

# The sensory world of bees

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ALSO IN THIS ISSUE: • One X-ray technique better than two• Haber's rule and toxicity • Madeira wines worth the wait

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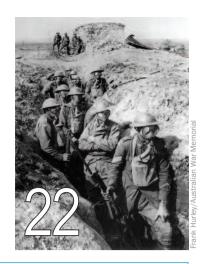
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Royal Australian Chemical Institute

# chemistry in Australia

# June 2015



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# Research and reviews roll on

You may have noticed that someone new is steering the Research section here at *Chemistry in Australia*. After nine years at the helm, Matthew Piggott compiled his final Research highlights for the April edition. Matthew joined the magazine's management committee in 2005 and soon after suggested starting a Research highlights section: 'I had always enjoyed reading the Science and Technology Concentrates in *C&EN*; the Research column was inspired by that.' The committee and the magazine have been very lucky to benefit from Matthew's good ideas and hard work since then.

In Matthew's first batch of Research highlights, CSIRO's Chris Elvin and colleagues summarised their research (published in *Nature*, doi: 10.1038/nature04085) into production of a semisynthetic version of resilin, the rubbery cross-linked protein found in the legs of some insects (see picture). 'Synthetic resilin has potential for medical use in situations requiring a resilient elastomer with a long fatigue lifetime,' said the authors in the February 2006 edition of *Chemistry in Australia* (p. 33).

In 2013, Linqing Li and Kristi Kiick at the University of Delaware reported on recent developments in resilin's biomedical applications (*ACS Macro Letters*, doi: 10.1021/mz4002194): 'The outstanding mechanical properties of natural resilin have motivated recent research in the



engineering of resilin-like polypeptide-based biomaterials, with a wide range of applications including use as biorubbers, nanosprings, elements in biosensors, and tissue engineering scaffolds.'

Matthew thanks those who have contributed research summaries for publication – particularly those who did so on their own initiative and who took note of style and word length! He is also thankful to the many people who provided positive feedback. Matthew hopes that:

... researchers have valued and will continue to value the opportunity to publicise their work among the RACI



community, and that the readers have enjoyed finding out about what the heavy hitters are up to. My apologies if I've annoyed anyone with my editorial tinkering, and sorry to those whose work I was unable to include.

David Huang, a senior lecturer in the chemistry department at the University of Adelaide and treasurer of the RACI's South

Australian Branch, revealed his inaugural Research highlights in the May edition, and we look forward to many more. Ever since his undergraduate days editing student publications at the University of Sydney, David has had an interest in journalism and in science communication in particular. Compiling the column, he says, will be a good way to pursue these interests, while becoming acquainted with the many chemists in Australia doing cutting-edge research. He thinks that the section can help to inspire chemists by making them aware of



David Huang

Matthew Piggott



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Contributors' views are not necessarily endorsed by the RACI, and no responsibility is accepted for accuracy of contributions. Visit the website's resource centre at chemaust.raci.org.au for information about submissions.

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developments in other fields. David comments that the Research highlights section:

... provides an important service by collating outstanding new Australian research from across all chemistry disciplines. The scale of chemistry research in Australia is small compared with that in many other countries, and it can be easy to forget how much excellent research is done here – I think it's important that this excellence be acknowledged.



Those with sharp eyes will have noticed a new addition to our contacts section: Damien Blackwell is our new book review editor. Damien is the president of the RACI's Tasmanian Branch and has served on that

Damien Blackwell

branch committee for more than 10 years. For *Chemistry in Australia*, he is busy sourcing books and other resources for review, and finding homes for them. We are grateful for his services and those of a good number of reviewers from a range of professional backgrounds.

Damien relishes opportunities to read and write, and enjoys the review process and providing constructive feedback, whatever the subject matter. He appreciates the opportunity to:

... be exposed to a new group of scientists, their styles, interests, interpretation and knowledge of chemistry.

The research landscape is always changing. Clearly, Matthew, David and Damien want to be part of this. What's more, they all enjoy and see the importance of an involvement in the RACI that is greater than membership alone. This magazine, the Institute and its members are so much richer for it.



Sally Woollett (editor@raci.org.au) With thanks to Matthew, David and Damien for their contributions to this editorial.

#### Adding colour to Yellowstone's thermal springs

This is a brief historical comment on the item on the March news item 'Yellowstone's thermal springs – their colours unveiled' (p. 8) originally from the American Institute of Physics. It may not only be tourists in recent years who have changed the colours of the thermal springs with discarded coins and detritus.

There is the case of R.W. Wood, a brilliant experimental physicist and practical joker, throwing a bottle of fluorescein into the Emerald Spring at Yellowstone in 1892 when on his honeymoon. As a result, the pool 'was glowing in the hot sunshine with the brilliance and colour of an emerald', which amazed the other tourists and the guide (Seabrook W. *Doctor Wood, modern wizard of the laboratory: the story of an American small boy who became the most daring and original experimental physicist of our day – but never grew up New York: Harcourt, Brace and Company, 1941, pp. 47–8).* 

William P. Palmer FRACI CChem

#### Chemists, laborateurs and pharmacists

The letter from Chris Embery (April issue, p. 5) and the President's message (Dec 2014/Jan 2015 issue, p. 4) reminded me that when I joined the staff of the South Australian Brewing Co Ltd in Adelaide in early 1946, it was with the title 'assistant brewer and analyst'. Although the company was then expanding its laboratory facilities, the title 'chemist' was not used (nor was it employed for about 30 years thereafter), as it was considered that its use may support the then prevalent, but ignorant, rumours about the existence of 'chemical beer'. Another major Australian brewing company then used the French term *laborateur* rather than 'chemist'.

In an association spanning nearly seven decades with the beverage and food industries in Australia, plus involvement with RACI and other relevant professional associations, I can recall various attempts to improve the general level of scientific literacy among the general public and of food and beverage consumers in particular. There is no doubt that education is the key but obviously there is much still to be done to dispel the myths surrounding 'chemicals' and to discourage the use of terms such as 'chemical free' and others with similar connotations. It is encouraging to note from the President's message that the Decadal Plan for Chemistry, initiated by the Australian Academy of Science's National Committee on Chemistry, recognises the importance of education and, to use the President's phrase, of 'taking our word back'.

The confusion that still exists regarding the roles of 'the chemist' and 'the pharmacist' still remains to some extent ... but that is another story!

John Harvey FRACI CChem

#### Colour and cyanobacteria

I enjoyed reading 'A spectrum of seasonal change' by Colin Scholes (April issue, p. 14). It reminded me of work I did on nutrient-rich eutrophic ponds. The idea was to add 'dye' to inhibit cyanobacteria. We found pine bark leachate absorbs at about the same wavelength preferred by blue-green algae. I first became interested in this by noticing that 'tea-coloured' waters, as at Tidal River, Victoria, don't appear to suffer from algae blooms. Experiments on a treated wastewater storage lagoon in South Gippsland found that salinity and pH fluxes, induced by adding sea water, were effective in controlling algal densities (August 1997 issue, p. 6).

Max Thomas

#### **Pantone colours**

Many thanks for your note about Pantone colours in the April issue (p. 4).

The initiation and batch matching of requisite printed colours to a Pantone standard is a basic in label design and periodic receipt of the printed labels. There would be many chemists who have needed to acquire working knowledge of their use in their day-to-day dealings with marketing personnel and printers for labels, logos and advertising copy.

Ultimately, Pantone colours rely on the inertness of their components and packaging/containment to maintain their integrity, analogous with any other chemical reference standard. As such, their storage conditions must minimise any effects of light, humidity and heat.

David Edmonds FRACI CChem

#### Colours and 'chemical free'

*Chemistry in Australia* of April 2015 is another masterpiece as collaged by the Editor, Sally Woollett. Members of RACI are fortunate to receive monthly editions of high quality and variety that will appeal to the whole membership. Personally, I start with Ian Rae's 'Letter from Melbourne' and then the obituaries, this being a symptom of my ageing.

None-the-less, over the month I read cover to cover, enjoy and learn something new.

The cover of autumn leaves includes a purple leaf, which is not as common as the reds, oranges, yellows and browns with which we in suburban Melbourne are familiar. This purple colour finds its way into the editorial where Sally's favourite colour is Pantone 2058. Officially, Pantone 2058 is known as 'Crocus' but to my eyes it is strongly reminiscent of the colour mauve (Pantone Mauve Mist 15-3207 TPX) a popular clothing colour of the 1950s and early 1960s. Unfortunately, in 2000s Melbourne you can be clothed in any colour as long as it is black (paraphrased from Henry Ford's early 1900s famous quote regarding his Model T Ford.)

Mauve is virtually unknown to today's children, and some other words from that 1950s era have a completely new meaning as expressed by Chris Embery in his letter 'Dangers of "chemical free''' (April issue, p. 5). It makes me wonder what Henry Bolte and Arthur Rylah would have done with the book *The gay provider* by Alan Marshal, published by F.W. Cheshire in 1961 (subtitled *The Myer story*, i.e. Myer Emporium), with the present day meaning.

As a chemist of over 50 years in the food and pharmaceutical industries, I am extremely perturbed by the highjacking of the ancient word 'organic'. I support Chris completely but we chemists lost the race many years ago. At this time, Standards Australia are reviewing Australian Standard AS6000 – Organic and Biodynamic Products. This Standard contains lists of food additives that may be used in manufactured foods that can be approved as 'organic' even though many of these additives are inorganic or synthetic.

Tony Zipper FRACI CChem

#### Knowledge versus thinking

Professor Ian Chubb was quoted in the March issue (p. 32). Of chemistry: 'It's more than a discipline, said Chubb, it's a way of thinking.'

This reminded me of Richard Dawkins' essay 'Science, Genetics and Ethics: Memo for Tony Blair' from about 12 years back (*A devil's chaplain: reflections on hope, lies, science, and love,* Mariner Books, 2004). In this essay, Dawkins wrote:

Senior Ministers could be forgiven for seeing scientists as little more than alternate igniters and quenchers of public panic. If a scientist appears in a newspaper today, it will usually be to pronounce on the dangers of food additives, mobile phones, sunbathing or electricity pylons. I suppose this is inevitable, given the equally forgivable preoccupation of citizens with their own personal safety, and their tendency to hold governments responsible for it. But it casts scientists in a sadly negative role. And it fosters the unfortunate impression that their credentials flow from factual knowledge. What really makes scientists special is less their knowledge than their method of acquiring it – a method that anybody could adopt with advantage.

Later in the same issue of *Chemistry in Australia*, in 'Why students should study STEM', Kieran F. Lim writes that: 'Studying chemistry develops critical thinking skills such as synthesising and evaluating information, record-keeping and documentation skills, and the ability to interpret data and use evidence to support a line of reasoning.'

In other words, what makes scientists and especially chemists special is less *what we know*, important though that may be, but rather *how we think*.

This is now more important than ever because most of the knowledge that used to be the preserve of the scientific research section of a university library is now visible to anyone with a broadband connection. Journalists – and politicians – are adept at grabbing this knowledge, often out of context, for purposes not always aligned with the welfare of the community or its citizens. This makes it all the more important that, when representing our profession, we must not let the media use us as just an 'expert witness', which, in Dawkins' words, would be 'as though one met Picasso and devoted the whole conversation to the dangers of licking one's brush. Or met Bradman and talked only of the best box protector to put down one's trousers.'

Nigel Simpson MRACI CChem

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### NASA Mars rover's weather data bolster case for brine

The Rover Environmental Monitoring Station (REMS) on NASA's Curiosity Mars rover includes temperature and humidity sensors mounted on the rover's mast. One of the REMS booms extends to the left from the mast in this view. Spain provided REMS to NASA's Mars Science Laboratory Project. The monitoring station has provided information about air pressure, relative humidity, air temperature, ground temperature, wind and ultraviolet radiation in all Martian seasons and at all times of day or night.

Martian weather and soil conditions that NASA's Curiosity rover has measured, together with a type of salt found in Martian soil, could put liquid brine in the soil at night.

Perchlorate identified in Martian soil by the Curiosity mission, and previously by NASA's Phoenix Mars Lander mission, has properties of absorbing water vapour from the atmosphere and lowering the freezing temperature of water. This has been proposed for years as a mechanism for possible existence of transient liquid brines at higher latitudes on modern Mars, despite the red planet's cold and dry conditions.

New calculations were based on more than a full Mars year of temperature and humidity measurements by Curiosity. They indicate that conditions at the rover's near-equatorial location were favourable for small quantities of brine to form during some nights throughout the year, drying out again after sunrise. Conditions should be even more favourable at higher latitudes, where colder temperatures and more water vapour can result in higher relative humidity more often.

'Liquid water is a requirement for life as we know it, and a target for Mars exploration missions,' said the report's lead author, Javier Martin-Torres of the Spanish Research Council, Spain, and Lulea University of Technology, Sweden, and a member of Curiosity's science team. 'Conditions near the surface of present-day Mars are hardly favourable for microbial life as we know it, but the possibility for liquid brines on Mars has wider implications for habitability and geological water-related processes.'

The weather data in the report published in *Nature Geosciences* comes from the Curiosity's Rover Environmental Monitoring Station (REMS), which was provided by Spain and includes a relative-humidity sensor and a groundtemperature sensor. NASA's Mars Science Laboratory Project is using Curiosity to investigate both ancient and modern environmental conditions in Mars' Gale Crater region. The report also draws on measurements of hydrogen in the ground by the rover's Dynamic Albedo of Neutrons (DAN) instrument, from Russia.

'We have not detected brines, but calculating the possibility that they might exist in Gale Crater during some nights testifies to the value of the roundthe-clock and year-round measurements REMS is providing,' said Curiosity project scientist Ashwin Vasavada of NASA's Jet Propulsion Laboratory, Pasadena, California, one of the report's co-authors.

Curiosity is the first mission to measure relative humidity in the Martian atmosphere close to the surface and ground temperature through all times of day and all seasons of the Martian year. Relative humidity depends on the temperature of the air, as well as the amount of water vapour in it. Curiosity's measurements of relative humidity range from about 5% on summer afternoons to 100% on autumn and winter nights.

Air filling pores in the soil interacts with air just above the ground. When its relative humidity gets above a threshold level, salts can absorb enough water molecules to become dissolved in liquid, in the process of deliquescence. Perchlorate salts are especially good at this. Since perchlorate has been identified both at near-polar and nearequatorial sites, it may be present in soils all over the planet.

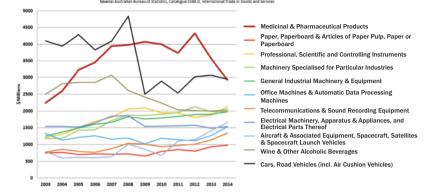
Researchers using the High Resolution Imaging Science Experiment (HiRISE) camera on NASA's Mars Reconnaissance Orbiter have in recent years documented numerous sites on Mars where dark flows appear and extend on slopes during warm seasons. These features are called recurring slope lineae, or RSL. A leading hypothesis for how they occur involves brines formed by deliquesence.

'Gale Crater is one of the least likely places on Mars to have conditions for brines to form, compared to sites at higher latitudes or with more shading. So if brines can exist there, that strengthens the case they could form and persist even longer at many other locations, perhaps enough to explain RSL activity,' said HiRISE principal investigator Alfred McEwen of the University of Arizona, Tucson, also a co-author.

In the 12 months following its August 2012 landing, Curiosity found evidence for ancient streambeds and a lakebed environment more than 3 billion years ago that offered conditions favourable for microbial life. Now, the rover is examining a layered mountain inside Gale Crater for evidence about how ancient environmental conditions evolved. JPL, a division of the California Institute of Technology in Pasadena, manages the Mars Science Laboratory and Mars Reconnaissance Projects for NASA's Science Mission Directorate, Washington. NASA

# Pharmaceutical exports dive

Pharmaceutical Exports v. Other Manufactured Exports, Australia, 2003-2014 Source: Australian Bureau of Statistics, Catalogue 5368.0, International Trade in Goods and Services



Recent figures from the Australian Bureau of Statistics show Australian pharmaceutical exports declined by 18% to \$2.9 billion in 2014, compared to \$3.6 billion in the year before.

Since 2012, when they peaked at around \$4.3 billion, Australian pharmaceutical exports have declined by more than 30%.

'These figures are extremely disappointing,' said Medicines Australia CEO, Tim James.

'Pharmaceutical manufacturing is precisely the sort of activity that Australia should excel at. We have a highly skilled labour force, a world-class infrastructure, a history of excellence in manufacturing innovation and, above all, a long-standing and well-justified reputation for manufacturing safe, highquality medicines and vaccines.

'Despite this, new investment in pharmaceutical manufacturing in Australia remains negligible, which clearly shows that all these factors are simply not enough to keep Australia competitive.'

Unfortunately, the decline in Australian pharmaceutical exports comes at a time when the global market for medicines and vaccines is booming. It is already worth over US\$1 trillion per year in sales, and is expected to nearly double in size by 2020.

'Much of this growth is going to come from emerging markets in Asia,' James said.

'But right now, we just don't have the correct policies in place to capitalise on this growth. If this continues, we will no doubt miss out on this once-in-ageneration opportunity, regardless of how good we may look "on paper".

Last year, Medicines Australia, in partnership with AusBiotech, submitted a joint proposal to the Australian Government on steps it should take to build a stronger pharmaceuticals industry in Australia.

Broadly, the proposal called on the Government to:

- ensure a stable, predictable and efficient business operating environment
- strengthen Australia's intellectual property system
- enable growth in Australia's local biotechnology sector
- enact globally competitive incentives such as tax breaks to encourage investment.

'Implementing these policies would show that the Australian Government is serious about attracting investment and that Australia is truly "open for business", James said.

'Globally, the pharmaceutical industry invests billions each year in manufacturing. If we want to attract a bigger share of this investment, we be must be proactive, decisive and coordinated, especially with respect to the policy environment.' MEDICINES AUSTRALIA

# Forging a future in green steelmaking



The dry slag granulation rig is fitted to blast furnaces to produce granulated slag and heated air.

Australian smart technology that harvests blast furnace waste and converts it into a new product to make cement is being trialled for commercialisation in China where 60% of the world's iron waste is produced.

The process, known as dry slag granulation, also reduces water use and greenhouse gas emissions, and is the focus of an agreement signed by CSIRO and the Beijing MCC Equipment Research & Design Corporation (MCCE).

The signing of the agreement, to demonstrate CSIRO's dry slag granulation (DSG) technology at industrial scale, is a landmark for Australia–China research collaboration and for environmentally friendly metal production, according to CSIRO Director of the Mineral Resources Flagship, Jonathan Law.

'Our collaboration is an exciting step towards the uptake of an innovation with real prospects of transforming the productivity and environmental performance of global iron smelting,' Law said.

'The benefits from wide uptake of DSG technology on blast furnaces will be profound in helping the global industry to

reduce water and energy use and greenhouse gas emissions while sustaining metal production.

The DSG technology that is fitted to blast furnaces includes a spinning disc and granulation chamber that separates molten slag into droplets under centrifugal forces, uses air to quench and solidify the droplets, and extracts a granulated slag product as well as heated air.

The process produces a 'glassy' product that is ideal for cement manufacture, but has significantly lower associated greenhouse gas emissions than cement produced by conventional methods.

Air at 500–600°C extracted from the DSG process can be used onsite for drying, preheating or steam generation.

The technology also saves water and eliminates the underground water pollution that can be associated with alternative wet granulation processes.

'The benefits each year from full commercialisation and adoption of DSG technology are in the order of 60 billion litres of water, 800 petajoules of heat energy and 60 million tonnes of greenhouse gas emissions,' Law said.

'Those savings are equivalent to 14% of Australia's energy use and about 10% of our greenhouse gas emissions each year.'

In entering the collaboration with MCCE, CSIRO has recognised the R&D reputation of the Beijing-based company and its ability to scale up the technology and introduce it into China – where 60% of the world's 300 million tonnes of iron blast furnace slag is produced each year.

Under the agreement, MCCE is to scale up and demonstrate the technology at industrial scale and, upon success, commercialise it in China and then potentially world wide.

The agreement is the culmination of more than a decade of DSG technology development by CSIRO and industry partners, including Arrium and BlueScope. CSIRO

# Smartphones as personal, real-time pollution monitors

As urban residents know, air quality is a big deal. When local pollution levels go up, the associated health risks also increase, especially for children and seniors. But air pollution varies widely over the course of a day and by location, even within the same city. Now scientists, reporting in *Environmental Science & Technology*, have used smartphone and sensing technology to better pinpoint where and when pollution is at its worst.

Mark J. Nieuwenhuijsen and colleagues note that many studies have

investigated people's exposure to air pollution, which is associated with respiratory and cardiovascular problems. But they usually create a picture of exposure based on air pollution levels outside people's homes. This approach ignores big differences in air quality in school and work environments. It also ignores spikes in pollution that happen over the course of the day, such as during peak hour. Nieuwenhuijsen's team wanted to test technology's ability to fill in these gaps.

The researchers equipped more than

50 school children with smartphones that could track their location and physical activity. The children also received sensors that continuously measured the ambient levels of black carbon, a component of soot. Although most children spent less than 4% of their day travelling to and from school, commuting contributed to 13% of their total potential black carbon exposure. The researchers conclude that mobile technologies could contribute valuable new insights into air pollution exposure. AMERICAN CHEMICAL SOCIETY

### Caging of molecules allows investigation of equilibrium thermodynamics

A team of scientists from Technische Universität München (TUM) (Germany) and Linköping University (LIU) (Sweden) has developed a methodology to investigate the equilibrium thermodynamics of single molecules.

In the search for high performance materials for applications such as gas storage, thermal insulators or dynamic nanosystems it is essential to understand the thermal behaviour of matter down to the molecular level. Classical thermodynamics average over time and over a large number of molecules. Within a threedimensional space single molecules can adopt an almost infinite number of states, making the assessment of individual species nearly impossible.

The breakthrough study is based on two pillars: a technology that allows molecules to be caged within two-dimensional nanopores and extensive computational modelling.

At the Chair of Molecular Nanoscience and Chemical Physics of Interfaces at TU München, led by Professor Dr Johannes V. Barth, Dr Florian Klappenberger developed the method to produce high-quality metal-organic networks on a silver surface. The network forms nanopores that restrict the freedom of movement of adsorbed single molecules in two dimensions. Using scanning tunnelling microscopy, the researchers were able to track their motions at different temperatures with sub-nanometre resolution.

Parallel to the experiments, the researchers worked with

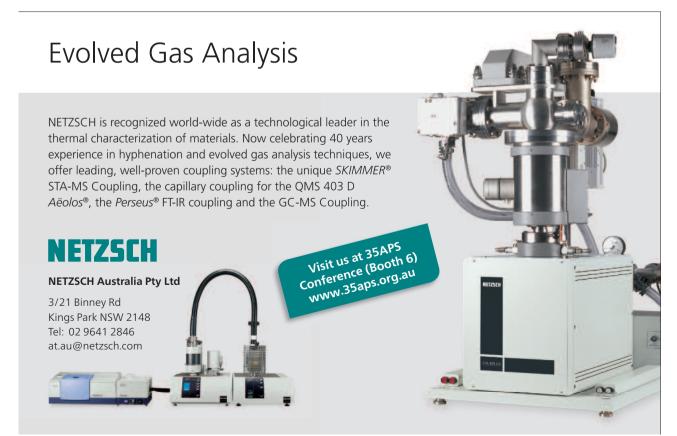
sophisticated computer models to describe the temperature dependence of the dynamics of these single trapped molecules.

Comparing experimental and modelled data, the scientists unravelled that under certain conditions the integral theory approaches a simple projection of the molecular positions in space. This approach is central to statistical mechanics, but has never before been challenged to reproduce an experiment, due to the practically infinite molecular positions and energies one needed to consider without the nanoscale confinement.

'It was extremely exciting to employ two-dimensional networks as a confinement strategy to reduce the available conformational space of a single molecule, like a chaperone does with a protein', said Dr Carlos-Andres Palma, the lead author of the study. 'In analogy to biology, such a form of confinement technology has the potential to establish sensors, nanomachines and possibly logics controlled by and made of molecular distributions.'

Applying their knowledge of characteristic equilibrium configurations, the researchers carefully modulated the nanopore, thus making a single molecule write letters of the alphabet such as L, I and U, just by fine-tuning the temperature.

Their work has been published in *Nature Communications* (doi: 10.1038/ncomms7210). TECHNISCHE UNIVERSITÄT MÜNCHEN





# Trajan and UTAS secure top postdoctoral fellows for ASTech

Trajan Scientific and Medical (Trajan) and the University of Tasmania (UTAS) have secured three top scientists to oversee innovative research programs at ASTech, the ARC Training Centre for Portable Analytical Separation Technologies, supported by the Australian Research Council (ARC).

ASTech is a collaboration between Trajan and UTAS combining industry knowledge and research to innovate in product design, development and manufacturing techniques.

Professor Emily Hilder, ASTech Training Centre Director, said that she is looking forward to working closely with the three new postdoctoral fellows who were selected from a pool of applicants from around the world.

Dr Greg Barbante has a PhD in electroanalytical/synthetic chemistry and Honours in the development of sensors based on immobilised microcrystals, and has recent experience in the food industry, including HPLC and GC method development, and project management.

Dr Masoomeh Tehrani Rokh completed her PhD in Engineering in the field of bio-microelectromechanical systems and microfluidics, a Master of Science in microengineering and nanoelectronics, and has extensive experience in microfabrication processes and facilities.

Stephen Tomisich, Trajan's Chief Executive Officer said, 'We are thrilled to have recruited these high-calibre researchers for ASTech. Each has unique expertise that will complement R&D at Trajan, and this month we have welcomed Dr Lapierre at Trajan's global headquarters in Melbourne to commence his industry placement.'

Dr Florian Lapierre has a PhD in micro and nanotechnology in the field of sophisticated microfluidic device design, also a Master of Science and Technology in microfluidic systems and a Master of Engineering in scientific measurement and applied business. Lapierre has worked as an engineer consultant in biomaterial development and designing digital microsystems for pathogen detection.

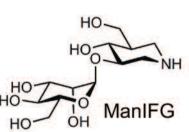
Tomisich said the development of new micro-materials could play a critical role in next generation portable analytical devices.

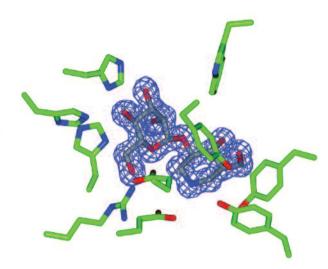
Hilder encourages scientists to seize the opportunity while ASTech PhD scholarships are still available.

'Applications will be accepted until all HDR positions have been filled, so budding scientists should visit the ASTech website and apply to join us in developing innovative separation technologies,' said Hilder. ASTech

# Yeast-eating bacteria in the human gut

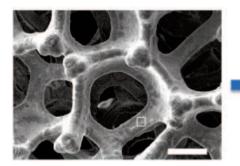
Yeasts have been a regular part of our diet since their domestication some 7000 years ago. A joint study between groups in the US, the UK, Belgium and Canada, and that of Associate Professor Spencer Williams at the University of Melbourne has worked out how a common component of the human microbiota, Bacteroides *thetaiotaomicron*, acquired the capacity to use the yeast cell wall as a food source (Cuskin F., Lowe E.C., Temple M.J., Zhu Y., Cameron E.A., Pudlo N.A., Porter N.T., Urs K., Thompson A.J., Cartmell A., Rogowski A., Hamilton B.S., Chen R., Tolbert T.J., Piens K., Bracke D., Vervecken W., Hakki Z., Speciale G., Munōz-Munōz J.L., Day A., Peña M.J., McLean R., Suits M.D., Boraston A.B., Atherly T., Ziemer C.J., Williams S.J., Davies G.J.,



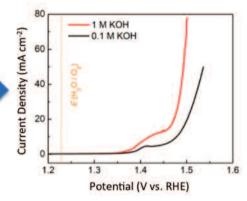


Abbott D.W., Martens E.C., Gilbert H.J. Nature 2015, **517**, 165–9). A critical role in this work was played by the bespoke azasugar inhibitor  $\alpha$ -mannosyl-1,3isofagomine synthesised by the Williams group, which was used in X-ray crystallographic structural studies to determine on a molecular level how a glycoside hydrolase enzyme cleaves complex chains of the polysaccharide mannan found in yeast cell walls. The discovery that mannan is a micronutrient degraded by *B. thetaiotaomicron* may be relevant to the health-promoting effects of the human microbiota.

## Nanostructured electrodes for efficient water splitting

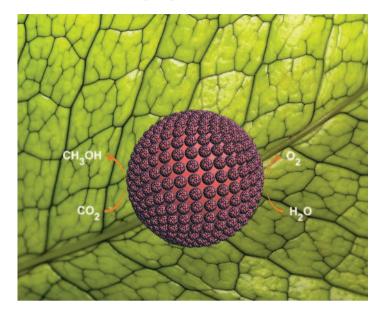


Electrolytic water splitting holds promise for large-scale storage of energy generated from renewable sources, such as solar and wind, in the form of hydrogen fuel. But the sluggish kinetics of the oxygen evolution reaction on the anode means that expensive catalysts such as oxides of iridium ( $IrO_2$ ) or ruthenium ( $RuO_2$ ) must often be used to lower reaction barriers. The group of Associate Professor Chuan Zhao at the

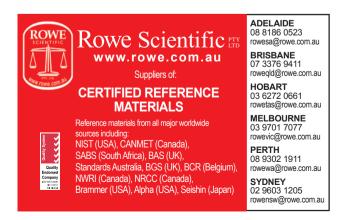


University of New South Wales has recently developed a highly efficient oxygen electrode by electrodepositing amorphous mesoporous nickel-iron composite nanosheets directly onto macroporous nickel foam substrates (Lu X., Zhao C. *Nat. Commun.* 2015, **6**, 6616). The hierarchically structured porous electrode exhibits high catalytic activity towards water oxidation in alkaline solutions, initiating the reaction at an overpotential of only 200 mV and delivering current densities of 500 and 1000 mA cm<sup>-2</sup> at overpotentials of 240 and 270 mV, respectively. The electrode is also stable to prolonged use at high currents. The results suggest the electrode is the most efficient oxygen evolution electrode in alkaline electrolytes reported so far and can potentially be used for industrial water electrolysis.

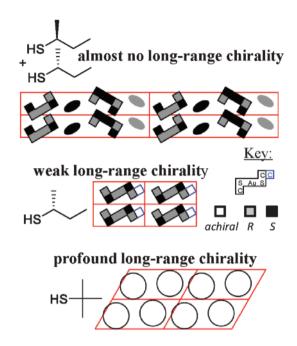
### Harnessing light for fuel



Researchers at Monash University have made significant progress towards developing a method of artificial photosynthesis that could replace the use of fossil fuels in the future. Artificial photosynthesis is the industrial process of preparing fuels and chemicals from nothing more than carbon dioxide, water and sunlight. The researchers, led by Professor Douglas MacFarlane, discovered a new way to convert carbon dioxide to methanol (Li H., Zhang X., MacFarlane D.R. Adv. Energy. Mater. 2015, 5, 1401077). They created a photo-catalyst based on copper oxide, the surface of which is decorated with tiny carbon dots about 2 nm in size. This nano-composite material can directly convert carbon dioxide dissolved in water into methanol, using only sunlight as an energy source. The key to this process in chemical terms is the development of catalysts - one to oxidise water and another to absorb and reduce carbon dioxide. When the catalysts are coupled with materials that can absorb light energy, fuels such as methanol can be generated efficiently.

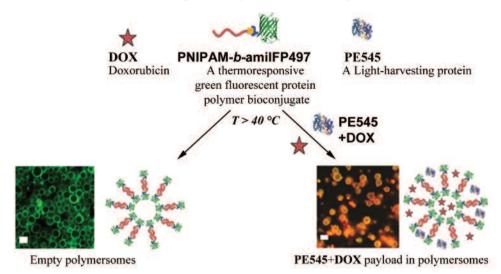


# Chirality on surfaces unlike that in solution or crystals



Chirality in solution is controlled simply by molecular stereocentres, while that in crystals has the added complexity that all molecules in the crystal unit cell must be considered. Crystal packing typically involves centrosymmetric arrangements of enantiomeric pairs, meaning that chiral crystals are rare. On surfaces, however, self-assembled monolayers (SAMs) usually pack into units containing internal rotational symmetry, preserving chirality. In addition, the combined molecule-surface geometry, or the arrangement of achiral molecules above a surface, can generate chirality. Recently, researchers at the University of Technology, Sydney, led by Professor Jeff Reimers, and at five other institutions (Yan J., Ouyang R., Jensen P.S., Ascic E., Tanner D., Mao B., Zhang J., Tang C., Hush N.S., Ulstrup J., Reimers J.R. J. Am. Chem. Soc. 2014, 136, 17087-94) combined to observe and characterise seven SAMs formed by the butanethiol family on Au(111). Racemic 2-butanethiol mixtures self-assemble, both directly on the surface and on Au-adatom stereocentres, into units containing 12 chiral centres each, yet this structure is rectangular with an approximate internal symmetry plane, negating long-range expressions of surface chirality. On the other hand, achiral oblate-like t-butanethiol self-assembles without chiral head groups into near rhombic shapes with profound long-range chirality. While the whole surface is racemic, independent large domains are chiral, offering the prospect of chiral catalysis.

### Capture and sensing of payloads in polymersomes



Thordarson group at the University of New South Wales and collaborators recently reported the synthesis of a protein-polymer bioconjugate PNIPAM-b-amilFP497 composed of thermo-responsive polv(Nisopropylacrylamide) (PNIPAM) and a green-fluorescent protein variant (amilFP497) (Wong C.K., Laos A.J., Soeriyadi A.H., Wiedenmann J., Curmi P.M.G., Gooding J.J., Marguis C.P., Stenzel M.H., Thordarson P. Angew. Chem. Int. Ed. 2015, 54, 5317-22). Above 37°C, this bioconjugate forms

Polymersomes – vesicles formed by self-assembly of polymer amphiphiles – provide a good platform for targeted drug delivery and for creating complex (bio)catalytically active systems for research in synthetic biology and systems chemistry. To realise these applications requires both spatial control over the encapsulation components in the polymersomes and a means to determine where the components are in the polymersomes. Addressing these twin challenges, the polymersomes that can (co-)encapsulate the fluorescent red drug doxorubicin and the fluorescent pink light-harvesting protein phycoerythrin 545 (PE545). Using fluorescence lifetime imaging microscopy and Förster resonance energy transfer (FLIM-FRET), the researchers were able to distinguish PE545 protein found only in the polymersome membrane from doxorubicin found in both the polymersome core and membrane.



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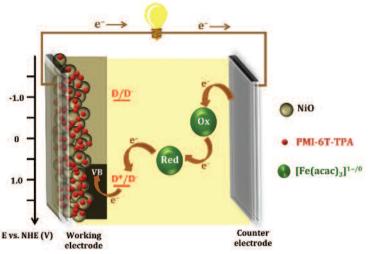


The world of chromatography

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#### New benchmark in p-type dye-sensitised solar cell performance

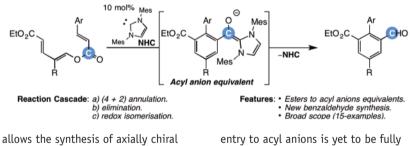
The development of renewable energy technologies is vital for meeting the increasing energy demands of the modern world and for lowering greenhouse gas emissions and environmental pollution from fossil fuel combustion. Towards this end, many approaches to harvesting solar energy have been explored. The dyesensitised solar cell (DSC) is one promising device that can potentially be constructed at low cost and with environmentally friendly components. Efforts are being made to develop n-type and p-type DSCs that can be combined into high-efficiency tandem DSC devices. But the poor efficiency of p-DSCs has hampered the performance of such tandem devices. The Spiccia and Bach groups at Monash University have recently tackled this problem by developing a new electrolyte for p-DSCs based on the tris(acetylacetonato)iron(II/III) redox couple that better matches the energy levels of the p-type semiconductor and sensitiser used (Perera I.R., Daeneke T., Makuta S., Yu Z., Tachibana Y., Mishra A., Bäuerle P., Ohlin C.A., Bach U., Spiccia L. Angew. Chem. Int. Ed. 2015,



**54**, 3758–62). The devices made with this redox couple have the highest efficiency (2.5%) and current density (7.65 mA cm<sup>-2</sup>) of any p-type DSC reported to date.

### Esters provide acyl anion equivalents too

The generation of acyl anion equivalents from aldehyde-containing materials underpins many studies in the field of *N*-heterocyclic carbene (NHC) catalysis. Recent studies from the Lupton group at Monash University have uncovered a pathway that allows esters to provide access to acyl anion equivalents as well. The specific reaction proceeds via a novel cycloisomerisation, elimination, redox isomerisation cascade. The transformation is quite general (15 examples) and, using chiral catalysts,



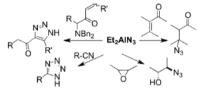
biaryls via a novel point to axial chirality transfer event (Candish L., Levens A., Lupton D.W. *Chem. Sci.* 2015, **6**, 2366–70). The potential of this new entry to acyl anions is yet to be fully exploited, and may lead to other novel complexity-generating cascades starting from ubiquitous ester-containing substrates.

Compiled by **David Huang** MRACI CChem (david.huang@adelaide.edu.au). This section showcases the very best research carried out primarily in Australia. RACI members whose recent work has been published in high impact journals (e.g. *Nature, J. Am. Chem. Soc., Angew. Chem. Int. Ed.*) are encouraged to contribute general summaries, of no more than 200 words, and an image to David.



### Aust J Chem

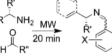
In the May issue, an interesting Highlight on the synthetic uses of diethylaluminium azide (Et.AlN.) by Monticelli and Pace (Vienna) summarises the formation of tetrazoles and bistetrazoles from (di)nitriles, triazoles and beta-azidoketones (by Michael addition) from alpha-beta unsaturated ketones, beta-azidoalcohols from the ring opening of epoxides, which effectively corresponds to the addition of HO-N, to C=C double bonds. Numerous other reactions are also described, including the formation of acvl azides from esters (by substitution) and of azidofunctionalised  $C_{60}$  (by addition). The reactivity of this reagent arises from a combination of the Lewis acid nature of Al and the nucleophilic and cycloaddition properties of the azide group.



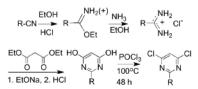
Hypervalent iodine compounds constitute another powerful group of reagents in organic synthesis. A Highlight by Hartrampf and Toombs-Ruane (Munich) describes the use of diaryliodonium salts in the difunctionalisation of alkynes, where they act as highly electrophilic aryl transfer reagents. Such reactions yield inter alia 3-methyleneoxindoles from propargylic amides, 3-alkoxymethylfurans from betaacylalkenynes, guinolines from acetylenes and nitriles, and triazoles from acetylenes and azides. Many other useful reactions are also described.



Imines (Schiff bases) are well-known and highly useful compounds, e.g. for the synthesis of secondary (chiral) amines and bio-organic compounds such as alkaloids. They are usually prepared by condensation of an aldehyde or ketone with an amine at reflux, often with the help of a catalyst such as zinc or titanium chloride, alumina or copper sulfate. Philip Andrews and co-workers (Monash University) report the rapid and facile preparation of a variety of aromatic and heterocyclic, chiral and achiral imines by using microwave irradiation. The yields are high, often quantitative, and the reactions are finished in a matter of minutes.



The importance of pyrimidines in biology and in medicinal chemistry is well established. However, the preparation of simple 4,6-dihydroxypyrimidines (6-hydroxypyrimidin-4-ones) and the corresponding 4,6-dichloropyrimidines can be tedious, requiring the isolation of hygroscopic intermediates, viz. imido acid ester and amidine hydrochlorides. Opitz, Sulger, Daltrozzo and Koch (Konstanz and Oldenburg) have now developed a one-pot, high-yielding (up to 93%), large-scale (1 mol) synthesis of 2-substituted 4,6-dihydroxypyrimidines as well as their conversion to the 4,6-dichloropyrimidines with POCL in up to 86% yield on a similarly large scale. These well-worked procedures will be of interest to synthetic and medicinal chemists. In addition, the mechanism of the chlorination reaction was investigated computationally.



Curt Wentrup FAA, FRACI CChem (wentrup@uq.edu.au), http://uq.edu.au/uqresearchers/researcher/wentrupc.html?uv\_category=pub

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# The tale in the

BY DAVE SAMMUT

SHIT

Working and sensory lives of bees



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Bees have a well-earned reputation for pollination and honey-making, but their lesser known skills in electrocommunication are just as impressive.

ccording to the United Nations, 'of the 100 crop species that provide 90 per cent of the world's food, over 70 are pollinated by bees' (bit.ly/1DpiRYF). It's little wonder, then, that bees continue to be a subject of study around the world. More surprising, perhaps, is that so much remains to be learned.

Bee-keeping (apiculture) is believed to have started as far back as about 4500 years ago; sculptures in ancient Egypt show workers blowing smoke into hives as they remove honeycomb. In ancient Greece, Aristotle either kept and studied bees in his own hives or examined the observations passed to him by beekeepers. In doing so, he made some astute conclusions; for example, that there are three classes of bees, one of which is sterile. Along with his better observations, he thought incorrectly that bees do not make honey and instead that it is distilled from dew.

In reality, the manufacture of honey by bees is both complex and elegant. Honey varies in composition depending on many factors (such as the different species of flower from which the inital nectar is collected), but in general terms it is dominated by two key simple sugars: dextrose (glucose isomer) and levulose (fructose isomer), constituting over 70% by mass. It also contains aromatic volatile oils (giving it rich flavour), mineral elements, some proteins, enzymes, vitamins and colouring matter.

Worker bees collect nectar from selected flowers. Containing about 80% water, together with complex sugars, this nectar is stored in a special stomach (the 'honey stomach') where the invertase enzyme secreted by the bee's salivary glands begins the process of breaking down the sucrose in the nectar into simple glucose and fructose. Some of the glucose reacts with a second enzyme, glucose oxidase, to form gluconic acid and hydrogen peroxide, creating conditions of low pH (3.2–4.5). sucrose +  $O_2$  inverse fructose + glucose Once the worker bee's honey stomach is full, it returns to the hive and regurgitates the partially modified nectar for a hive bee. The hive bee ingests this material to continue the conversion process, then again regurgitates it into a cell of the honeycomb. During these processes, the bees also absorb water, which dehydrates the mixture.

Hive bees then beat their wings to fan the regurgitated material. As the water evaporates (to as little as around 10% moisture), the sugars thicken into honey – a supersaturated hygroscopic solution of carbohydrates (plus oils, minerals and other impurities).

Some researchers think that the hive bees inject a venom into each comb, giving the honey its antibacterial properties; others dismiss this idea, saying that the high concentration of sugars means that fermentation cannot happen. Either way, there seems to be general agreement that the acidic nature of the honey is hostile to bacteria, mould and fungi.

In its entire lifetime (approximately seven weeks, as compared to Aristotle's estimate of seven years), an average bee will produce less than a gram of honey.

But how does the worker bee select its flowers in the first place? In 2013, Professor Daniel Robert and his team at the University of Bristol made a fascinating discovery (*Science*, doi: 10.1126/science.1230883).

It was already well known that bees generate a positive charge as they move, and most particularly as they fly. It was also known that flowers generate a weak negative charge over time. Using a Faraday pail (a sort of electrically shielded bucket, similar to the wire cage in a microwave oven), Robert and his team measured this positive charge on individual bees. They went on to demonstrate that when the bee lands on a flower, this charge is temporarily passed to the flower, and that for a period of minutes after the visit the flower will have a measurably more positive charge.

# **Sensational species**

The multiple senses that humans and animals possess beyond the 'standard five' are fascinating. In humans, this includes mechanical senses for balance ('equilibrioception') or for locomotion ('propioception'), and many more.

Electroreception is the biological ability to perceive electrical stimuli. In some species of the animal kingdom, these senses are highly developed – particularly in aquatic or wet terrestrial environments where charge is carried better. As an example, some species of shark can detect DC fields as low as 5 nV/cm.

ockphoto/vladosk

The most common usage is in electrolocation in predation. Living organisms generate small electrical fields in the movement of their muscles and in their nerves, while fish also generate fields from the ion pumps associated with osmoregulation at the gill membrane. Some predators use this to detect their prey (sharks have been shown to attack any source of an electric field, which was a problem for early telegraph cables), while others use the sense to avoid predators.

This has led to an 'arms race', for example in the evolution among some fish species towards more complex or higher frequency electrical fields that are harder for their predators to detect.

Conversely, some species of fish communicate by modulating the waveform of their electrical field, for mating and territorial displays. This electroception is caused by a multitude of biological mechanisms. Sharks use field sensors called the ampullae of Lorezini: electroreceptor cells connected to seawater by pores in their snout and head. Monotremes (particularly the platypus, but also two species of echidna) use free nerve endings located in the mucous membranes of the snout.

In species with 'active electrolocation', the animal generates its own electrical field using a specialised organ of modified muscle or nerves, and then modifies the frequency and waveform in a manner that might be unique to the species or even the individual.

Most importantly, using artificial flowers with a controlled electrical charge, the Bristol team was able to show that the bees could sense the electrical charge on the flowers, and that they could be trained to use that charge to guide their activities. This was a breakthrough – the first time that electroreception had been documented in an invertebrate species (see Sensational species box).

It now seems that bees also use electrocommunication. In a paper to the Royal Society in 2013, Greggers et al. note that 'the electric fields emitted by dancing bees consist of both lowand high-frequency components. Both components induce passive antennal movements in stationary bees according to Coulomb's law. Bees learn both the constant and the modulated electric field components in the context of appetitive proboscis extension response conditioning.' (*Proc. R. Soc. B*, doi: 10.1098/ rspb.2013.0528)

The 'waggle dance' is itself a remarkable note in the journals of science. Much like the Rosetta Stone unlocking the secrets of hieroglyphics, the seminal work of zoologist Karl von Frisch unlocked in the mid-20th century the secrets of the movement of successful foragers returning to the hive. He correlated the dance to directions on flower patches via relative position of the sun and the distance from the hive, with different dances particular to different bee species. It was the first demonstration of non-human communications for learning, and it won von Frisch the 1973 Nobel Prize in Physiology or Medicine. And now we know that electrical fields also play their part in this communication.

However, the waggle dance is not without controversy. Some experts argue that the waggle dance cannot give guidance on a nectar source, and that floral odour is actually the dominant method of recruiting bees to the source. For most of us, this is a matter of nuance. It would seem that most scientists would agree that both mechanisms contribute, and that it is only the relative weighting that is in contention. For the antagonists, it is often a matter of polarised principle, even outright hostility.

#### 20 Chemistry in Australia

The honeybee can see only four basic colours, compared to the 60 distinct colour combinations from the three primary colour photoreceptors in humans.



Electroreception in bees is associated with a collection of sensory cells in the second segment of the antennae called the Johnston's organ, which detects motion in the flagellum (the final antennal segment). As with other animals, the sense is mechanical, but it represents yet another mechanism for electroreception. It is a truly wondrous demonstration of the ability of evolution to take up every advantage available in the physical world. And because the presence of the Johnston's organ is a defining characteristic that separates the class insect from other hexapods, it opens the possibility of yet undiscovered behavioural triggers in invertebrates.

Returning to the Bristol study, the researchers found that the electrical charge stimulus worked best in combination with colour triggers, and this brings me to another remarkable aspect of bees and the animal kingdom more generally.

The honeybee can see only four basic colours, compared to the 60 distinct colour combinations from the three primary colour photoreceptors in humans. Their visible spectrum stretches from about 300 to 650 nm, and they are red-blind. Yet with their vision in the UV portion of the spectrum, bees can see a guite remarkable amount of detail in flowers that we cannot, which is obviously an evolutionary response between the two organisms. Indeed, the extensive publications of Professor Lars Chittka of Queen Mary University of London suggests that the photoreceptor abilities of ancestral bees pre-dated the existence of flowers by more than 100 million years, and that the colouration of flowers evolved in response to the bees' ability, rather than the other way around.

That there is a topic so thoroughly researched over such a long period, and with so many insights yet to offer, is simply delightful. Given the importance of bees to our global food supply, these advances in our understanding are of more than mere esoteric interest. They might one day become critical to our existence.

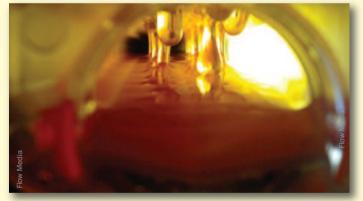
Dave Sammut FRACI CChem is principal of DCS Technical, a boutique scientific consultancy, providing services to the Australian and international minerals, waste recycling and general scientific industries.

# Investigating bee decline

Bee populations, both wild and commercialised, are in decline globally. Current research is largely focused on trving to identify the causes of decline (called colony collapse disorder in the US). The main areas under investigation are bee parasites (most particularly the varroa destructor mite), use of pesticides and the build-up of toxins in the foraging environment, loss of biodiversity and foraging rich environments, spread of the Africanised honey bee (in the US), and extremes of weather associated with changing climates. Work is being done in gene manipulation of honey bees to protect them from mites, as well as research into alternative pollinators that can be used should bee populations fail catastrophically.

Some recent good news in Australia is an innovative beehive design using a slight flexing of a plastic framework to allow honey to flow directly out of the hive (literally honey on tap) for collection. This could have implications in the fight to strengthen bee colonies, by allowing more user-friendly beekeeping set-ups for the rapidly expanding urban apiarist markets. No smoking or bee suits required!

Chantelle Craig



The cells of the honeycomb fracture during this new type of process, allowing the honey to flow down, but they don't actually break.



Honeybees on the plastic beehive framework.

# Exposure time and chemical toxicity

# A new approach

iStockphoto/khvost

BY DES CONNELL

Over the past century, few scientific relationships have survived unaltered. Haber's rule has not only survived, it has prospered in its application.



Australian infantry wearing small box respirators. The soldiers are from the 45th Battalion, Australian 4th Division at Garter Point near Zonnebeke, Ypres sector, 27 September 1917.

he introduction of a new weapon was heralded to the Queen Victoria Rifles in April 1915 when the startled soldiers, resting after being at the front, saw coming at them from the French lines galloping teams of frenzied horses. The soldiers could see that something terrible was happening in the ominous green–yellow cloud moving slowly towards them. It was the start of one of the first mass gas attacks of the Great War using chlorine, and it became the weapon the soldiers feared the most.

World War I is described by some commentators as the chemists' war. The originator of chlorine gas as a weapon of war was Fritz Haber, controversial recipient of the Nobel Prize in Chemistry in 1918. This was awarded for his development of the process for fixation of nitrogen from the atmosphere to produce crop fertilisers, and greatly accelerated food production. It is possibly the most important industrial process for the human race ever devised; it was, and still is today, a great service to humanity.

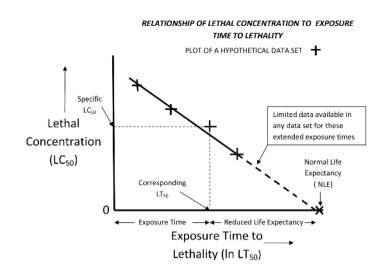
Another result of the involvement of the 'father of chemical warfare' is Haber's rule (Haber F. 'On the history of gas warfare', In: Five lectures from the years 1920-1923. Springer, Berlin, pp. 75–92, 1924). It is used to predict the influence of exposure time on toxicity in medical, occupational and other industrial applications. In recent times, the occurrence of toxic chemicals at low environmental concentrations and for long periods of time have become important. These new factors need to be considered when setting environmental and occupational quidelines for toxic chemicals, thus leading to new requirements for accounting for the exposure time (Yu Q. et al. Chemosphere 1999, vol. 38, pp. 909-18; Zhao Y., Newman M.C. Environ. Toxicol. Chem. 2004, vol. 23, 2147-53).

# Haber's rule and lethal concentration

Toxicological data is usually reported as the  $LD_{50}$  or  $LC_{50}$ , while the exposure time to reach the toxicity, often 24, 48 or 96 hours, is recorded but fixed and not considered as a quantifiable

variable (Ashauer R., Escher B. J. Environ. Monit. 2010, vol. 12, pp. 2056-61; Rozman K.K., Doull J. Toxicology 2000, vol. 144, pp. 169–78; Rozman K.K., Doull J.J. Pharmacol. Exp. Ther. 2001, vol. 296, pp. 663–8). Usually broad and imprecise terms such as acute. subacute. chronic and subchronic are used to describe the exposure time conditions. The lethal toxicity, at another exposure time other than that reported, may be required to set guidelines in air, food, soil and water. This is usually obtained by extrapolation using Haber's rule. Haber formulated a rule to do this extrapolation from observations of the effects of poisonous gases and used it to calculate the lethal effects in the dispersal of chlorine on the Western Front. Haber's rule is usually expressed as:

 $LC_{50} \times exposure time = constant (K)$ where  $LC_{50}$  is the lethal concentration of the toxic chemical to the average organism over the time the organism is exposed and the empirical constant K is related to the organisms being evaluated, experimental conditions and units used. The RLE model ... solves the problems apparent with the traditional Haber's rule, which cannot be applied to long-term exposure to chemicals in the environment.



Representation of the RLE model fitted to hypothetical observed data with fish and zooplankton.

Thus a lethal gas with an  $LC_{50}$  of  $10 \text{ mg/m}^3$  taking 24 hours to reach lethality to an average mammal, gives a calculated *K* of 240. The lethality of the gas at 48 hours would be 240/48, which is 5 mg/m<sup>3</sup>. Other toxicities at other exposure times can be similarly calculated. The inherent toxicity of the substance does not change during the exposure, irrespective of the time involved, but the toxic effects on the organism have a longer duration with longer exposure times and consequently have a lethal toxic effect at a lower concentration.

This rule has been used for evaluation of effects of exposure time on toxicity for about a century with a high degree of success. Many variants of Haber's rule have been proposed that preserve the essential nature of the relationship, with the two variables, toxicity and exposure time, modified in some way.

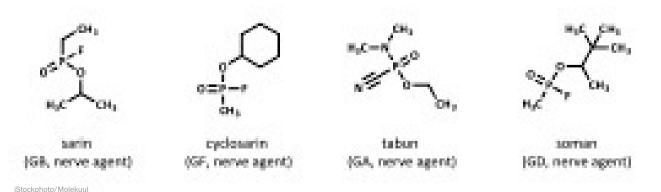
Haber's rule has stood the test of time in setting standards, extrapolating effects from chronic to subchronic exposure, setting exposure limits for workplaces and even setting guidelines for maximum permissible limits for chemicals in spaceships. Generally, Haber's rule has been extremely valuable with toxicants at relatively high levels and short exposure times.

#### Faults of Haber's rule

Management of toxic chemicals has expanded over recent decades. The relatively high exposures with pharmaceuticals as well as workplaces and other industrial applications remain important. But the environmental occurrence of chemicals poses new challenges, with long exposure times and low levels of exposure. In these situations, Haber's rule has two major faults.

First, according to Haber's rule when the toxicity approximates zero, as occurs in most environmental situations, then the exposure time should approach infinity since the value of K needs to remain constant to satisfy Haber's rule – thus zero multiplied by infinity should give K. This is an inappropriate result, which does not give any useful values in the extrapolation.

Second, there is no limit to Haber's rule – it can be applied to very long exposure times, in fact well beyond the lifetime of any organism (specifically humans) being considered. This is also inappropriate and yields no useful results.



#### Reduced life expectancy model

Our research (Connell D.W., Yu J. Mar. Pollut. Bull. 2008. vol. 57. pp. 245-9: Verma V. et al. Chemosphere 2012, vol. 89, pp. 1026-33) evaluates the importance and use of the normal life expectancy (NLE) as a totally new variable in quantifying the effects of exposure time on toxicity. The new model addresses the two major faults with Haber's rule. It is based on an observed negative linear relationship between the lethal toxicity of a chemical,  $LC_{50}$ , and the natural logarithm of the exposure time,  $LT_{50}$ . Thus it describes the fall in  $LC_{50}$  as the exposure time increases until  $LC_{50}$ decreases to zero and  $LT_{50}$  becomes the NLE. The organism exhibits a reduced life expectancy (RLE) as the exposure time increases (see figure). The model takes the form:

$$\label{eq:LC_50} \begin{split} \mathrm{LC}_{50} &= -a\ln(\mathrm{exposure\ time,\ LT}_{50}) + b \\ \mathrm{where\ LC}_{50} \text{ is the\ lethal\ concentration} \\ \mathrm{to\ the\ average\ organism,\ LT}_{50} \text{ is the} \\ \mathrm{average\ exposure\ time\ for\ the} \\ \mathrm{expression\ of\ lethality\ LC}_{50} \text{ also\ when} \\ \mathrm{the\ LC}_{50} \text{ is zero\ and\ the\ LT}_{50} \text{ is the\ NLE} \\ \mathrm{and\ } a \text{ and\ } b \text{ are\ empirical\ constants.} \end{split}$$

Our extensive investigations (Verma V. et al. *Environ. Poll.* 2014, vol. 185, pp. 234–9, 2014; Verma V. et al. *ISRN Toxicology* 2013, doi: org/10.1155/2013/230763) of data from the literature with the RLE model for fish and marine invertebrates involving 88 data sets and with a wide range of organic and inorganic toxicants gave high linear statistically significant correlations ( $R^2 > 0.8$ ). These plots take the form of the hypothetical plot shown.

The NLE introduces a fixed limiting point for a species and at the same time it is a reference point. This valuable reference point is available with most data sets where the NLE of the test organism is known. It utilises the fact that when the exposure to a chemical is zero, it follows that the time to reach lethal toxicity is the NLE.

It should be noted that the toxicity of the chemical being considered is constant all the time although the  $LC_{50}$ values are declining. But the exposure time increases and is responsible for the observed change in  $LC_{50}$  of the compound. In fact, with increasing exposure time, the contribution of the constant toxicity of the compound to the observed toxicity ( $LC_{50}$ ) declines as the significance of the exposure time increases. Finally when  $LC_{50}$  is at its minimum, at zero, then the exposure time is the normal life expectancy.

#### Use of the RLE model

The RLE model can be used to calculate  $LC_{50}$  values for a specific organism and toxicant at any exposure time from a set of data comprising LC<sub>50</sub> and corresponding exposure time. The RLE model is used together with the NLE of the organism being considered to develop the RLE equation for the particular organism and specific toxicant. However, the set of  $LC_{50}$  values and corresponding exposure times are supplemented with the NLE at an  $LC_{50}$  of zero. The equation of best fit is obtained for this data for a plot of  $LC_{50}$  against  $\ln LT_{50}$ , as in the graph, which gives values for all

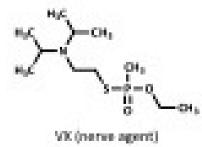
the constants in the RLE equation:

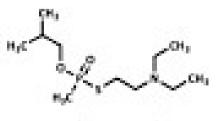
 $LC_{50} = -a \ln(LT_{50}) + b$ In this situation, only one actual measured data point is needed, together with the NLE, to obtain the RLE equation. Once the RLE equation is obtained, the  $LC_{50}$  can be calculated at any exposure time with a reasonable level of accuracy.

# New parameters, new applications

The RLE model is a new approach to evaluating the influence of exposure time on toxicity. It solves the problems apparent with the traditional Haber's rule, which cannot be applied to longterm exposure to chemicals in the environment. The model has been proven to be accurate in predicting the change in toxicity with different exposure times with a range of different chemicals and different organisms. The NLE is a new parameter that has never been used for this purpose before. From a limited database consisting of a minimum of a single data point with fish and zooplankton, in addition to the NLE of an organism, the RLE equation can be obtained. From this, the  $LC_{50}$  at any exposure time can be calculated. The new model is simple and has many applications, particularly in relation to health risk assessment and the setting of guidelines for exposure to toxicants.

**Emeritus Professor Des Connell** AM, FRACI CChem is at the Griffith School of Environment, Griffith University, Queensland.





VR (nerve agent)



(blister agent)

# New X-ray spectroscopy gives better look at the chemistry of interfaces

#### BY LYNN YARRIS

The Lawrence Berkeley National Laboratory has combined key features of two highly acclaimed X-ray spectroscopy techniques.

new technique, developed by researchers working at the Advanced Light Source (ALS) of the US Department of Energy (DOE)'s Lawrence Berkeley National Laboratory (Berkeley Lab), offers sub-nanometre resolution of every chemical element to be found at heterogeneous interfaces, such as those in batteries and fuel cells. This new technique is called SWAPPS for standing wave ambient pressure photoelectron spectroscopy, and it combines standing-wave photoelectron spectroscopy (SWPS) with high ambient pressure photoelectron spectroscopy (APPS).

Researchers working at the Advanced Light Source (ALS) of the US Department of Energy (DOE)'s Lawrence Berkeley National Laboratory (Berkeley Lab) have combined key features of two highly acclaimed X-ray spectroscopy techniques into a new technique that offers sub-nanometre resolution of every chemical element to be found at heterogeneous interfaces, such as those in batteries and fuel cells. This new technique is called SWAPPS for standing wave ambient pressure photoelectron spectroscopy, and it combines standing-wave photoelectron spectroscopy (SWPS) with high ambient pressure photoelectron spectroscopy (APPS).

'SWAPPS enables us to study a host of surface chemical processes under realistic pressure conditions and for systems related to energy production, such as electrochemical cells, batteries, fuel cells and photovoltaic cells, as well as in catalysis and environmental science,' says Charles Fadley, a physicist who holds joint appointments with Berkeley Lab's Materials Sciences Division and the University of California Davis, where he is a Distinguished Professor of Physics. 'SWAPPS provides all the advantages of the widely used technique of X-ray photoelectron



spectroscopy, including element and chemical-state sensitivity, and quantitative analysis of relative concentrations of all species present. However with SWAPPS we don't require the usual ultrahigh vacuum, which means we can measure the interfaces between volatile liquids and solids.'

Fadley is one of three corresponding authors of a paper describing SWAPPS in Nature Communications. The paper is titled 'Concentration and chemical-state profiles at heterogeneous interfaces with sub-nanometer accuracy from standing-wave ambient-pressure photoemission' (doi: 10.1038/ ncomms6441). The other two corresponding authors are Hendrik Bluhm, with Berkeley Lab's Chemical Sciences Division, a pioneer in the development of APPS, and Slavomír Nemšák, now with Germany's Jülich Peter Grünberg Institute.

In terms of energies and wavelengths, X-rays serve as excellent

SWPS ... made it possible for the first time to selectively study buried interfaces in a sample with either soft or hard X-rays.

probes of chemical processes. In the alphabet soup of X-ray analytical techniques, two in particular stand out for the study of chemistry at the interface where layers of two different materials or phases of matter meet. The first is SWPS, developed at the ALS by Fadley and his research group, which made it possible for the first time to selectively study buried interfaces in a sample with either soft or hard X-rays. The second is APPS, also developed at the ALS by a team that included Bluhm, which made it possible for the first time to use X-ray photoelectron spectroscopy under pressures and humidities similar to those encountered in natural or

practical environments.

'Heterogeneous processes at solid/gas, liquid/gas and solid/liquid interfaces are ubiquitous in modern devices and technologies but often difficult to study quantitatively, Bluhm says. 'Full characterisation requires measuring the depth profiles of chemical composition and state with enhanced sensitivity in narrow interfacial regions at the nanometre scale. By combining features of SWPS and APPS techniques, we can use SWAPPS to measure the elemental and chemical composition of heterogeneous interfaces with subnanometre resolution in the direction perpendicular to the interface.'

Says Fadley, 'We believe SWAPPS will deliver vital information about the structure and chemistry of liquid/vapour and liquid/solid interfaces, in particular the electrical double layer whose structure is critical to the operation of batteries, fuel cells and all of electrochemistry, but which is still not understood at a microscopic level.'

Fadley, Bluhm, Nemšák and their collaborators used their SWAPPS technique to study a model system in which a nanometre layer of an aqueous electrolyte of sodium hydroxide and caesium hydroxide was grown on an iron oxide (hematite) solid. The spatial distributions of the electrolyte ions and the carbon contaminants across the solid/liquid and liquid/gas interfaces were directly probed and absolute concentrations of the chemical species were determined. The observation of binding-energy shifts with depth provided additional information on the bonding and/or depth-dependent potentials in the system.

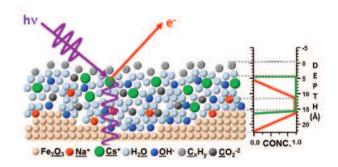
'We determined that the sodium ions are located close to the iron oxide/solution interface, while caesium ions are on average not in direct contact with the solid/liquid interface,' Bluhm says. 'We also discovered that there are two different kinds of carbon species, one hydrophobic, which is located exclusively in a thin film at the liquid/vapour interface, and a hydrophilic carbonate or carboxyl that is evenly distributed throughout the liquid film.'

A key to the success of this study was the use of X-ray standing waves to excite the photoelectrons. A standing wave is a vibrational pattern created when two waves of identical wavelength interfere with one another: one is the incident X-ray and the other is the X-ray reflected by a mirror. Interactions between standing waves and core-level electrons reveal much about the depth distributions of each chemical species in a sample.

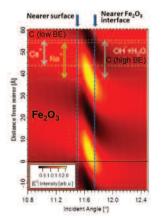
'Tailoring the X-ray wave field into a standing wave can be used to achieve greater depth sensitivity in photoelectron spectroscopy,' Fadley says. 'Our combination of an oscillatory standing-wave field and the exponential decay of the photoelectron signal at each interface gives us unprecedented depth resolution.'

In their *Nature Communications* paper, the authors say that future time-resolved SWAPPS studies using freeelectron laser or high-harmonic generation light sources would also permit, via pump-probe methods, looking at the timescales of processes at interfaces on the femtosecond time scale.

'The range of future applications and measurement scenarios for SWAPPS is enormous,' Fadley says. Reproduced with permission from Lawrence Berkeley National Laboratory/Phys.org APPS ... made it possible for the first time to use X-ray photoelectron spectroscopy under pressures and humidities similar to those encountered in natural or practical environments.



By utilising X-ray standing waves to excite photoelectrons, SWAPPS delivers vital information about all the chemical elements at the heterogeneous interfaces found in batteries, fuel cells and other devices. Slavomír Nemšák



SWAPPS measures the depth profiles of chemical elements with sub-nanometre resolution in the direction perpendicular to the interface, utilising an X-ray standing wave field that can be tailored to focus on specific depths, i.e. near the surface or near the iron oxide interface.

Chuck Fadley

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### New Fellow

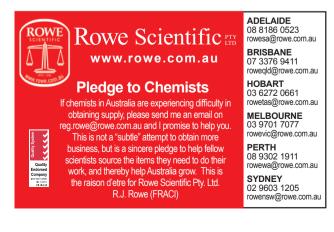
Anthony O'Mullane was born in Cork, Ireland; he received his BSc from University College Cork in 1997 and completed his PhD at the same university in 2001 in the field of gold electrocatalysis. He undertook postdoctoral fellowships at Technische Universität Darmstadt, Germany (organic electronics), University of Warwick, UK (electrochemical imaging studies) and then in Australia at Monash

University (organic semiconductors, large amplitude Fourier transformed AC voltammetry). In 2008, he worked briefly as a research scientist at CSIRO before taking a position at RMIT University where he was then awarded a Vice Chancellor Senior Fellowship. In 2012 he was awarded an ARC Future Fellowship and in 2013 continued this fellowship and started a senior lectureship at Queensland University of Technology.

O'Mullane's research is multidisciplinary in nature and includes the electrochemical synthesis and characterisation of nanostructured materials such as metals, metal oxides and conducting organic materials; electrocatalysis; catalysis; photocatalysis; lithium metal batteries; liquid metals and in particular the application of electrochemical methods to various aspects of physical, chemical and biological science. In essence, his work focuses on applying electrochemical principles to understand electron transfer processes that are at the core of most technologies, devices or applications. He thoroughly enjoys collaborative research projects and to date this has led to the publication of over 100 journal articles.

He and his colleagues were awarded the John A. Brodie Medal (2010) and he recently received an RACI Citation Award (2014) for his contribution to chemistry and the chemistry profession.

O'Mullane served as the RACI ambassador for RMIT during his time there, and also as the secretary (2010–13) and now Chair of the Electrochemistry Division of the RACI. He is married to Linda (an economist). They have two daughters Meesha and Maya, Meesha (5) having the current ambition to be a 'doctor scientist'.



### **Notice of Special General Meeting**

A special general meeting is planned for Thursday 9 July 2015 at 7 pm in Lecture Theatre 4, School of Chemistry (Building F11), University of Sydney, NSW 2006. The agenda will be:

- 1 Welcome
- 2 Apologies
- 3 Proxies received
- 4 Resolution
  - Accept the revised constitution
- 5 Vote
- 6 Result of vote (To be accepted, 75% of the votes must be in favour.)
- 7 Meeting close

The sole topic of the meeting will be a vote on a resolution to accept the revised constitution.

The revised constitution is included as an insert in this magazine. It is also available, together with a comparison with the current constitution document, on the RACI website at www.raci.org.au/theraci/corporate-governance/notice-of-general-meeting.

The constitutional revision has been formulated through an extensive consultation process within the Board, the Assembly and the membership in general through a progression of green papers, white papers and drafts all open for comment.

Eligible voters include all individual members except undergraduate students and Associates.

If you are unable to attend the meeting, you can still vote by use of a proxy form. A proxy form is included as an insert in the magazine together with a stamped return envelope or it is available on the website listed above.

Complete the proxy form and either return it to the CEO at the National Office before 8 July 2015 or give it to a colleague who is attending the meeting.



# George Victor Meehan A gifted teacher

It is with great sadness that we note the passing of George Victor Meehan in the Adelaide Hills on Saturday 15 March 2015. George devoted most of his professional career to James Cook University over four decades, and had a distinguished career in both teaching and research. He is very

warmly remembered by all his students and colleagues.

George Meehan was born in Western Australia and did his BSc and Honours degrees in Chemistry at the University of Western Australia. He then moved to the Australian National University, where he undertook his PhD in synthetic organic chemistry. He subsequently held two postdoctoral positions at Ohio State University and University College London before being appointed to the staff of the University of Strathclyde as a lecturer in organic chemistry (1970–5). In 1976, he returned to Australia to take up a position as a senior lecturer at James Cook University – from where he retired as a professor in 2009.

George was a supremely gifted teacher and he was invariably deeply admired by students he dealt with at both the undergraduate and postgraduate levels. He was uncompromising about the standards required at the tertiary level for graduates, and while challenging students, he displayed infinite patience to ensure they not only reached that standard, but also realised their own talents.

In his research, his primary interests were in synthetic organic chemistry for specific chemical and biological purposes. The emphasis of his medicinal/bioorganic chemistry work was on the synthesis of molecules that exhibited significant pharmacological activity or were useful as biochemical tools. However, perhaps he was ultimately more widely recognised for his collaborative work on supramolecular chemistry/molecular and metal-ion recognition with Professor Leonard Lindoy - who was on the chemistry staff at JCU from 1970 to 1996 and then at the School of Chemistry, University of Sydney. This collaborative program was substantially funded (>\$1 million) by the Australia Research Council (inter alia) from 1992 until after his retirement, and was very productive - with nearly 40 joint publications and many invitations (usually presented by Professor Lindoy) for plenary or section lectures at national and international conferences.

George Meehan had an encyclopaedic knowledge of synthetic organic chemistry and he was always a wonderful and very generous source of wise information, advice and guidance about strategies in organic chemistry. His record boasts some 80 publications – almost invariably in leading international peer-reviewed journals.

George Meehan also provided significant academic leadership throughout his career – his voice was always one of adherence to best practice and the maintenance of the highest academic standards. Among many contributions, he played an extremely significant role in the establishment of the very successful pharmacy program at JCU, and for a time he had a significant role in the activities of the Staff Association. George was the quintessential team player.

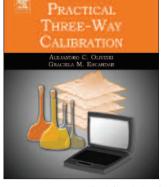
George was also involved in RACI activities: he was the Secretary of the North Queensland Section 1977–9, and was subsequently the Section Chairman in the early 1980s. In 1989, he was the Secretary for the National Conference of the RACI Division of Organic Chemistry, which was held in Townsville, and he was a regular visitor to primary schools in the region for the 'Chemistry in Schools Program' run by the Chemical Education Division of the Queensland Branch.

George Meehan had an encyclopaedic knowledge of synthetic organic chemistry and he was always a wonderful and very generous source of wise information, advice and guidance about strategies in organic chemistry.

On his retirement, George and Susan moved to Adelaide where they built a beautiful home in the Adelaide Hills. However, during 2014, George became seriously ill as a complication of some procedures associated with his contraction of emphysema and his health deteriorated all too quickly. He is survived by his wife Susan – herself a faithful servant of JCU in administration for many years (particularly the Graduate Research School) – and their four sons – Malcolm, Gareth, Anthony and Leon – and their families.

George Meehan was a very major force in the establishment of the research profile of James Cook University and there are very fond memories of his time in Townsville. Vale George – you were a very good friend and valued colleague. May you rest in peace.

Emeritus Professor Richard Keene FRACI CChem



# Practical three-way calibration

Olivieri A.C., Escandar G.M., Elsevier, 2014, hardback, ISBN 9780124104082, 330 pp., \$176.95, e-book US\$150

Quantitative analysis is subject to a variety of constraints, which vary from situation to situation, but universally has an over-riding aim of getting an appropriate answer to a chemical problem, in a timely

manner and with minimal effort. Chemical data is very important; considerable effort, time and expense are often required to get it, so it is important that efficiency of acquisition and its utility be maximised. Chemometrics offers a way to facilitate this, by melding the chemist's art with principles of experimental design and statistical data processing. It is probably fair to say that chemometrics exists on the fringes of chemistry. Most chemists know very little about it; a good number think it is probably important but lack the detailed understanding to either use its techniques or grasp its applicability; and others view it as 'black magic'. Further, it usually requires a reasonable level of computer programming skill and an understanding of difficult concepts in mathematics and statistics.

Practical three-way calibration, available both as a text and an e-book, is intended as an introductory-level guide to analytical calibration with three-way instrumental data (for example, data from a diode array HPLC detector in the form of wavelength vs signal vs time). The authors claim that prior programming experience is unnecessary and that there is no need to learn programming languages. Freely available software such as MATLAB (a high-level language and interactive environment that lets you explore and visualise ideas across a range of disciplines from signal processing to finance) and MVC2 (model view controller software) is used throughout the text and the authors walk the reader through examples from analyses. These are of graduated complexity and their explanations are aided by computer screen shots. The mathematics and statistics are kept to reasonable levels throughout.

The book begins with a discussion of calibration scenarios before investigating the attributes of various forms of data. After introducing the MVC2 software, a series of quite complex chapters follow, covering, inter alia, factor analysis for tri-linear and non-linear data, multivariate curve resolution, partial leastsquares, and three-way/second-order standard additions. *Introductory*, yes, but these are certainly not trivial concepts. There is danger of reaching erroneous conclusions if the underlying concepts are not clearly grasped. (If you don't believe me, consider some of the guff people drag out of Excel statistics routines: the machine spits out the number, so it must be right and pregnant with meaning!)

# Chemometrics [melds] the chemist's art with principles of experimental design and statistical data processing.

*Practical three-way calibration* is far from an 'easy read'. You really need to work at it, preferably in front of a computer. If you do that, I'm reasonably confident it will enrich your analytical chemistry perspectives, help you better plan and process your experimental data, and enhance the level of cunning you bring to hunting the analytical snark. For me, at least, there is a very steep hill to be climbed. The authors are Argentinian and there is a delightful Spanish flavour to their writing. They cogently quote Saint Augustine (re time). Let me requote, slightly altered: 'If no one asks me about it (practical three-way calibration), I know what it is, but if I wish to explain it to him who asks me, I do not know'. The book has moved me from total ignorance to educated uncertainty.

R. John Casey FRACI CChem

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## Can sharing your personal data protect your freedom?

We increasingly live in an age of big data, but does that equate to an Orwellian dystopia where 'Big Brother is watching you'? Are privacy and data sharing directly in conflict, or can an organisation's decision to share your personal data be compatible with protecting your freedom and choice?

The European Union is proposing a new Data Protection Regulation, which could curb data sharing in Europe, including for research purposes. Could legislation that is designed to protect individuals from unwanted use of their data actually undermine the wellbeing of the people it seeks to protect?

At the Wellcome Trust Sanger Institute, big data is our bread and butter. In January 2014, we reached a major milestone, having collected one petabyte (one million gigabytes) of genomic data and we continue to collect about one terabyte (one thousand gigabytes) each day.

The data that we collect is used around the world to improve knowledge of human and animal health. We pride ourselves on our expertise in sequencing and analysing genomes. Our research is overwhelmingly supported by charitable and public funds, so we believe it right and in the public interest that others benefit from the science we create by sharing our expertise, resources and the data we generate. Doing great science is of limited benefit if others cannot use it.

So, if sharing genomic data is in the public interest where does that leave our participants' privacy? Our human data is generated from volunteers who donate samples. Whether they are apparently healthy people or people with specific illnesses, they appreciate the fact that their data is beneficial to society. For many participants, they do not simply donate for an individual project, but instead expect and want us to share the data we derive from their donation freely with other researchers.

Our participants recognise that it is not possible to predict the future uses for their data but they still consent to and want their data shared for research purposes. This is typically done in a coded anonymised form that prevents researchers from knowing individuals' identities.

Alongside consent, the Sanger Institute also operates a managed system whereby researchers must apply to access data. An application to access data is never judged on the merits of the science or whether it competes with our own research, but simply on whether the applicants are seeking to use data for legitimate and ethical research purposes.

As we have the consent of our participants to share data, it is not unreasonable to ask why we have managed access. Consent is a fundamental and critical cornerstone of research, the importance of which cannot be underestimated, but believing that consent completely protects participants from having their privacy breached is, perhaps, a mistake.

Every day people give commercial organisations consent to use their data when they sign up for their services, and yet often feel their privacy has been invaded if an organisation uses their data in a way they did not expect. This was exemplified in the backlash that accompanied publication of the experiment Facebook carried out on its users. Every user had given consent but many still felt that Facebook had breached their privacy.

At the Sanger Institute, we believe that guarding data from misuse stands alongside consent as the best means to guarantee we protect our participants' privacy.

Given that consent is rightly enshrined in research and permeates our society, it is understandable that the European Parliament put consent at the heart of their proposed Data Protection Regulations, which will include health-related and genetic data. Under the proposals, individuals need to provide purpose-limited consent for their personal data to be used and they must re-consent on a case-by-case basis for their personal data to be shared.

On the face of it, this sounds reasonable, but, in reality, vital research that is legal and ethical would not be possible because of the difficulties of re-consenting thousands of participants each time their data was shared for new research.

We believe that these regulations will make research at the Sanger Institute and worldwide extremely difficult in a way that would be detrimental to research and health care, but critically they also undermine the autonomy of research participants throughout Europe. We should all have the right to say how our data is used.

For these reasons the Sanger Institute has chosen to support the Data Saves Lives Campaign, which aims to persuade the EU to recognise the importance of sharing data for research and to revise its restrictions on research. The Sanger Institute is committed to protecting the privacy of our participants, without whom our work would not be possible.

Over the coming months we will campaign to be allowed to do the research that we believe is so important to patients and beneficial for wider society and in the process we will be campaigning for our participants' autonomy and their right to self-determination.

Sarion Bowers is the Research Policy Advisor at the Wellcome Trust Sanger Institute. She has a PhD in Biochemistry. Before joining the Institute, she did postdoctoral fellowships in Leeds and Connecticut. She recently completed an MSc in Science and Technology Policy, in which she researched the adoption of genomics into the NHS. First published at https://sangerinstitute.wordpress.com/ 2015/01/28/can-sharing-your-personal-data-protect-your-freedom.

# Hate the peer-review process? Einstein did too

Most academic papers today are published only after some academic peers have had a chance to review the merits and limitations of the work. This seems like a good idea, but there is a growing movement that wants to retort as Albert Einstein did to such a review process.

Academic review process was different in Einstein's time. In his brilliant career, the only time his work was subjected to blind peer review – the authors don't know the reviewers and vice versa – he showed contempt for what is now the gold standard of science. Was Einstein right to be so suspicious of the peer-review process? Should we learn from him and begin to question the widespread use of peer review in academic science?

The first part of Einstein's career was in the German-speaking world. The German physics journals, in which Einstein published his breakthrough work, didn't have the same peer-review system we use today.

For instance, the *Annalen der Physik*, in which Einstein published his four famous papers in 1905, did not subject those papers to the same review process. The journal had a remarkably high acceptance rate (of about 90–95%). The identifiable editors were making the final decisions about what to publish. It is the storied editor Max Planck who described his editorial philosophy as:

To shun much more the reproach of having suppressed strange opinions than that of having been too gentle in evaluating them.

Many of the core scientific discoveries were not peer reviewed to modern standards. For example, the publication of the foundational paper describing the double helical structure of DNA by James Watson and Francis Crick in 1953 would have been jeopardised in the context of the classic review system as we know it, because of its speculative nature.

At the prestigious journal *Nature*, the peer-review system was only formally introduced in 1967. More recently, the discovery of distortion in gravitational waves by a telescope at Harvard – which has crucial consequences for our understanding of the formation of the universe – was presented as preliminary and treated with extreme caution and even sometimes with denigration, because it had not been peer-reviewed.

#### American adventure

It was only after Einstein came to the US in 1935 that he came face to face with the peer-review process. He and his younger colleague, Nathan Rosen, sent a paper on gravitational waves to *Physical Review*, a journal which had established its reputation as the premier physics journal in the US. The paper had the potential to be highly controversial as it challenged the idea that gravitation was a wave.

John Tate, the editor of the journal, hesitated over Einstein's paper for a month. He then sent it to a reviewer for comments – his selected reviewer was probably the famously gossipy Howard Percy Robertson, one of Einstein's colleagues at Princeton. The reviewer returned ten pages of comments which cast doubt on many of the central claims in the paper. The editor returned these comments to Einstein, asked him to consider the issues, and make any changes he saw necessary. Here is how Einstein reacted:

We (Mr. Rosen and I) had sent you our manuscript for publication and had not authorised you to show it to specialists before it is printed. I see no reason to address the – in any case erroneous – comments of your anonymous expert. On the basis of this incident I prefer to publish the paper elsewhere.

Although he withdrew the paper from *Physical Review*, Einstein went on to publish it in a much more low key outlet, the *Journal of the Franklin Institute*. However, the published version contains substantial revisions. It appears these revisions were largely on the basis of a discussion he had with Robertson at Princeton. The revised version toned down many of his original huge claims. These revisions may have saved him from public embarrassment.

#### What would Einstein say today?

Some might see this as an amusing historical incident. But we think it contains some important lessons for scientists of all kinds today. This is because it reflects the current tension regarding the peer-review system.

The story reminds us that double-blind peer review is only a relatively recent invention. For most of history of science, scientific advances were judged in a much more open and public fashion. It also shows us that the peer-review process can provoke displeasure among even the greatest. It can mean scientists not listening to criticism. Sometimes the result is that many ideas don't see the light of day.

These anecdotal lessons point to wider issues with the peerreview process, which itself hasn't been studied in much detail. The review process was meant to save scientists from mistakes and public embarrassment. The idea was that peers help to improve our work, and the review process of high-status journals can serve as 'stamps of approval' or simply signal of quality.

But sometimes a collegial discussion rather than formalised peer review can be a better way of getting the message across. So far the peer-review process has been largely an item of faith – something that probably produces better science. However, there is a growing body of evidence which is challenging this notion.

An extensive review of the literature on peer review in 1998 identified problems. They found that there is a low level of reliability and agreement over the quality of submitted papers, largely because of a lack of objective evaluation criteria. Even worse, reviewers make mistakes in their evaluation and often accept papers they should have rejected. As a direct consequence, established journals are usually biased against innovative work.



communities have experimented with making reviewing process public.

In the hard sciences, there are those who post papers online and other scientists decide whether they are worth being cited. PLOS ONE publishes any paper that has been considered as 'technically sound' after a round of editorial review, and readers then judge the relevance of the research. Another alternative system would be to have a set of reviewers rating all

In our own field of management science, some have claimed the peer-review system means academic work can simply end up losing its integrity during the review process, and can result in trivial and boring research.

On a more positive note, when reviews are perceived of quality by authors, they tend to generate more citations, which is a measure of the number of times a research paper is mentioned in other journals and is considered a mark of quality. Also, reliability is not necessary for an efficient review process – often it is the process of peer review itself that contributes to improving the paper. Reviewers play a developmental role in the construction of knowledge, and the energy they deploy in this process is primarily driven by moral motives rather than any material interest.

#### Bad review for peer review

Perhaps the most gentle solution would be to improve peer review. There are clearly disagreements about how this might be done. Some claim the peer-review system needs to become more objective through the introduction of clearer criteria and better trained reviewers who are able to systematically apply these criteria. Others claim that some subjectivity is important because it can stop reviewers herding to established ideas, thereby crowding out alternative and often more innovative approaches.

The frustration regarding the peer-review system has led to new hybrid systems to emerge. For instance, some scientific the papers submitted online, and revising their judgement in case of resubmission. The growing number of open access journals has raised concerns that peer review would be progressively abandoned and search engines and metrics will replace editors and peer reviewers.

#### Let's try something new

Some, like Einstein before them, think that the peer-review system should be abandoned in favour of a 'market of ideas' where the best research would naturally be identified by the crowd, hence reducing the cost of the review process. There are many potential dangers of these alternatives to peer review, the most obvious being expanded opportunities for 'bad science' to masquerade as legitimate work. However, given the immense cost and frustrations associated with the peer-review process, we think it may be worth considering alternatives.

Peer reviewing is an important scientific institution. But there might need to be a range of forums in which scientific results and discussion takes place – peer-reviewed journals only being one among a number of options. Such options would then compete for both the attention of the readers and the best papers. We think this mixed scientific landscape would have pleased Einstein.

Andrew Spicer is Professor of Organisational Behaviour, Cass Business School at City University London. Thomas Roulet is Novak Druce Research Fellow at the University of Oxford. First published at www.theconversation.com.

### **Biofuels and biochemicals**

Renewable resources are often touted as the route to a carbonfree economy. In today's climate of low oil prices, the economics of biofuels and biochemicals production need consideration. Production of ethanol and the conversion of ethanol into ethylene are a useful basis for discussion.

Ethanol is produced by a wide variety of fermentation processes, of which the most widespread is the conversion of carbohydrates (such as sugar) into ethanol and carbon dioxide. For sucrose, the reaction stoichiometry is:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 4C_2H_5OH + 4CO_2$$

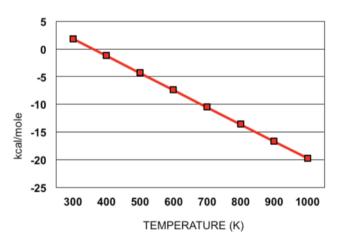
This route to ethanol is widespread as it is the basis for the production of potable ethanol (booze). In most jurisdictions, the product attracts large excise taxes (currently \$80/L for whisky). It is also used in the production of ethanol fuels in the US and Brazil and at Sarina (using sugar molasses) and Dalby (using sorghum) in Queensland. Note that most Australian fuel ethanol is produced as a by-product from starch manufacture at Manildra in NSW and this process is not considered here.

One point to note is that a typical fermentation takes place in a relatively dilute solution so that one of the main operating costs is the separation of the ethanol from the excess water.

Ethanol can be dehydrated to produce ethylene at temperatures usually over 200°C (500 K):

 $C_2H_5OH \rightarrow C_2H_4 + H_2O$ 

This is an equilibrium reaction (see below) with a large portion of industrial-grade ethanol being produced by hydration of ethylene at low temperatures.



Free energy change  $C_2H_5OH \rightarrow C_2H_4 + H_2O$ 

High potable excise results in heavy regulation of industrial ethanol, which is generally tax free, and fuel ethanol, which is generally taxed at fuel levels (\$0.389/L), to ensure the integrity of the excise system.

Prior to the advent of the petrochemical industry, ethylene was often produced by dehydration of ethanol and is still found in small facilities in some countries (India, China) and was once used in Australia by CSR Chemicals at Rhodes. Recent interest in renewable plastics has reinvigorated work in the process.

The table gives illustrative economics using sucrose (as molasses) as the feedstock. The first two columns give scenarios for two typical scales of operation – capital and operating costs are in 2013 US dollars. Feedstock for this example was priced as sugar at \$US300/t.

#### Statistics for ethanol production

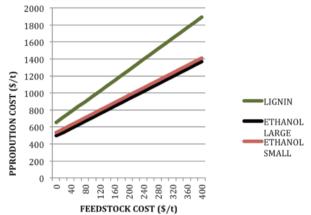
Feedstock	Molasses	mol + sugar	Lignin
Ethanol output (ML/year)	56.79	37.86	56.79
Capital cost (\$million)	49.63	37.10	65.91
Capital costs (c/L)	11.86	13.30	15.75
Operating costs (c/L)	27.35	29.09	35.70
Feedstock costs (c/L)	51.78	51.78	4.89
Ethanol production costs (c/L)	90.99	94.17	56.34
Gasoline at current oil price (c/L)	43.73		
Typical US ethanol traded price (c/L)	40.00		
Capital costs (\$/t)	150.31	168.55	199.60
Operating costs (\$/t)	346.67	368.75	452.47
Feedstock costs (\$/t)	656.26	656.26	61.98
Ethanol production costs (\$/t)	1153.24	1193.56	714.05
Gasoline at current oil price (\$/t)			594.71

The data illustrates that the ethanol production cost is more than 90c/L, which is more than double the cost of gasoline (petrol) at the current oil price (about \$65/bbl for Tapis crude) and the traded price for ethanol on the US market. At this time, the cost of sucrose (\$300/t) is higher than its value as ethanol.

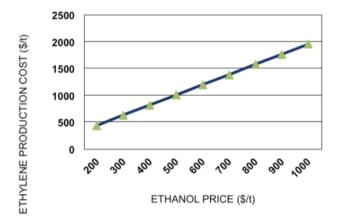
Because of the impact on the use of arable land for fuel production forcing increases in food prices, there is much effort in developing non-food feedstock such a lignocellulose (e.g. wood fibres, corn stover, bagasse). There is a paucity of information on the cost of this process but in the last column of the table I have placed some indicative costs for a similar output. There are three main points:

- Capital costs are higher due to a more complex process and a lower overall efficiency. Large volumes of primary feedstock will require additional processing such as drying and shredding. Also specialist enzymes are needed for the process, which will be produced on-site in a separate facility.
- Operating costs are higher, reflecting a more complex process, which will include the disposal of significant volumes of waste material
- Feedstock cost is not zero, as might be assumed. Proposed sources will require collection and transport to the facility. The transport cost in energy terms limits the scale of the operation to a relatively small facility so that economy of scale is limited. The notionally free feedstock may have a value (such as mulch), which will have to be recompensed in some way.

Assuming a value of \$20/t for the cost of the feedstock and a 65% efficiency in the process, then production costs are reduced to 56c/L, which is still higher than the price of ethanol and gasoline at current oil prices. Without on-going subsidy, this revolutionary new route only makes sense at significantly higher oil prices. The sensitivity of the cost of production to feedstock price is shown.



Ethanol production cost versus feedstock price.



Sensitivity of ethanol production cost to ethanol price.

Rather than use ethanol for a relatively low value commodity such as fuel, what about conversion to higher value ethylene? The salient economics are illustrated.

With a typical ethylene value of about \$1300/t, ethanol prices have to be below about \$600/t to make this route viable. As noted from Figure 2, this is only likely to be achieved by new (unproven) routes using low-cost lignocellusosic feedstock with cost below \$40/t.

An alternative view is that using ethanol priced at \$1000/t to give ethylene at \$2000/t, the difference (approximately \$700/t) is the premium a user would have to pay to use 'renewable' ethylene for 'renewable plastics'.

Although there is much interest and political will to develop and promote ethanol as a renewable fuel, this economic analysis shows that, without high government subsidies such as tax breaks, grants and fuel mandates, the current technology is only viable at high oil prices (>\$100/bbl). At current oil and sugar prices, the level of subsidy required is very high and would present a major hurdle for private investment in this sector.

This study also shows that new routes using lignocellulose as a feedstock would also require high oil prices to succeed. At present, the technology is marginally viable at best and still requiring a subsidy at the current oil price.

Converting ethanol to ethylene is marginal unless the ethanol was available at energy equivalent prices when the production cost would be similar to the product of ethylene from ethane by steam cracking (May issue, p. 36).

Using the route to produce renewable ethylene and hence renewable plastics implies a premium of at least 50% relative to conventionally produced products.



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# Whodunnit?

Television shows with a forensic science theme are a popular genre at the moment. The combination of 'high-tech science', the nerdy/edgy lab experts and the standard mystery solved in 55 minutes is grabbing the attention of TV audiences around the world. In the real world, the field of environmental forensics has become an important set of tools for environmental regulation and enforcement of environmental compliance. Besides the trendy high tech, there is a lot of sound, basic science that also goes into nabbing the environmental baddies.

In my time at EPA Victoria, the Environmental Chemistry team was an integral part of gathering the evidence that would stand up in Court and identify the guilty parties. EPA's field staff had an important role to play, too, because the integrity of the samples they collected, and the ability to demonstrate custody of those samples through the analysis chain, was critical in establishing facts beyond reasonable doubt.



Abestos cement roofing, Uglich, Yaroslavl Oblast, Russia.

In one case, the field team investigating a fish kill in an urban creek used chemical analysis to identify that the fish had died from ammonia poisoning. The source was not obvious, there being no discoloured discharges from the stormwater system to provide any clues. One of the chemistry team recognised that fertilisers are sources of ammonia, so the field staff searched for warehouses and other storages that might have been holding fertilisers. This identified one premises that had been storing urea in bulk, in stockpiles on the floor of a large shed. Somehow, the powder made its way into the stormwater system and hydrolysed, releasing ammonia into the creek. In this case, it was the chemical reasoning about the possible source that drove the good outcome (at least from the perspective of nabbing the culprit).

The major part of EPA's work involved GC-based analysis of hydrocarbon mixtures. This is hardly surprising given the widespread use of petroleum mixtures and the highly mobile nature of the liquids themselves. Hydrocarbon 'fingerprinting' is the main game here, and it even takes its name from another well known forensic science technique. The overall envelope of a GC trace can be a good starting point to try and either match a suspected source sample with one from the environment, or rule out possible sources. High-resolution GC enables several marker compounds to be targeted, and measurement of their relative abundances enables a high level of certainty to be achieved in matching samples. We typically used GC-FID techniques to achieve a match, but occasionally the added diagnostic power of GC/mass spectrometry came into play.

While it might be possible to use GC techniques to match petroleum samples with a high degree of certainty, one needs a good idea of where to look for a source in the first place. When a marine oil spill washed up on Phillip Island, impacting on Victoria's famous little penguin colony, finding a source might have been a daunting prospect. Bass Strait is wide and wild, and the currents are strong. However, in this case, the Bureau of Meteorology and the Australian Maritime Safety Authority (AMSA) were able to apply computer modelling to track the path of the petroleum mass washed up on the beach. The chemical fingerprint indicated how long the spill had been in the environment, and tracking of the winds and current established, in concert with satellite signals that track vessels, the one ship that had been in the likely source zone at the time. AMSA intercepted the ship at its next Australian port of call and seized its log, which showed that the bilge tanks had been cleaned illicitly in the location and at the time modelling had predicted.

Like satellite imagery, conventional aerial photography can be used for surveillance and environmental monitoring. In Lombardy, Italy, a multi-year program of aerial surveillance using multispectral infrared and visible imaging has been used to map densely populated areas for the presence of asbestos cement roofing materials. By examining the images from two different points in time, the regional EPA could identify the houses from which asbestos cement materials had been removed. Staff then visited houses to confirm that the asbestos-containing materials had been disposed of properly. From my observations of rural housing in Russia, a similar approach might be applicable there if the authorities were so inclined. Asbestos cement seems to have been a popular roofing material, possibly in the Soviet era, but there is a trend of replacing it with coated steel sheeting, often in bright colours. When I saw the apparent trend, my immediate thought was about what had happened to the waste materials.

One of the most effective tools in environmental forensics is the dog-walking citizen. Any number of environmental spills and other incidents, not to mention even more sinister offences, are first brought to light by those civic-minded people who value canine companionship and fresh air. Which just goes to show that it doesn't have to be all high tech and nerdy lab geeks in order to find the guilty party.

**Paul Moritz** MRACI CChem is a Principal Environmental Scientist with Douglas Partners, and an EPA-appointed Environmental Auditor in Victoria and the Northern Territory. He is also a dog owner who walks by the local creek.

# The wine of Madeira

The general knowledge crossword in Melbourne's *Sunday Age* occasionally seeks a word for a 'heating process used in wine production'. While there are perhaps a few options, the one that came to my mind initially was the production of Madeira, although the crossword compiler required the specific name of 'estufagem' for the heating process. In reality, there are two versions of the estufagem process as well as another heating strategy known as 'canteiro'.

Madeira wine comes from the island of the same name, part of the Portuguese archipelago in the north Atlantic Ocean. The capital, Funchal, is located at latitude 32°N. For comparison, this is similar to Rottnest Island in our hemisphere. On the other hand, Funchal is about a 90-minute flight from Lisbon and is in fact closer to the African coast than mainland Europe. The island area is around 800 km<sup>2</sup> (references vary!), and importantly for grape production it is hilly with most of this area at slopes over 25%. This presents a challenge to viticulture.

The vines are planted on terraced land, with about 1700 hectares under vine. The actual holdings are small, with the average around 0.3 hectare, requiring wineries to purchase grapes from many growers. The common trellis used is a pergola system, with the vines fruiting below wires running between posts at 1–2 metres above the ground. Some farmers will even plant vegetables for domestic use under the vines – a great way to make use of the limited space.

Mechanisation is a challenge and most work, including harvesting, is done by hand. The older practice involved crushing the grapes on site and transferring the must into goatskin vessels of about 70 litres volume. These vessels would then be carried by hand, often across the carrier's back, along the narrow pathways between the terraces to the winery. The journey may be up to 20 kilometres. Check out bit.ly/19ZQTYO and the following page for some great images. Trucks are now used to transport the grapes.

The initial part of the winemaking process is similar to that for fortified port wine. After the grapes are crushed, the fermentation is allowed to continue until the selected sweetness level is achieved. Fermentation may be performed either in stainless steel vats or in oak casks. The fermentation is stopped by the addition of neutral alcoholic spirit around 96% strength. As less 'natural' alcohol is produced in the shorter fermentation for sweeter wines, more spirit is required to achieve the desired final alcohol concentration around 19-20%. This results in greater dilution of the wine compared to the drier styles. Bual and Malvasia (sometimes called Malmsey) grape varieties tend to be used for the sweeter wines and may be fermented on skins for more effective extraction of phenolic compounds. The longer fermentation results in a drier wine and this is normally performed 'off-skins'. Verdelho, Sercial and Tinta Negra Mole varieties are more commonly used for the drier wines.

### What to try

The wines from Madeira are not common in Australia, but they have a significant historical and international reputation. Tradition has it that Madeira wine was used for the toast at the signing of the US Declaration of Independence. A pipe was sent to Napoleon *Le Premier* in exile, although he apparently declined to open the cask. For those readers who remember Flanders and Swann, Madeira seems to be favoured by roués (bit.ly/1CNHTjN).

My experience with these wines is limited to those made from Verdelho. The off-dry versions are suitable as aperitif wines. The nose tends to show caramel, smokiness and maybe dried stone fruits while the palate normally shows good acid structure to hold the wine through a long finish. A 500-millilitre bottle of a 10-year-old wine is about \$50. If you are keen to try an aged wine, the Solera 1898 is available as a medium dry wine at \$1350 (750-millilitre bottle), although one website was offering a 10% discount for a dozen purchase!

The uniqueness in the production of Madeira wines comes from the heating process employed after the fermentation and fortification steps. Heating is utilised to enhance the ageing and maturation of the wine. The estufagem process involves placing the wine in large stainless steel tanks and heating the wine to between 45°C and 55°C for at least three months, after which it is allowed to cool and then aged in old oak casks. A variation of this process uses casks in a warm room at 30–40°C for at least six months to achieve the same degree of development. Wines destined for the upper end of the market go through the canteiro process that involves the wine in 480litre pipes (oak barrels) being placed under the eaves in wine company lodges in Funchal. Heating is by the sun only and the maturation takes at least two years, although some may be left under the eaves for 20 years or longer.

Serendipity played a significant part in the development of this winemaking process. Tradition has it that a ship loaded with Madeira on its way to England deviated via the Indies. When the wine was opened, it was regarded as the 'best ever' and so a sea voyage was introduced as standard practice. After some time, it was realised that perhaps heating of the wine in the ship's hold as it passed over the Equator may have been the basis for its development and thus heating in the winery replaced the ship voyage. Exposure of Madeira to heat and oxygen (through ingress via barrel staves) means that the wine will not oxidise when opened and so will keep well for years, if one can wait that long!



Geoffrey R. Scollary FRACI CChem (scollary@unimelb.edu.au) was the foundation professor of oenology at Charles Sturt University and foundation director of the National Wine and Grape Industry Centre. He continues his wine research at the University of Melbourne and Charles Sturt University.

# 1300 days later

An enormous, 3-storey tall blue plastic bear cups his hands around his eyes and presses his face up against the glass of the Denver convention centre, trying to peer inside. What he would have seen, had his plastic eyes worked on the 28th of August would have been ten thousand chemists from all over the world gathered together to talk about their research during the 242nd American Chemical Society (ACS) National Meeting.

It was with these words that I began my report to the RACI on my 2011 experience at the ACS. It was a memorable trip and remains one of my most fruitful conference experiences. I was a PhD student and filled with enthusiasm and awe at the breadth of research that was being undertaken in the field of chemistry.

Two weeks ago, I found myself at the ACS again, this time as a postdoctoral researcher. By sheer coincidence, it was again held in Denver, so it was a good opportunity to see what had changed in the last 1300 days and what hadn't.

The first thing that struck me was just how competitive the field is now that I am a postdoctoral researcher. As a PhD student, the atmosphere seemed to be more benign – I was, after all, in a cohort of relatively inexperienced researchers. As a postdoc, I am in a far more brutally competitive cohort. My peers are postdocs looking towards the next stage of their career. This inevitably means an assistant professorship – a position for which there is intense and seemingly insurmountable competition.

Sharing the experiences of two of my almost-peers may give you an idea of what the competition is like. (I say 'almostpeers' because they are a couple of years ahead of me with their careers.)

The first researcher graduated from the same group as I did and went on to postdoc for one of the top five polymer scientists in the US. In his three years with the group, he co-authored over 30 peer-reviewed papers. To put this number in perspective, I authored seven in my three and a half years as a PhD student, so he did very well indeed. When he landed a job, I was happy for him; he is clearly one of the bright young It seems that the assistant professorship is a much more difficult pond to get into than the postdoctoral one, but once you make it there, the fish are all pretty friendly and the bigger fish aren't looking to gobble you up.

postdoccing before landing his assistant professorship. He applied for 20 jobs and received nine offers. Much better, right? Ah, but he did his postdoc at Caltech. In the US, Caltech carries a lot of weight and, in addition to this, his advisor also actively worked to get him a job.

I write about these colleagues because it may be interesting for young PhDs to know what lies ahead in the job market. It is an especially sharp contrast with the process of finding a postdoc: I was working at the labs of my first-choice supervisor 12 months after approaching him!

While this may sound discouraging for aspiring researchers, there is good news. The assistant professors at the conference were a really supportive bunch. Each of them seemed genuinely warm and cordial towards their peers. Even more encouraging was the respect shown by the established professors towards the young up-and-comers. It seems that the assistant professorship is a much more difficult pond to get into than the postdoctoral one, but once you make it there, the fish are all pretty friendly and the bigger fish aren't looking to gobble you up.

I've moved from a small pond in New Zealand to a larger one in Australia to a larger one still in Europe. Now I look across the

iStockphoto/Diane Labombarbe

Atlantic to see an apparently enormous one in the US. The barrier to entry looks

high indeed, but I hope I have what it takes to make it. And with luck, 1300 days after today, the big blue bear may see an enthusiastic New Zealander addressing the ACS yet again, this time as an assistant professor!

The author is a small fish in Lausanne, Switzerland, and is aware of the irony that he wishes to swim in a pond in plain view of a giant blue bear.

chemistry. Then I found out that his advisor (the aforementioned top-five scientist) wrote him 40 reference letters before he secured a job. 40! That is a staggering number. Especially since you consider that I am approximately a third as productive as he is (publicationwise). Does this mean my referees will have to write me 120 letters of reference?

The next story is a little more positive. The researcher graduated from a wellrespected group and spent a year with a start-up and then 18 months

minds of polymer

# Neville Currey: interwar chemist?

In 1934, publisher Maurice G. Henderson produce a volume entitled *500 Victorians*, labelled as the Centenary Edition. It was not the latest edition of a regular publication but a one-off to take advantage of interest aroused by the centenary of settlement of the colony. It was normal for people to pay to be included in publications like this, but nothing in the book alludes to this and there was no press coverage that I could find.

All sorts of worthies were included, with photographs of their heads placed on top of sketched bodies wearing appropriate clothing, mostly suits. I was interested, of course, to see if there were any chemists. Indeed there were, and I found four. They were Professor Sir David Orme Masson ('you will need several APCs before tackling Sir David's literature'), Albert Cherbury David Rivett, Masson's successor in the Melbourne chair but by 1934 the CEO of CSIR, and Arthur Victor Leggo, metallurgist, chemical manufacturer and merchant. I was aware of these three, but the remaining chemist was unknown to me.

He was Neville Burton Currey, who was educated at Brighton Grammar, served in the Great War and 'on return founded the chemical works of which he is proprietor'. In 1917-19, he was a driver in a Signal Company in France. His membership of several clubs was mentioned, as well as his recreations - golf, yachting, aviation and tennis, each of which was illustrated by a little cartoon. There was no evidence of technical or university education; records at the National Archives of Australia show that he applied, as an ex-serviceman, for assistance in undertaking a course in gold assaying with Mr W. Levy of Melbourne but there is no evidence that this request was granted or that he did undertake such training that could have been the basis for a chemical business. It was noted that his father was Registrar of Titles and Registrar General of Victoria, so it seems unlikely that there was a family business for him to take over.

The 1934 volume gave his birth year as 1898, and his World War I service record shows that he was 19 years old when he enlisted in 1917. His World War II record gives the birth year as 1905. This may have been adjusted so as to make him seem under 40 years of age when he enlisted, because the correct date was implied upon his death in 1969 at age 71. During this second period of service, he faced a court martial in December 1942 but no details of the charge and the outcome are available.

From 1921 until the late 1930s, Currey was listed in directories as a chemical manufacturer with an office in a city building but no factory was listed. No advertisements or listing

in directories gave any clue as to what Currey's company manufactured, so I spent some time hunting around to see what he was up to.

There is one clue about what his chemical company was doing. In 1927, describing himself as a manufacturing chemist, Currey applied for an Australian patent for 'a process and apparatus for decorating purposes'. It concerned the decoration of a glass container such as 'a fancy shaped bottle' or a pottery object by coating it with a coloured film like that formed by a solution of shellac and 'gamboge saffron or the like' in clear varnish. Patterns in a variety of colours are formed by brushwork and a clear outer coating was to be applied to protect the design. A sketch of a typical product was included in the application. The patent was granted in 1928.

More robust materials such as ceramics are decorated by china painters, often using flower motifs, and this art draws on a culture going way back into history. The pigments, mostly metal oxides, are mixed with liquids and painted onto the ceramic. The liquid may be oil, often a mixture of mineral oil and an unsaturated vegetable (drying) oil, but water or glycols can be used and even glue or milk. The paint is allowed to dry and then the object is fired at 600–700°C. Several layers may be applied, with successive firings, to build up a threedimensional decoration. While unglazed material can be painted, most china painters prefer to work with glazed pieces. Dilute hydrofluoric acid was used to prepare the surface before application of the paint, but increasing hazard classification has made this acid almost impossible to purchase by hobbyists, so cleaning with alcohol, mainly to remove fingerprints, has to suffice. I see from recent press coverage of some antique glassware that painting could even be done on the inside of vessels.

Similar techniques were used to prepare most of the 'stained glass' that we see in decorative windows in churches and other places. I had always imagined that the glass was coloured (tinted) by including the metallic oxides or salts in the original melt. Some of it was made that way but much of it had the coloured layer painted after it was cut to size and shape and before it was fired to 'fix' the pigment. The more modern windows I have seen make use of tinted glass in bright colours with better light transmission, but the old techniques are still used for special pieces.



Ian D. Rae FRACI CChem (idrae@unimelb.edu.au) is a veteran columnist, having begun his Letters in 1984. When he is not compiling columns, he writes on the history of chemistry and provides advice on chemical hazards and pollution.

#### events

#### cryptic chemistry

18th International Conference on Organometallic Chemistry Directed Towards Organic Synthesis (OMCOS-18) 28 June – 2 July 2015, Barcelona, Spain

www.omcos2015.com

**11th International Symposium on Ionic Polymerization** 5–10 July 2015, Bordeaux, France

http://ip15.sciencesconf.org

#### 35th Australasian Polymer Symposium

13–15 July 2015, Gold Coast, Qld www.35aps.org.au

# 12th International Conference on Materials Chemistry (MC12)

20–23 July 2015, York, UK www.rsc.org/events/international

## 24th International Symposium: Synthesis in Organic Chemistry

20–23 July 2015, Cambridge, UK www.rsc.org/events/international

#### IUPAC 2015

48th General Assembly 6–13 August 2015, 45th World Chemistry Congress 9–14 August 2015, Busan, Korea www.iupac2015.org

13th Conference on Laser Ablation (COLA-2015) 31 August – 4 September 2015, Cairns, Qld http://cola2015.org

#### 13th Annual UNESCO/IUPAC Workshop and Conference on Macromolecules and Materials

7–10 September 2015, Port Elizabeth, South Africa http://academic.sun.ac.za/unesco

#### 22nd International Clean Air and Environment Conference

20-23 September 2015, Melbourne, Vic. http://casanz2015.com

#### 4th Federation of Asian Polymer Societies – International Polymer Congress

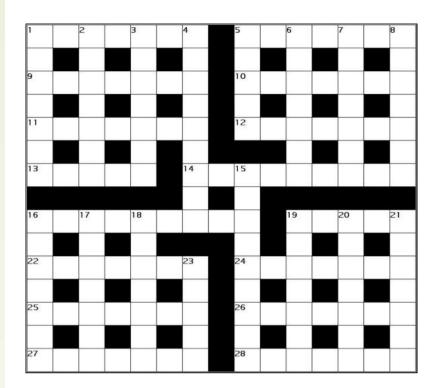
5-8 October 2015, Kuala Lumpur, Malyasia www.4faps-ipc.org.my

#### 2015 Sustainable Industrial Processing Summit and Exhibition

9 October 2015, Turkey www.flogen.org/sips2015

#### Pacifichem 2015 15–20 December 2015, Honolulu, Hawaii www.pacifichem.org

RACI events are shown in blue



#### Across

- Combine hydrogen, thorium, protactinium, nitrogen and a hydrocarbon mixture. (7)
- 5 Oi! Catch! Fumbled! What a shambles! (7)
- **9**  $(CH_3)_3N^+(CH_2)_2OHX^-$  618310. (7)
- **10** New relay behind bismuth film two molecules thick. (7)
- **11** Fifty-fifty is fair. (7)
- 12 Confused if Lusitanian comes back holding anion. (7)
- **13** Piddle in the street? Nice! (5)
- **14** Adept at organising titanium, carbon, iron, neon, iodine and fluorine. (9)
- **16** New niche in coal producing dyestuff. (9)
- **19** Little one's cat gets into the arsenic! (5)
- 22 Yank to admire and beautify Spooner macromolecule. (7)
- 24 It's late in the day to aim for treating 11 Across. (7)
- 25 Sent out diet met change. (7)
- **26** Triangular one, dope, with xenon and iodine mixed in. (7)
- 27 Indicators in glass bottles. (7)
- **28** Perhaps iron in a place where one feels comfortable. (7)

Graham Mulroney FRACI CChem is Emeritus Professor of Industry Education at RMIT University. Solution available online at Other resources.

#### Down

- **1** Clue: sun explosion in the middle. (7)
- **2** Bear show. (7)
- **3** Travel grant one of three. (7)
- 4 Eyelet can filter  $C_2H_2$ . (9)
- 5 Dice, perhaps, changes 2 into 8. (5)
- It describes a group attached to CH<sub>2</sub>=CHCH<sub>2</sub>- in a legally licensed business. (7)
- Your old place for digging up 5-methyluracil. (7)
- 8 Contemporary flow. (7)
- **15** Less room: points to carbon allotrope. (9)
- **16** Machines modified  $\pi$  score. (7)
- **17** Chilling  $O_2$  in the hold. (7)
- **18** Passivity of Iranite reaction. (7)
- **19** Expert pitch for compound. (7)
- 20 Crack if hard water follows oxygen radical. (7)
- 21 Imply offer. (7)
- 23 Bumps small numbers over Dextrose Equivalent. (5)



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# www.raci.org.au/awards

# **2015 NATIONAL AWARDS**

The RACI is a professional membership organisation and one of the most important duties of the organisation is the recognition and promotion of the contributions and achievements of our members.

There are a range of prestigious awards covering a broad range of areas from school education to applied research that are aimed at the full range of members from Post Graduate Students to Distinguished Fellows.

These awards are open to all members of the RACI who meet the specific award requirements. Some can be applied for while others require nomination by third parties.

The awards are listed on the website at www.raci.org.au/awards together with the criteria requirements and proposed methods. Any other information can be requested from awards@raci.org.au or by contacting the RACI National Office directly on (03) 9328 2033.

Presentation of the awards will be at a special dinner held in November 2015.

ON 30 JUNE OR 31 MAY FOR POST GRADUATE STUDENTS.

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