPIONs covered with different coating ligands

Keywords: Superparamagnetic iron oxide nanoparticles (SPIONs), Magnetic particle imaging (MPI), magnetism, surface coating and silica thickness.

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Spatial controlled chemical reaction in plasmonic nanoparticle using external stimuli

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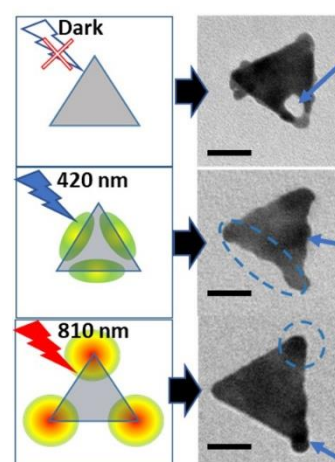
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Surface plasmons are collective oscillations of free electrons by an incident electromagnetic field and are prominently exhibited by noble metals such as Ag, Au, and Cu at nanoscale dimensions. The localised surface plasmon resonance (LSPR) resulting from this light-matter interaction leads to remarkable opto-electronic effects such as optical near field enhancement close to nanoparticle surfaces, generation of hot carriers and finally thermalization (photo-thermal effect) of the plasmon excitation. These phenomena have been of significant research interests, particularly to harness them for driving chemical reactions. Anisotropic nanoparticles such as silver nanoprisms exhibit multiple LSPR modes, like the in-plane and out-of-plane dipolar and quadrupolar modes. These modes can be selectively photo-excited using light of narrow bandwidth which leads to localised hot spots within the nanoparticle depending on the mode excited.¹ These



plasmonic hotspots also act as chemical hotspots and can be used to drive and control chemical reactions on nanoparticle surfaces. Galvanic replacement is a spontaneous reaction that occurs due to the difference in the standard electrode potential of two components participating in the reaction. The GR reaction leads to the corrosion (oxidation) of the component having the lower reduction potential, while simultaneously reduction of the second component leading to interesting nanoparticle morphologies such as nanoshells, nanocages, nanoframes.^{2, 3} We report selective photoexcitation of LSPR modes as a means to control the chemical reaction sites in silver nanoprisms by taking galvanic replacement between silver nanoprisms and chloroaurate ions as a probe for the site-selectivity.⁴ When the reaction between silver nanoprisms and chloroaurate ions is carried out under excitation of the in-plane dipole mode, the reaction occurred at the vertices of the nanoprisms; whereas it occurred at the nanoprism edges when carried out under excitation of in-plane quadrupole mode. No such site-selectivity was observed when the reaction was performed in dark conditions (no photoexcitation) We attribute this effect to hot-electron injection process at the sub-particle sites (plasmonic 'hot-spots') where localised plasmon eigenmodes drive selective reactivity. Our approach allows mapping of plasmon-driven sub-particle reaction sites with a high spatial resolution. We also probe the changes in the LSPR of Ag-Au alloy nanoprisms obtained under different photoexcitation conditions using Electron Energy Loss Spectroscopy (EELS), which reveals peculiar changes in the optical properties of the resultant bimetallic particles. The selective photoexcitation of different LSPR modes of anisotropic metal nanoparticles during a chemical reaction presents an exciting opportunity to control and spatially bias chemical reactions on the nanoparticle surface.

Keywords: plasmon, galvanic replacement, PMCR, chemical reaction, Silver prisms

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Enhancing the Electrochemiluminescence of Tris(2,2'-bipyridine)ruthenium(II) and Tri-*n*-propylamine

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The co-reactant electrochemiluminescence (ECL) reaction of tris(2,2'-bipyridine)ruthenium(II) ($[\text{Ru}(\text{bpy})_3]^{2+}$) and tri-*n*-propylamine is used for highly sensitive detection for clinical diagnostics.[1] Recent research by our group[2] has shown that the ECL intensity of this reaction can be enhanced by an order of magnitude by adding an iridium(III) complex (*fac*- $[\text{Ir}(\text{sppy})_3]^{3+}$, where sppy = 5'-sulfo-2-phenylpyridinato-*C*²,*N*). Moreover, the green emission from the iridium(III) complex can be used for internal standardisation of the red ECL of $[\text{Ru}(\text{bpy})_3]^{2+}$. The enhancement was proposed to arise from a novel 'redox mediator' pathway, although other mechanisms, such as energy transfer from the excited Ir(III) luminophore, are also possible. In this project, we examine a range of possible alternative enhancers to explore the mechanism of enhancement and design more efficient enhancers. This includes metal complexes that emit green or blue light, and several that are non-emissive, with a wide range of redox potentials.

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Phthalocyanine tattoo pigments: The effect of ageing and laser removal

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The number of individuals getting tattoos has increased recently, as has the size of tattoos people are getting. A significant part of the tattooed community have second thoughts and regret their tattoo. Therefore, the demand for laser tattoo removal has increased. Laser removal of tattoos has been reported to result in the production of potentially carcinogenic and acutely toxic compounds. Notably, hydrogen cyanide, benzene, and 1,2-benzenedicarbonitrile have been detected as degradation products after Q-switched ruby (694 nm) laser irradiation of one of the commonly used pigments, pigment blue 15 [1]. Furthermore, evidence suggests that aged pigments may degrade differently [2]. In this study, the degradation of aged phthalocyanine pigments (pigment blue 15, green 7 and green 36) was investigated to assess whether there were differences in the removal of an older tattoo compared with a fresh tattoo.

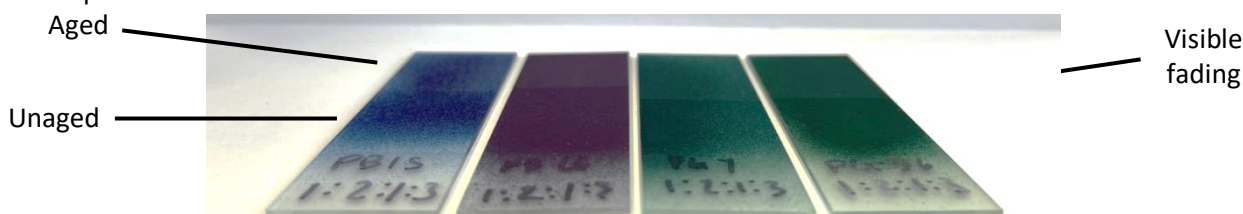


Figure 1. Pigment mixtures of copper phthalocyanine tattoo pigments, aged for 3 months under 660 nm light using the Red-Light Therapy LED. The lower half was covered with aluminium foil and kept as an unaged reference, whilst the upper areas were exposed to the red light.

The work presented here examined the effects of ageing phthalocyanine tattoo pigments under simulated light. The degradation products generated upon laser (Nd: YAG (532 nm) laser) and thermal destruction techniques were then examined. Raman analysis of the aged pigments over time was undertaken to assess any chemical structural differences as fading by ageing occurred. The Py-GCMS instrument was used to mimic the thermal breaking of bonds in the aged pigments. Similar compounds were observed in all aged and unaged pigments. This included 1,2-benzenedicarbonitrile and benzonitrile, characteristic degradation products of phthalocyanine pigments. Pigment green 7 was found to have chlorobenzene as a major degradation product upon pyrolysis, whilst both green pigments showed evidence of di- and tri- chlorine substituted benzene products. All detected compounds are likely to elicit potential toxic effects in the skin or bloodstream if present in large quantities. In summary, the potential generation of toxic products upon laser removal is evident. This research describes the toxic products that could originate from the destruction of phthalocyanine tattoo pigments. Further research should be conducted in aged tattoo pigments to aid in laser removal strategies and help in the regulations of removal procedures.

Key words: tattoos, phthalocyanine pigments, laser removal.

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Extending photocatalyst activity through choice of electron donor

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Reactivity of photocatalytic systems are generally predicted using the ground and excited state reduction potentials of the catalyst. Sacrificial additives are used in photoredox catalysis as a convenient source of electrons, but what occurs after electron transfer is often overlooked. Tertiary alkylamines initially form radical cations following electron transfer, which readily deprotonate to form strongly reducing, neutral α -amino radicals.¹ Similarly, the oxalate radical anion ($C_2O_4^{\bullet-}$) rapidly decomposes to form $CO_2^{\bullet-}$ ($E^0 \approx -2.2$ V vs SCE). We show that these reactive intermediates impact the desired photochemistry, both positively and negatively. By monitoring reductive dehalogenation reactions with high performance liquid chromatography, we identify that photoredox systems using oxalate as an electron donor can engage substrates with greater energy demands, extending reactivity past the energy limits of single and multiphoton transition metal catalysts. Using UV-vis spectroscopy we also identify the impact of photosensitization on substrate reactivity. Furthermore, oxalate offers better chemoselectivity than the commonly employed triethylamine when reducing substrates with moderate energy requirements.

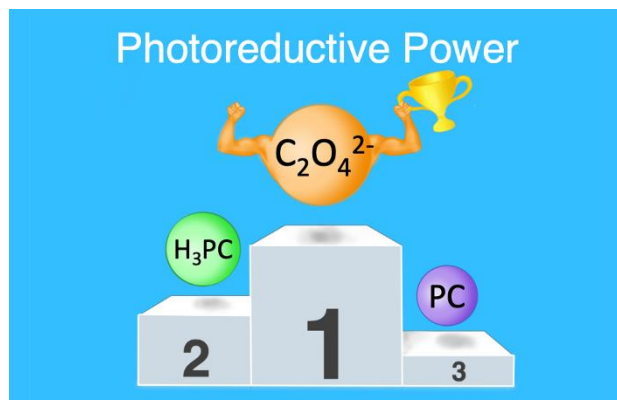


Figure: winners and loser of photocatalytic systems

Keywords: photoredox catalysis, transition metal, electron donor, CO_2 radical anion

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Development of aquaculture feed using food waste residues from an unconventional approach

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Worldwide food waste has been roughly assessed as one-third of the food production that causes from the food supply and consumption chain each year. The global food waste creates environmental impacts and food insecurity. It is estimated that the annual greenhouse gas emission is eight percent by landfilling food waste¹. Therefore, food waste management strategies and food waste recycling technologies should be implemented to mitigate the socio-economic and environmental issues. There are promising industrial approaches to minimize food waste footprint; Green Eco Technologies has introduced an innovative, efficient, and beneficial on-site food waste recycling solution using WasteMaster mechanism². The organic food waste is processed through this technique to convert waste into dry pathogen free residue that can be re-purposed the food waste as reusable resources. The focus of the study is to determine the nutritional composition of WasteMaster processed residue to as potential develop aquafeed ingredients. The global aquafeed industry is projected to reach high value-market in future, which has shown high demand for the aquafeed products. Therefore, food waste can be utilized for aquaculture feed development by reducing landfill. This framework will lessen the requirement of raw crop cultivation for aquafeed development. In the present study, the nutritional elements of processed residue are consistent with the input food waste type, which has showcased that the WasteMaster is not affecting the expected nutritional distribution. The sensitive food components including omega 3 and omega 6 fatty acids, amino acids, and phenolic compounds have been found intact in each residue material. Moreover, significant nutritional fatty acids and amino acids that are essential in the aquafeed diet have been detected in processed residue. Results suggest the high potentiality for the development of aquafeed products from processed food waste across green chemistry applications within a biorefinery setting while ensuring environmental sustainability.

Key Words: WasteMaster, Food Waste, Residues

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Microfluidic Fabrication and Characterization of core-shell Micro Polymer Inclusion Beads (μ PIBs) for Thiocyanate Extraction

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Polymer inclusion membranes (PIMs) are a green alternative to solvent extraction (SX) in the removal of thiocyanate ions (SCN^-) as they require minimal use of diluents [1]. Micro polymer inclusion beads (μ PIBs) are a recent innovation based on PIMs, with similar composition and more advantages, including a larger exposed surface area for high rates of extraction and back extraction [2]. This project aims to improve the performance of μ PIBs by fabricating them with a core-shell design using microfluidics. With poly (vinyl chloride) (PVC) as the base polymer, the PVC core will be coated in a polymer shell composed of PVC, Aliquat 336 (A336) as the extractant, and 1-tetradecanol (TD) as the plasticizer. With only the outer layer carrying the extractant, the effective diffusion distance for SCN^- would be reduced, allowing for faster extraction and back extraction. This study aims to optimise the conditions for the microfluidic fabrication of core shell μ PIBs and compare their extraction performance to conventional μ PIBs. Currently, 3 w/v % PVC as the core μ PIB solution and 45/45/10 wt% (PVC: A336: TD) in 0.4 w/v% shell μ PIB solution successfully produced core shell μ PIBs with an average shell thickness of $8.11 \pm 3.80 \mu\text{m}$.

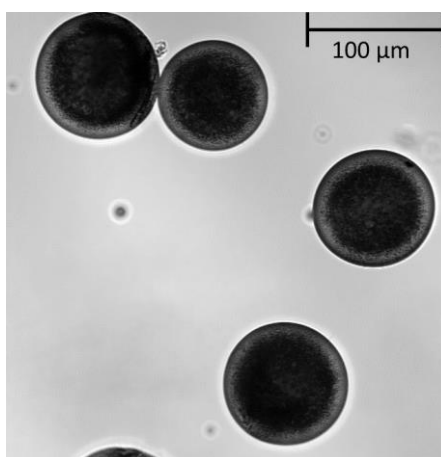


Figure: Core-shell μ PIBs imaged using a confocal microscope in brightfield (white light).

Keywords: core-shell polymer inclusion bead, polymer inclusion membranes, extraction, microfluidics, thiocyanate

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Quantification of pharmaceuticals in water and flora along an Australian river system

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Pharmaceutical pollution is known to spread into biota from surface waters of receiving environments. Research within surface waters and flora within natural environments has become a high focus overseas, with some using constructed wetlands to alleviate pollution. In the context of native Australian ecosystems however, research is limited. Here, samples from the Yarrowee / Leigh / Barwon river system were analysed for the presence of carbamazepine, primidone, propranolol, venlafaxine and tramadol within surface water and flora species. The aim of this research is to further establish and broaden the knowledge of pharmaceutical concentrations in regional Australian river systems and to establish accumulative properties for a select number of native aquatic flora species. Concentrations of tramadol and venlafaxine exceeded 500 ng/L closest to the outfall into the river system. Outfall concentrations of carbamazepine, primidone, and propranolol were observed as 498, 12.6, and 22 ng/L respectively. Concentrations of pharmaceuticals decreased with increasing distance, with some following first-order rates of decay. Carbamazepine and venlafaxine were found within the leaves of the flora species *Phragmites australis* (common weed) and *Vallisneria australis* (ribbonweed). Carbamazepine was detected in all *Phragmites australis* and *Vallisneria australis* samples with a range 11.5 ng/g to 30.5 ng/g, following a negative correlation with distance. The presence of venlafaxine was only detected in quantifiable amounts in the flora species near the outfall, with concentrations up to 22 ng/g. This research provides a basis of future research involving native flora species, with a promising avenue for the use of these flora species to aid in the remediation of pharmaceutical pollution.

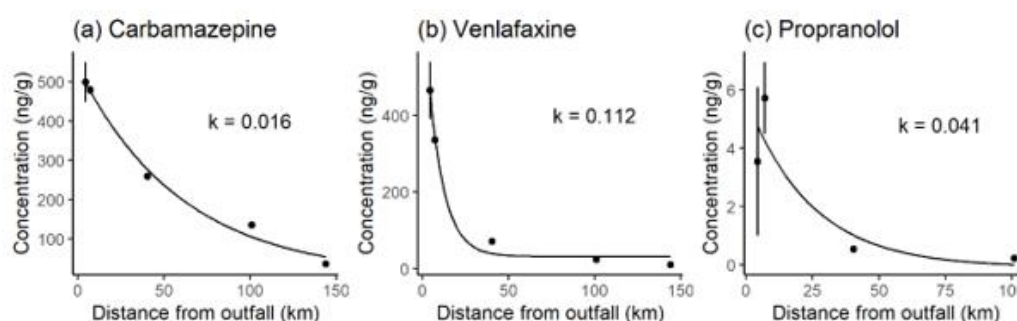


Figure: Modelled rates of decay of carbamazepine (a) venlafaxine (b) and propranolol (c) within surface water using first-order rate of decay model, $C_i(d) = a * e^{k*d}$. The decay constant (k in km⁻¹) for each curve is shown.

Keywords: pharmaceuticals, pollution, bioconcentration, riparian, macrophytes

PFAS capture using MOFs with functionalised biphenyl linkers

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Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a class of fluorinated aliphatic molecules, considered as harmful and persistent environmental pollutants. Thousands of PFAS have been identified, but the most widely referenced in literature and studied are Perfluorooctanesulfonic acid (PFOS) and Perfluorooctanoic acid (PFOA). These compounds are also bioaccumulative and very resistant to degradation due to their chemical stability. Owing to their adverse effects on human health and the environment, new and effective methods of their removal from various complex matrices needs to be developed. In this review, we focused on PFOS, and how it would most efficiently remove from environmental water using a new class of porous nanomaterials called Metal Organic Frameworks (MOFs). This study explores computational chemistry methods to screen and design mono-functionalised and bi-functionalised biphenyl linkers, which are the bridging organic linkers in the MOF UiO-67 (University of Oslo). Quantum chemical analysis vis Density Functional Theorem (DFT) and MP2 method are implemented for the structural characterisation and prediction of the thermodynamic properties of the biphenyl linkers in selective capture of PFAS. The information from quantum chemical calculations is incorporated in multiscale models to carry out Grand Canonical Monte-Carlo (GCMC) calculations in order to predict the uptake capacity of PFAS in several functionalised UiO-67 frameworks.



Figure: PFAS sources in many household products: non-stick pans, personal care products, etc.

Keywords: PFAS, Pollution, DFT, MP2, GCMC

References:

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Synthesis and characterization of luminescent heteroleptic cyclometalated iridium(III) complexes.

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Luminescent iridium(III) complexes have many applications such as biological imaging, photocatalysis, luminophores for organic light emitting diodes (OLEDs) and chemical and biological detection using electrochemiluminescence (ECL).^{1,2} Developing highly emissive novel metal complexes and exploring the electrochemical and the photophysical properties is highly beneficial for the advancement of these applications, especially for the analytical applications such as ECL-based sensors. Hence, in this work, a series of novel luminescent Ir(III) complexes is synthesized and the electrochemical and photophysical properties are explored.

Due to their high ligand field stabilisation energy (LFSE), Ir(III) complexes have tuneable redox and optical properties by altering the energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).² This can be achieved by modification of the coordinated ligands resulting in a red or blue shift in the emission maxima.² In this work, the functional group attached to the cyclometalated ligand is changed as shown in Figure 1. Furthermore, full structural characterization, absorption and emission spectroscopy, cyclic voltammetry, and annihilation and co-reactant ECL properties are being explored.

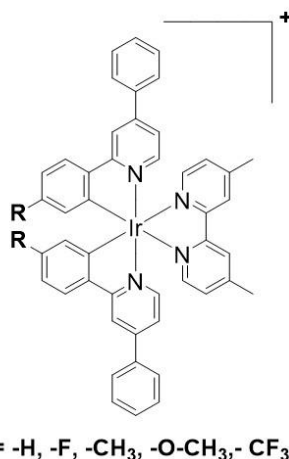


Figure 1: Structure of the synthesized cyclometalated heteroleptic Ir(III) complexes.

Keywords: luminescent iridium complexes, electrochemical and photophysical properties

References:

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Squid waste (viscera) oil processing: Enzymatic treatment to produce high quality omega-3 rich oil

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Squid viscera are non-edible 'waste' parts that are generated in large quantities by the seafood processing industry. Consequently, their valorisation is appreciated not only for preventing pollution but also for economic reasons [1]. Squid viscera consists of more than 40% of oil which contains a valuable antioxidant 'astaxanthin' and a health promoting omega-3 rich fatty acids viz. eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA). Various studies have demonstrated the extractability and processability of the oil derived from squid viscera to utilize its health benefits in complementary medicines for humans. However, in addition to having high levels of free fatty acids (FFAs), which have negative effects on the stability of the oil, squid visceral oils also frequently undergo processing that is not in favour to both human health and the environment [2]. As a result, researchers across the globe are inclined to develop alternative methods to process the squid wastes, with the rising interests in proposing safe, environmentally friendly, and green methods, that would either mitigate or eradicate the potential risks of the conventional squid waste processing [3]. Therefore, in the present work, we study an environmentally friendly processing of the squid viscera oil using immobilized biocatalyst (i.e. immobilized Lipase enzyme) in a bioreactor system to specifically reduce the high levels of free fatty acids without affecting its healthy ω -3 rich fatty acid composition. This poster examines the effects of enzymatic processing on oxidative stability of the oil to support the development of a complementary medicine for humans. We compare the fatty acid composition of oil by gas chromatography before and after the enzyme processing to ensure ω -3 fatty acids are not adversely impacted and monitor changes in free fatty acid content with enzymatic treatment using lipid class analysis.

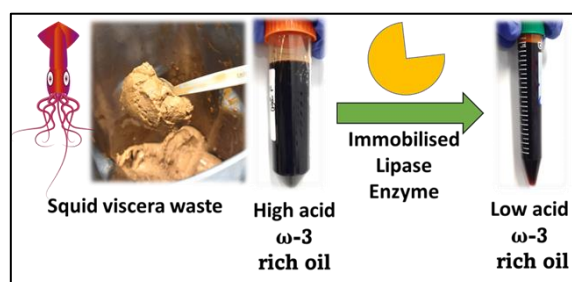


Figure: Immobilised enzyme mediated processing of Squid waste oil

Keywords: Squid, Waste, Oil, Lipase, Omega-3

References:

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Characterisation of layered double hydroxides aided by simple *ab initio* and crystallographic simulations

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Layered materials have lately called much attention, being a hot topic in materials research in the last few years. With all their advantageous features that are mostly due to their distinct physicochemical properties, especially related to their intrinsic anisotropy and diverse chemical composition, they have been applied in many different systems, from catalysis to nanocomposites for engineering materials, and also been studied for having the potential to be applied in other systems. Layered Double Hydroxides (LDHs) are a distinct class of layered materials. They are usually composed of bidimensional crystals of edge sharing metal hydroxide octahedra, $[M(OH)_6]$, intercalated with other species in the interlayer space, whose composition depends especially on the chemical composition and electrostatic properties of the 2D metal hydroxide layers. Whereas LDHs usually present positively charged layers, intercalating anions, a few layered materials might also intercalate cations along with anions, such as motukoreaite and other shigaite-like minerals. For being relatively new and presenting this peculiar feature, more research on these materials is still to be done in order to find more possible applications for them in technology.

Characterising these materials is therefore of great importance when developing and studying the many materials of this class. FTIR spectroscopy, for instance, may provide sensitive information of these materials, especially with regard to the interlayer space chemical environment, that might be the main interest depending on the application of the layered material, however, properly attributing the bands in the spectra might present a challenge, and it is usually done by comparing with previous works. Recently^[1] we showed that the use of basic computational chemistry as well as visualisation programs for structural models and crystal engineering might present a good help for attributing the FTIR bands, aiding the elucidation of structures, chemical interactions and geometrical properties of the chemical species present in the materials—especially in the interlayer space—and therefore contributing to the understanding of the chemical behaviour of the material.

In this work we describe the synthesis and characterisation of a negative result for obtaining a cation-exchanging motukoreaite phase intercalated with ammonium and sulphate^[2] and a MgAl LDH intercalated with carbonate, comparing the XRD and FTIR results with the computational results obtained by crystal engineering and *ab initio* quantum chemistry for interpreting experimental results.

Keywords: layered materials, layered double hydroxides, characterisation, visualisation, theoretical chemistry.

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Label-free detection of viral disease agents through their cell surface proteins: Rapid screening SARS-CoV-2 in biological specimens

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Current methods for the screening of viral infections in clinical settings, such as reverse transcription polymerase chain reaction (RT-qPCR) and enzyme-linked immunosorbent assay (ELISA), are expensive, time-consuming, require trained personnel and sophisticated instruments. Therefore, novel sensors that can save time and cost are required specially in remote areas and developing countries that may lack the advanced scientific infrastructure for this task. Here we present. In this work, we present a sensitive, and highly specific biosensing approach for the detection of harmful viruses that have cysteine residues within the structure of their cell surface proteins. We utilized new method for the rapid screening of SARS-CoV-2 virus in biological fluids through its S1 protein by surface enhanced Raman spectroscopy (SERS). The protein is captured from aqueous solutions and biological specimens using a target-specific extractor substrate. The structure of the purified protein is then modified to convert it into a bio-thiol by breaking the disulfide bonds and freeing up the sulfhydryl (SH) groups of the cysteine residues. The formed biothiol chemisorbs favorably onto a highly sensitive plasmonic sensor and probed by a handheld Raman device in few seconds. The new method was used to screen the S1 protein in aqueous medium, spiked human blood plasma, mucus, and saliva samples down to 150fg/L. The label-free SERS biosensing method has strong potential for the fingerprint identification many viruses (e.g. the human immunodeficiency virus, the human polyomavirus, the human papilloma virus, the adeno associated viruses, the enteroviruses) through the cysteine residues of their capsid proteins. The new method can be applied at points of care (POC) in remote areas and developing countries lacking sophisticated scientific infrastructure.

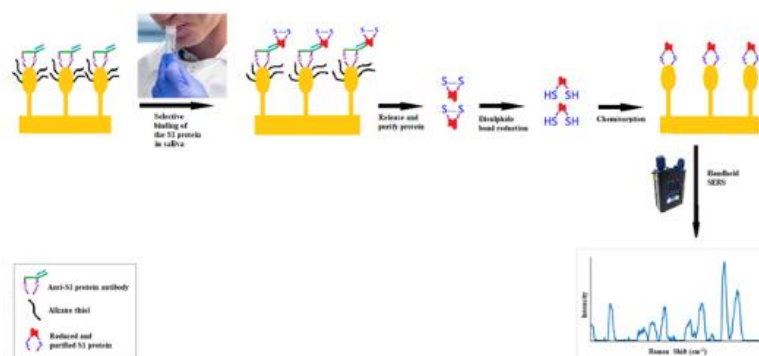


Figure 1: Graphical abstract of experimental method.

Keywords: S1 protein, viral capsid proteins, thiol chemistry, label-free SERS, saliva, human blood plasma.

Heavy metal concentrations in three species of ducks from south-eastern mainland Australia.

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Heavy metals are pollutants of increasing concern in aquatic systems. These contaminants are found in increasing concentrations in waterways since they are often found in industrial effluents and agricultural runoff. These chemicals bioaccumulate in the food web, potentially causing harmful effects on avian species such as ducks through processes ranging from eggshell thinning to mortality. In Australia, studies of heavy metal exposure levels in waterbirds are limited. The aim of this study was to determine the body burden of heavy metals in Pacific black ducks, *Anas superciliosa* (PBD), grey teal, *Anas gracilis* (GT), and Australian wood duck, *Chenonetta jubata* (AWD). Breast feathers of ducks residing in the same location were collected, dried, and digested; and inductively coupled plasma-mass spectroscopy (ICP-MS) was used to measure heavy metal concentrations. The results showed that GTs tended to have higher heavy metal concentrations than the other two species, except for Cd. Mercury concentrations were significantly higher in GTs than in AWDs and PBDs. This was partially expected due to differences in feeding ecology, with GT being highly nomadic and dispersing more widely than the other two, more sedentary, species. This study provides important information on current trace metal levels in Australian freshwater systems.

Keywords: Ecotoxicology, Heavy metals, waterfowl, ducks, and environment

Development of a novel microfluidic paper-based ethanol sensor

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Microfluidic paper-based analytical devices (μ PADs) exploit the ability of cellulose fibres in paper to transport liquids via capillary forces. Such devices accommodate the expanding demand for rapid, accurate and low-cost environmental and clinical monitoring¹. This work demonstrates the development of a paper-based sensor incorporating the interaction between two triarylmethane dyes - ethyl violet and malachite green - and Nafion membrane for the determination of ethanol content in alcoholic beverages. Triarylmethane dyes belong to a class of synthetic polymethine dyes which has been widely applied in cell staining, dyeing and as indicators. Nafion is a perfluorinated sulfonic acid polymer developed in the 1970s. The acid-base properties of the dyes which were immobilised in Nafion were found to change when ethanol was present, which then resulted in a colour change. This ethanol sensor was characterised by a working range from 2.5 – 60 % (v/v) with analysis time per sample of 3 min. The sensor is advantageous in offering in-situ monitoring whilst requiring no sample pre-treatment, which is commonly required by conventional alcohol determination methods.

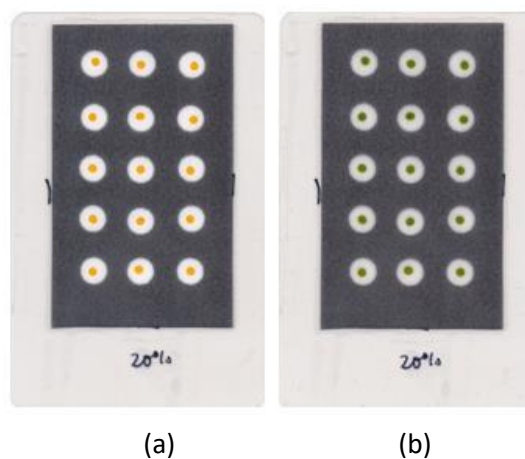


Figure 1: Scans of the proposed microfluidic paper-based device. (a) Before introduction of ethanol. (b) After introduction of ethanol.

Keywords: Microfluidic paper-based device (μ PADs), ethanol detection, Nafion[®], alcoholic beverages

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Metal-Organic Framework/Polymer Coatings on Solid-Phase Extraction Frits for the Preconcentration of Phenols.

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Metal-organic frameworks (MOFs) are an exciting class of crystalline materials based on the coordination of metal ions or clusters with rigid organic linkers, creating extended ordered networks. Due to their large surface area, low density, and tunable composition, MOFs have been widely studied. However, due to their small size and non-spherical morphology, it is challenging to fully utilise MOFs properties for extraction or separation applications, requiring additional MOF processing strategies such as growth of MOFs on beads, monoliths, or membranes.

We present for the first time the application of metal-organic framework (MOF)/polymer coatings on commercial frits for the solid-phase extraction of environmental pollutants. Zirconium 2-aminoterephthalate UiO-66-NH₂ MOFs have been immobilized in commercially available polyethylene frits with the help of polyvinylidene difluoride as polymer binder. The performance of the resulting frits has been evaluated for the SPE of six phenols from water samples. Extraction efficiency increased towards the less polar analytes, making it an ideal material for the preconcentration of hydrophobic phenols, such as the endocrine disrupting 4-nonylphenol.

Typical SPE columns require sorbents based on beads with a size ranging from 50 µm to 150 µm, which are packed in between two porous frits. The developed MOF/polymer frits can be prepared with micro/nanomaterials regardless their particle size and shape, and the frits can be simply introduced in an empty SPE cartridge and directly applied.

Keywords: Zirconium 2-aminoterephthalate, polyethylene frits, solid-phase extraction, phenols.

Classifying Cheddar cheese based on maturity level and manufacturer using vibrational spectroscopy and chemometrics.

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Cheese is a nutritious dairy and an important commodity. Cheddar cheese is the most produced and consumed variety around the world, and the main one exported for Australia, figuring as the second most important in the agricultural sector, after meat. Despite its importance, the analytical methods to determine cheese quality rely on traditional, time and hazard chemical consuming, and requires qualified persons. Spectroscopic techniques provide instantly many molecular information, are non-destructive, fast, chemical-free methods. Combined with pattern recognition methods (chemometrics), they can identify small changes in composition or condition of cheeses. In this work, we combined FTIR and Raman with Principal Component Analysis (PCA) to investigate the effects of ageing in commercial Cheddar cheeses. Changes in the amide I and II bands were the main spectral characteristic responsible for classifying commercial Cheddar cheese based on the ripening time and manufacturer using FTIR, and lipids bands were more relevant changes in Raman spectra.

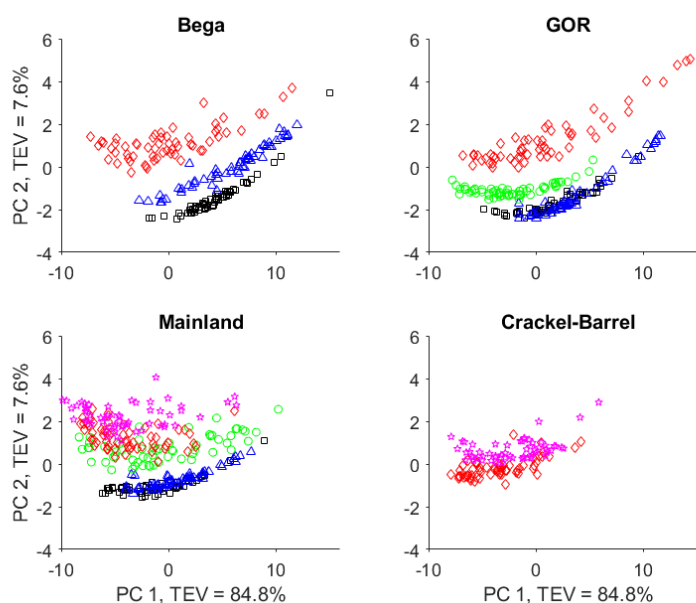


Figure: Score plot of PCs 1 x 2 of Bega, Great Ocean Road (GOR), Mainland and Cracker-Barrel Cheddar cheese FTIR spectra. Black square = Colby; blue triangles = Tasty; green circle = Extra-tasty; red diamond = Vintage; magenta stars = Epicure. TEV = total of explained variance.

Keywords: Ripening, Cheddar cheese, Spectroscopic techniques, Chemometrics.

TiO₂/CoAl-LDH nanocomposites for CO₂ photoreduction

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In 2017, 80% of global energy was produced by burning fossil fuels [1]. It is anticipated by 2040 that global energy demand will increase by 28%, with CO₂ levels reaching 750 ppm by 2050. This will increase average global temperatures by 2.7 °C with severe consequences for climate change [2]. Sunlight is the most abundant renewable energy source on Earth, providing 100000 TW per annum, exceeding annual global energy consumption [3], and hence offers a means to transitioning away from reliance on fossil fuels. Mimicking biological photosynthesis, inorganic semiconductors can harvest light energy to enable charge separation, and thereby drive the photocatalytic reduction of CO₂ and water to hydrocarbons [4].

Herein, cobalt aluminium layered double hydroxides (LDHs) were synthesized via coprecipitation and hydrothermal methods [5] to produce visible light photocatalysts with solid basicity. A modified alkali-free coprecipitation method produced pristine CoAl LDHs with 6 times greater surface area and CO₂ adsorption capacity than hydrothermal CoAl LDHs, reaching 120 m²/g and 91 μmol/g respectively. Physicochemical and optical properties of CoAl LDHs were tuned by tailoring the Co:Al molar ratio. Increasing Co:Al ratio from 1.3 to 3.2 lowered the band gap from 1.5 eV to 0.7 eV. At Co:Al ratios >2.3, limited availability of Al³⁺ ions and an abundance of Co²⁺ ions increased the proportion of tetrahedrally coordinated Co²⁺ ions in the hydroxide sheets, and increased absorbance in the near infrared region. High Co loadings can also induce defects and vacancies in the hydroxide layer to promote CO₂ adsorption and act as charge trap sites. To improve separation of photoexcited charge carriers, UV light active P25 was introduced to form P25-CoAl LDH nanocomposites [6]. Initial CO₂ photoreduction in a liquid phase batch reactor evidence photocatalytic activity of P25-CoAl LDHs exceeding that of either component. Fine-tuning of CoAl LDH surface and optical properties through heterojunction formation with TiO₂ to increase the interfacial contact area and CO₂ adsorption capacity is a promising route to an effective CO₂ photoreduction system.

Keywords: Photocatalysis, CO₂ conversion, Solar to fuel, Artificial photosynthesis

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Zirconia solid acid catalysts for sustainable chemical manufacturing

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Biomass conversion is of great importance for sustainable chemical manufacturing, whereby biofuels and specialty chemicals are generated from naturally produced biomass waste. Mesoporous solid acid catalysts are considered one of the most viable solutions to be applied in biomass conversion reactions since they offer high surface area, large pore diameters and tunable acidity. Zirconia, a polymorphic white crystalline ceramic material, is a promising catalyst or catalyst support due to its hydrothermal stability, amphoteric character, and possibility to tune acidity with dopants.

However, the wider application of ZrO₂ catalysts requires rational design to unravel structure-activity relationships and maximize catalytic productivity. In this study, pure monoclinic and tetragonal zirconia families with surface area of ~90 m²/g were synthesized and their physicochemical properties, such as porosity, microstructure, evolution of acid-base sites as a function of morphology, and hydrothermal stability determined. Sulphated ZrO₂ (SZ) families were also synthesized by doping zirconia with H₂SO₄ to enhance solid Brønsted acidity, while ZrO₂/SBA-15 families were synthesized using mesoporous SBA-15 frameworks to enhance ZrO₂ dispersion.

Levulinic acid is classified by the US DoE^[1] as a valuable platform chemical that is readily obtained by the dehydration of glucose, and is a precursor to the renewable solvent γ -valerolactone (GVL) (Figure 1). The production of GVL from levulinic acid proceeds via the Meerwein–Ponndorf–Verley (MPV) reduction reaction using iso-propanol as a hydrogen donor. The activity of these zirconia catalysts will be reported in both batch and continuous flow systems for the conversion of levulinic acid to GVL. Dual bed configurations will be explored in continuous flow reactors employing SZ and ZrO₂/SBA-15 catalysts for the tandem esterification of levulinic acid and subsequent MPV reduction to enhance the continuous production of GVL.

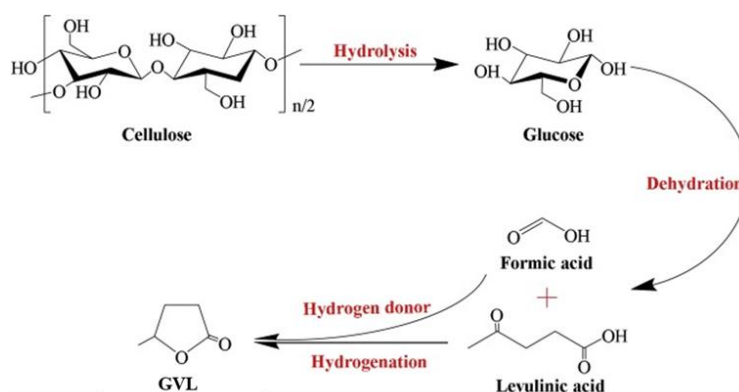


Figure 1: Proposed reaction pathways for the acid-catalysed hydrolysis of cellulose to GVL^[2]

Keywords: Heterogeneous catalysis, zirconia catalysts, biomass conversion

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Understanding the effects of ochre pigment processing on the physicochemical 'fingerprint'

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Ochre is a group of naturally-occurring red/yellow iron oxide/hydroxide based mineral pigments that commonly include several other minerals simultaneously such as silicates, carbonates, and clays (1). Within Australia, Indigenous communities have used ochre pigments for tens of thousands of years (2). Analysis of the physicochemical 'fingerprint' of Australian archaeological ochre pigments can be used to postulate their origin, as well as to obtain insight into archaeological exchange systems and cultural practices (3, 4). For example, researchers can compare factors such as variation in the composition (e.g. mineralogical profile, elemental composition) or physical profile (e.g. colour, particle size, morphology or other aspects) of ochres from a non-quarry setting to ochres from a known geological site (2, 3). However, it is known that ochre pigments may undergo various forms of cultural processing such as heating, grinding and/or mixing with binders or other pigments which may have altered the physical properties and chemical composition of the archaeological ochre (2-8). Such cultural alterations of ochre remain a complicating factor for postulation of origin, as the altered composition may not reflect the original source. This research has used Synchrotron XRD, FTIR, Py-GC-MS, microscopy, and colour studies to provide an insight into the effects of cultural processing on the physicochemical fingerprint of Indigenous Australian archaeological ochre. Factors including the effect of slow and rapid heating, grinding, and mixing with binders on the physicochemical profile have been studied. This presentation will highlight some of the key results obtained to date.

Keywords: Ochre, Physicochemical Properties, Australian Archaeology, Pigment Processing

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Cyclodextrins as chiral phase mobile additives in open-tubular liquid chromatography with a pseudophase coating

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The chiral separation of various anionic analytes (dichlorprop, mecoprop, ibuprofen, and ketoprofen) was demonstrated using different cyclodextrins (CD) as mobile phase additives in open-tubular liquid chromatography (OT-LC) using a stationary pseudophase semipermanent coating. The stable coating was prepared by a successive multiple ionic layer approach using poly(diallyldimethylammonium chloride), polystyrene sulfonate, and didodecyldimethyl ammonium bromide [1]. Increasing concentrations (0–0.2 mM) of various native and derivatized cyclodextrins in 25 mM sodium tetraborate (pH 9.2) were investigated. Chiral separation was achieved for the four test analytes using β -CD (resolution between 1.11 and 1.34), γ -CD (resolution between 0.78 and 1.27), carboxymethyl- β -CD (resolution between 1.64 and 2.59), and 2-hydroxypropyl- β -CD (resolution between 0.71 and 1.76) with the highest resolutions obtained with 0.1 mM carboxymethyl- β -CD. This is the first demonstration of chiral OT-LC using achiral chromatographic coatings and cyclodextrins as mobile phase additives [2].

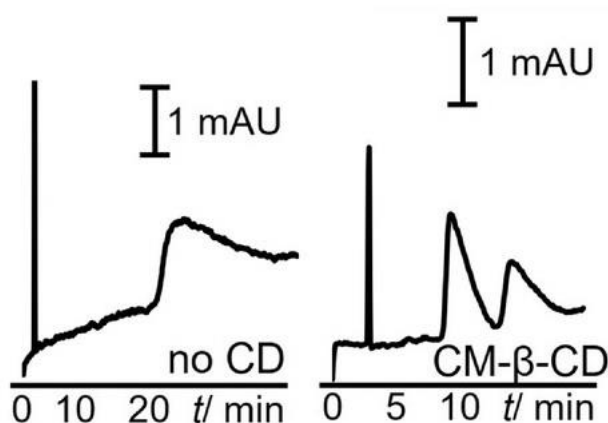


Figure 1: Representative OT-LC analyses of ibuprofen in a SMIL pseudophase coating without (left) and with (right) carboxymethyl- β -CD in the mobile phase

Keywords: chiral separation, cyclodextrin, open-tubular, liquid chromatography, semi-permanent coating

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Gold Nanoparticle Decorated Covalent Organic Polymers; Electrocatalysts for Water Splitting in Alkaline Medium

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The design and construction of a bimodal catalyst with magnificent performance and high stability is a debatable one for total water splitting. Herein, we report the synthesis of a covalent organic polymer network based on 1,4-phenylenediamine based covalent organic polymer (PD-COP) and its decoration with Au nanoparticles (Au NPs) as well as their confirmation using various analytical and surface techniques. The electrocatalytic activity toward total water-splitting reaction (OER and HER) in KOH solution (1.0 M) was investigated. Among the different electrocatalysts (PD-COP, Au@PD-COP-I, Au@PD-COP-II, Au@PD-COP-III and Au@PD-COP-IV) studied in this work, the Au@PD-COP-II demands a low overpotential of 288 mV and 184 mV to attain a 50-mA cm⁻² geometrical current density with a lowest Tafel slope value of 56 and 85 mV/dec for OER and HER respectively. From the OER and HER phenomenal activity, a two-electrode system was constructed, and it needs a cell voltage of 1.615 V to conquer a current density of 10 mA cm⁻² with outstanding stability for 34 h. The high electroactivity of Au@PD-COP-II may be allied with the presence of innumerable redox-active sites and high electrochemical active surface area (ECSA) towards effective water electrolysis.

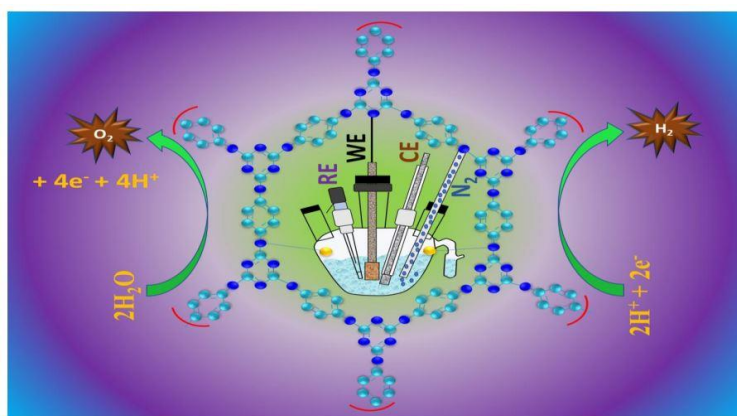


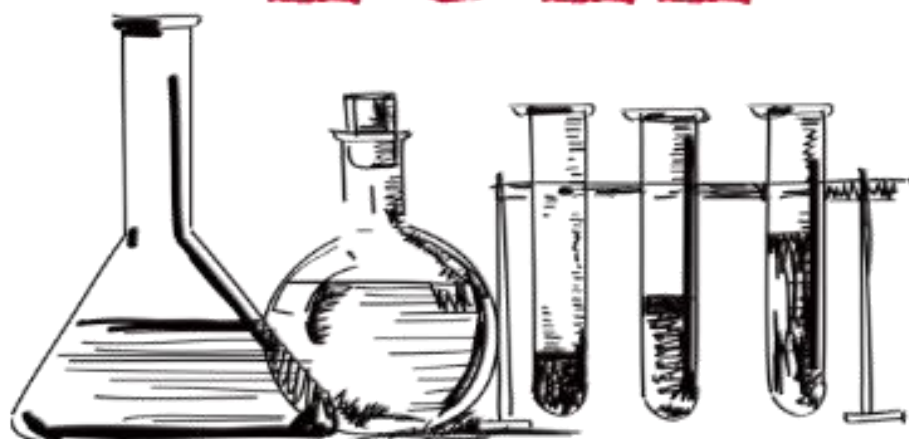
Figure: TOC represent the Au NPs decorated POP for Total Water Splitting reaction.

Keywords: Covalent organic polymer; Total water splitting; Gold nanoparticles.

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