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in Australia

March 2015

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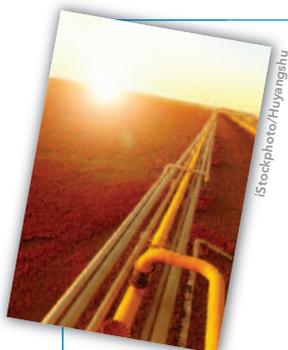
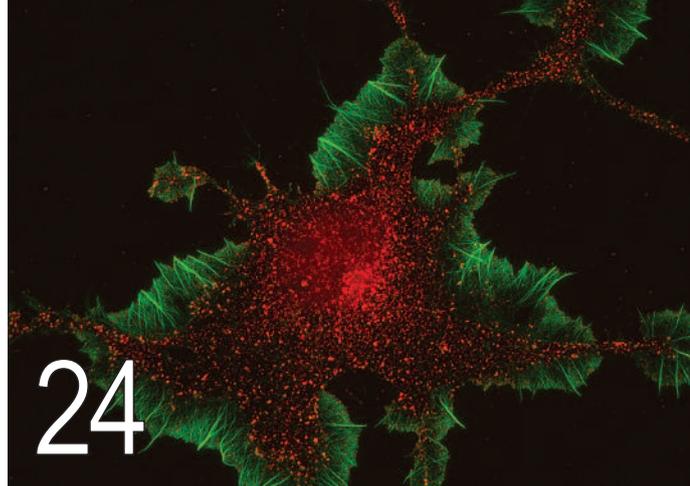
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cover story

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Hydrogen power should be afforded the same opportunity to shine as other renewable energy technologies, say the creators of a new fuel cell bicycle.

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24 Super resolution microscopy: it's all about the molecules. 2014 Nobel Prize in Chemistry II

Thanks to the properties of certain fluorophores, biological systems can be viewed at resolutions far beyond those theoretically possible with light microscopy. The challenge of obtaining real-time images of cellular events lies in design and synthesis of the right probes.

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From the President

As an incorporated organisation since 2001, RACI is governed according to its Constitution, which articulates not only its purpose for being but the rules that ensure it functions ethically, efficiently and in the best interests of the discipline of chemistry. Since incorporation, the Constitution has remained largely unaltered except for some minor operational changes made in 2007 and 2011. During 2014, there was considerable discussion about aspects of the current Constitution and its relevance 13 years onwards after incorporation. It is the firm view of the Board that the Constitution requires amendment for the reasons summarised below. All relevant documentation, including the proposed new Constitution, may be found at www.raci.org.au/theraci/corporate-governance/constitutional-change.

The proposed Constitutional changes can be partitioned into two different sections: (i) 'modernising' aspects of the Constitution that are no longer practical or relevant in 2015 and (ii) the structure of the RACI Board.

The first section contains a series of proposed minor amendments that remove some unintended operational restrictions. As an example, the RACI Constitution requires that its Annual General Meeting be held before 30 November of each financial year. For this reason alone, the Board was forced to hold its 2014 AGM in November (as opposed to in December to coincide with the 2014 RACI Congress and RACI Assembly meeting). This is but one example of relatively minor but restrictive or outdated aspects of the Constitution that should be changed. None of these changes is controversial.

The proposed structure of the Board requires clear articulation. The RACI Board currently comprises eight members: President (Chair), President Elect, Hon. Gen. Secretary, Hon. Gen. Treasurer, a nationally elected non-executive member, and three regionally elected board members (North East, South East and Western electorates). The three regionally elected Board members currently have ill-defined roles. During 2014, there was extensive discussion within the Board on the make-up of the RACI Board, followed by

consultation with the Assembly (Branches and Divisions), which culminated in a Green (discussion) paper. Based on RACI member feedback, a White (policy) paper was created (available at the above link).

In précis, the current positions of President, President Elect, Hon. Gen. Secretary, Hon. Gen. Treasurer and the single nationally elected non-executive Board member would remain unchanged. It is proposed to retire the three regionally elected Board positions at the end of their current terms and replace them with two nationally elected Board members, making a total of seven Board members elected by the entire RACI voting membership. Furthermore, the three non-executive Board members would take on defined portfolio responsibility, respectively, for matters such as liaison with RACI Divisions and Branches and overseeing the various operational matters (e.g. *Chemistry in Australia*, Australian National Chemistry Quiz etc.). The details would be defined in the RACI By-Laws.

A second proposed change to the Board structure is the appointment of up to two people with experience in areas where the Board has identified a gap in its expertise. These would be Board nominations, with AGM ratification, and could be from the membership or from outside the RACI. The Constitution currently forbids a non-member of RACI from holding a position on the Board and this will need to be changed. This change would enable someone from outside the immediate chemistry sector to bring valuable knowledge to the Board on the basis of their own professional experience, without the proviso that they be a chemist.

A Special General Meeting will be held to vote on these changes to the Constitution in mid-2015 where it is hoped that they will be ratified by the RACI membership. The details of this SGM will appear soon, but I urge you to support these proposed changes.



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Warm bloodedness and climate

A recent series of letters in 'Your Say' (Dec 2014/Jan 2015) caught my eye and interest as a mathematical physical chemist. The comments of Richard Corbett, Ronald Clarke and Tony Zipper span a wide area, but those of Ronald Clarke show not even a nod to much past work that is relevant.

For example, his simplistic comments about the 'Laws of thermodynamics' applied to an 'object' are anything but a 'logical application of the laws of thermodynamics'. When the 'object' is a warm-blooded animal as he is discussing, he is completely wrong.

All animals are open reactors, housing vast numbers of biochemical reactions and their associated energy changes, some of which are exothermic and others endothermic so we can only conclude that energy in = energy out + net energy change due to biochemical reactions.

Animals subjected to temperature stress, whether cold or hot blooded, have a vast array of sophisticated responses for survival, including (for humans) sweating, blood capillary dilation and contraction, as well as changes in body surface to volume ratio, diet, metabolism, panting and so on.

Sweating extends the range of possible viable temperatures for humans and makes excellent use of the Arrhenius temperature dependence of evaporation, which has a much steeper slope than the basal metabolic rate when plotted against temperature. It wards off hyperthermia by many degrees.

Similar modifications and more exist at lower temperatures where the problem is countering excessive heat loss. These are somewhat more numerous in the animal world (in humans, shivering, which increases the muscular metabolic rate, and in other smaller mammals, which can hibernate). The latter have much increased metabolic rates at low temperatures compared with non-hibernators, a good comparison being between squirrels, which show both types.

Such applications of physical chemistry were discussed many years ago (Gray B.F., Gray P., Kirwan N.A. *Combust. Flame* 1972, vol. 18, pp. 439–59), and it is clear from the letter by Tony

Zipper that a similar effort needs to be made with respect to the highly suspect application of physical-chemical concepts within climate 'science'. The Clapeyron–Clausius equation (limited to closed equilibrium systems) seems to get frequent mention in applications to the atmosphere, which is a highly non-equilibrium open system. No wonder discussions on water vapour as a greenhouse gas are few and far between!

B.F. Gray FRACI CChem, FAustMS CMath

Climate change is fundamentally not complex

While ostensibly advocating education and debate, Tony Zipper (Dec/Jan issue, p. 6) actually seems to want to overwhelm public discussion about climate change ('if it is really occurring') with every imaginable complexity.

This is a classic denier tactic: make the problem seem so obscure and difficult that nothing can be resolved and opposition to the denier's position becomes crippled by analysis paralysis.

But climate change is not like that. Yes, there are many complexities in the detail and thousands of scientists are engaged in their study, but the basics are straightforward and have been well understood for over a century. Both theory and observation are very accessible, especially to chemists who have the training to understand such material in depth, and the sort of issues raised by Zipper can be resolved with a visit to www.skepticalscience.com.

There is no doubt that both the atmosphere and the ocean are warming at an alarming rate, that the ocean is acidifying, that the consequences are already serious and widespread, and that things will get far worse.

Nor is there any doubt that the root cause is CO₂ produced by fossil fuel combustion. Water vapour and various feedback mechanisms amplify the effect; other greenhouse gases play a lesser role.

The damage already done will last for many centuries, but the solution to minimising further damage is obvious: stop burning brown coal, black coal, oil and gas – in that order of priority, and as rapidly as possible.

There are better ways to generate energy: we have enormous resources of wind and sunlight, both of which produce energy at near-zero variable cost with minimal environmental consequences, and private citizens using their own capital have already created a massive photovoltaic industry.

By all means let's try to better educate the public (especially our politicians) and enlighten debate – it would be a worthy activity for the RACI – but don't cloud the subject in confected difficulty.

Jim Bonham FRACI CChem

'Your say' guidelines

We will consider letters of up to 350 words in response to material published in *Chemistry in Australia* or about novel or topical issues relevant to chemistry. Letters accepted for publication will be edited for clarity, space or legal reasons and published in print and online. Full name and RACI membership status will be published. Please supply a daytime contact telephone number (not for publication).

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Comments on December issue

On reading I. Maxwell's 'A very large grain of salt' (Dec/Jan issue, p. 36), I found that my mind went back to the early 70s. At a hall of residence at Leeds University, one of the wardenial staff – a philosopher and theologian – asked me and another chemistry student whether it is possible for salt to 'lose its savour' – an expression that occurs in *Matthew* 5:13.

Neither I nor the other student was able to provide an answer. We did not have electronic access to information, and if we had attempted a library search (which neither of us did) it would have been difficult to know whether to go to the chemistry volumes or to the divinity volumes!

Some web pages offer the following plausible if pedestrian explanation. Salt for culinary purposes in those times contained 'salts' in the wider sense additional to the sodium chloride. When water vapour enters a pile of salt, it condenses and dissolves some and, according to the theory under consideration, this effect applies more than proportionately to the sodium chloride. Depletion of the sodium chloride in this way over a sufficiently long time would cause loss of the flavour-enhancing property of the salt: in other words it would have 'lost its savour'.

I do not know the extent to which this hypothesis has met with acceptance, or how closely it has been examined with reference to the known practices of the period when salt was used to preserve food as well as to flavour it. I. Maxwell might have some wisdom to offer on this, as might one or more readers of *Chemistry in Australia*. Otherwise, the 'loss of savour' might remain a conundrum like the passage of a camel through the eye of a needle of which we read in the 19th chapter of Matthew.

The article on Con and Ceci (pp. 33–34) reminded me of a similar biography within my own professional circle.

When I worked at the State Electricity Commission (SEC) Herman Research Laboratory (HRL) in Melbourne, the man who appointed me was Louis Kiss, who was from Hungary (his name being pronounced 'Keesh' in Hungary.) In the late 1940s, as a student in Budapest, he participated in a demonstration and found himself in difficulties so grave that he decided to flee to Australia. Before he was allowed to settle independently in Australia, he had to work for a year or so at whatever job was allocated to him. He was sent to Tasmania to work in the forests. After that, he came to the mainland and worked first for Heinz Foods in or near Dandenong. He left Heinz for the SEC and enrolled at RMTC (later RMIT) to study chemistry part time. He duly obtained his chemistry diploma from RMTC, and he remained with SEC for the rest of his career. On the basis of his diploma he was admitted to the RACI, and in due course became a Fellow. In about 1970, SEC sent him to the US to do a Masters at MIT. The postnominal acquired was SM and I heard him remark that in Australia that could be confused with 'Stipendiary Magistrate'. Louis was seconded from HRL to a UK electricity authority for a period, where he introduced and developed analysis techniques that he had devised in Australia.

Clifford Jones FRACI CChem

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The collage features several elements:

- A magazine cover for 'chemistry in Australia' dated November 2014, with the tagline 'for family and friends'.
- The word 'PUBLIC' in large white letters.
- The word 'EDITION' in large white letters.
- A 'Media guide 2015' logo with the 'raci' logo below it.
- A photo of a person with a tattoo, with the text 'Tatts: a novelty that won't wear off'.
- A photo of a person wearing goggles, with the text 'Chemistry at the movies'.
- A yellow banner at the bottom with the text: 'ALSO IN THIS ISSUE: Great minds behind the humble battery • Splendid science reading • Why wines taste different in the sky'.

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Yellowstone's thermal springs – their colours unveiled

Researchers at Montana State University, US, and Brandenburg University of Applied Sciences, Germany, have created a simple mathematical model based on optical measurements that explains the stunning colours of Yellowstone National Park's hot springs and can visually recreate how they appeared years ago, before decades of tourists contaminated the pools with make-a-wish coins and other detritus.

The model, and stunning pictures of the springs, were published in December in *Applied Optics* (<http://dx.doi.org/10.1364/AO.54.00B128>).

While the basic physical phenomena that render these colourful delights have long been scientifically understood – they arise because of a complicated interplay of underwater vents and lawns of bacteria – no mathematical model existed that showed empirically how the physical and chemical variables of a pool relate to their optical factors and coalesce in the unique, stunning fashion that they do.

'What we were able to show is that you really don't have to get terribly complex – you can explain some very beautiful things with relatively simple models,' said Joseph Shaw, a professor at Montana State University and director of the

university's Optical Technology Center. Shaw, along with his PhD student Paul Nugent and German colleague Michael Vollmer, co-authored the new paper.

Using a relatively simple one-dimensional model for light propagation, the group was able to reproduce the brilliant colours and optical characteristics of Yellowstone National Park's hot springs by accounting for each pool's spectral reflection due to microbial mats, their optical absorption and scattering of water and the incident solar and diffuse skylight conditions present when measurements were taken.

'When we started the study, it was clear we were just doing it for fun,' Vollmer said. But they quickly discovered there was very little in the scientific literature on the subject. That's when things got interesting.

Using handheld spectrometers, digital SLR cameras for visible images and long-wave infrared thermal imaging cameras for non-contact measurement of the water temperatures, the group took measurements at a number of pools in Yellowstone, including Morning Glory Pool, Sapphire Pool and Grand Prismatic Spring. Using these data, along with previously available information about the physical dimensions of the pools,

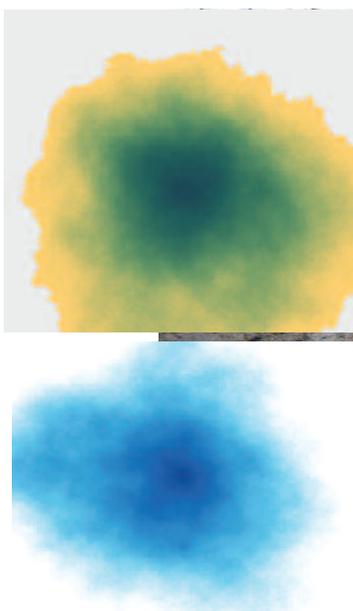
they were able to create a simple model whose renderings of the pools were strikingly similar to actual photographs.

In the case of Morning Glory Pool, they were even able to simulate what the pool once looked like between the 1880s and 1940s, when its temperatures were significantly higher. During this time, its waters appeared a uniform deep blue. An accumulation of coins, rubbish and rocks over the intervening decades has partially obscured the underwater vent, lowering the pool's overall temperature and shifting its appearance to a terrace of orange-yellow-green. This change from blue was demonstrated to result from the change in composition of the microbial mats, as a result of the lower water temperature.

A general relationship between shallow water temperature (hence microbial mat composition) and observed colours was confirmed in this study. However, colour patterns observed in deeper segments of the pool are caused more by absorption and scattering of light in the water. These characteristics – mats having greater effect on colour in shallow water, and absorption and scattering winning out in the deeper areas – are consistent across all the measured pools.

AMERICAN INSTITUTE OF PHYSICS

Joseph Shaw, Montana State University. Inset: Paul Nugent, Joseph Shaw and Michael Vollmer



Morning Glory Pool in August 2012 and (inset) simulated using a uniform orange microbial mat (top) and bare rock and pure water of varying depth (bottom).

Thousands of substances ranked according to potential exposure level

An overwhelming number of chemicals from household and industrial products are in the environment – and hundreds are in our bodies. But for most of them, scientists have yet to determine whether they cause health problems. Now they've taken the first step towards doing that by estimating which substances people are exposed to the most. Their new method is published in *Environmental Science & Technology* (doi: 10.1021/es503583j).

John F. Wambaugh (USEPA) and colleagues note that the risks to human health of any given substance depend primarily on two factors: the potential hazards a chemical presents, and how much of it people are getting exposed to. But public data on these variables are lacking for many substances already in widespread use. About 80 000 chemicals are registered in the US under the *Toxic Substances Control Act*, and industry adds 700–1000 new chemicals every year. Directly measuring how much of these substances people are getting exposed to

would be a Herculean task requiring the time-consuming analysis of thousands of blood or urine samples. Wambaugh's team sought a more practical approach.

The researchers developed a mathematical model to predict which household and industrial chemicals people are exposed to the most. They based their method on answering five simple questions about the substances, such as whether they are used in consumer products or whether they are pesticides. They used this approach to rank nearly 8000 chemicals, from highest potential exposure level to lowest. While a few of the top 10 were familiar compounds, such as DEHP, a common phthalate that has been shown to cause reproductive problems in rodents, most were substances that scientists know very little about. The researchers say the ranking could help prioritise future efforts that aim to understand potential health risks of thousands of chemicals.

AMERICAN CHEMICAL SOCIETY

Academy welcomes reinstatement of Science to Australian Cabinet

The Australian Academy of Science has welcomed the Prime Minister's announcement that Ian Macfarlane is now the Minister for Industry and Science.

Academy President Professor Andrew Holmes said he hopes the move will be more than simply a change in title.

'Having a Minister identifiably responsible for science is a very significant forward step for this Government. We very much hope that this signifies that the Government is placing greater value on the importance of science and technology to all Australians,' Holmes said.

'We take this shift in the Ministry as a signal that many important issues which have effectively remained dormant for the

last 18 months, while we've had no Minister with science in their title, will now have the additional horsepower they need to bring them back on to the agenda.

Holmes also welcomed the appointment of Karen Andrews as Parliamentary Secretary to the Minister for Industry and Science.

'We hope that the appointment of Ms Andrews boosts the leadership for science within the Government, and we look forward to working with her.

'We also welcome the new Minister for Health, Sussan Ley. This is an exceptionally important portfolio for medical sciences, at a critical juncture for medical research.

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2014 Rutherford Medal: understanding the fundamentals



Distinguished Professor Peter Schwerdtfeger, winner of the 2014 Rutherford Medal.

Distinguished Professor Peter Schwerdtfeger FRSNZ has been awarded the Royal Society of New Zealand's Rutherford Medal, its highest honour, for his world-leading contributions to fundamental aspects of chemical and physical phenomena in atoms, molecules and condensed matter. The Rutherford Medal is the highest honour awarded by the Royal Society of New Zealand and acknowledges a lifetime of significant scholarly research and the promotion of this knowledge to the benefit of New Zealand society.

'Distinguished Professor Peter Schwerdtfeger is one of New Zealand's most brilliant and internationally highly sought-after scientists,' the Rutherford Medal selection panel said.

'His research has provided a deep insight into how atoms and molecules interact at the quantum level.'

As one recent example, in 2013 he solved the long-standing problem of why mercury is the only metallic element that is liquid at room temperature. Through calculations and computational simulations, he showed that this is due to Einstein's special relativity. Without this effect, the melting point of mercury would be around +80°C, not -39°C as observed.

The selection panel noted that many of his papers have been revolutionary. Some of his papers were rejected initially by journals because the referees did not believe the results. They are now his most cited papers. In 2013, four of his research papers were selected for the cover of international journals and another one received this honour in 2014.

'I am in excellent company looking at the names of all the previous Rutherford Medal winners,' he said.

His approach is interdisciplinary, ranging from theoretical chemistry and physics to computer science and mathematics. His research interests include chemical evolution theory, why biomolecules prefer one-handedness (known as homochirality) and the structure and properties of superheavy elements. He designed a computer program to construct fullerene structures.

Schwerdtfeger is Director of the Centre for Theoretical Chemistry and Physics at the New Zealand Institute for Advanced Study at Massey University, Auckland and he is a strong advocate for a greater role for fundamental research in New Zealand universities. 'Many important developments of benefit to our society – including the development of lasers, treatments against illnesses such as cancer, or the world wide web – have emerged from fundamental science. It will be fundamental research which helps us to solve the many great challenges human beings face on our planet. If you focus solely on the commercial side without investing in fundamental science, you may get neither of them,' he said.

Schwerdtfeger was born in Stuttgart (Germany) and studied chemical engineering, chemistry and mathematics at university. He received his PhD in theoretical chemistry in 1986 and was then employed as a taxi driver for seven years while studying mathematics, taught chemistry and physics at intermediate schools, and held a permanent position as a software analyst at Stuttgart University. He undertook research at the University of Auckland and ANU before moving to Massey University at Albany to create a new research centre. He has received many prestigious grants, awards and prizes.

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R.J. Rowe (FRACI)



First structure measurements of molten uranium dioxide

Nuclear power is part of the worldwide energy mix, accounting for around 10% of global electricity supply. Safety is the paramount issue. Uranium dioxide (UO_2) is the major nuclear fuel component of fission reactors, and the concern during severe accidents is the melting and leakage of radioactive UO_2 as it corrodes through its protective containment systems. Understanding – in order to predict – the behaviour of UO_2 at extreme temperatures is crucial to improved safety and optimisation of this electricity source.

A paper published in *Science* (doi: 10.1126/science.aaa0163) by Lawrie Skinner and John P. Parise, from the Stony Brook University, New York, takes this understanding a big step further – providing the scientific and engineering community with the first structure measurements of molten UO_2 .

‘We melted uranium dioxide and studied its structure using X-rays; we also studied structural changes in hot, solid UO_2 before melting,’ Skinner said. ‘We found that, upon melting, the UO_2 structure goes from eight oxygen atoms surrounding each uranium atom down to an average of 6.7 oxygen neighbours. This affects the predicted physical properties of the liquid, like its viscosity.’

Even though the behaviour of UO_2 upon melting is of critical importance in extreme nuclear reactor accidents – such as Chernobyl in 1986 and Fukushima in 2011 – the very high temperatures needed for testing had severely limited investigation of this melt. This prevented structural studies and an accurate understanding of the inter-atomic interactions.

In fact, previous to the Stony Brook findings, no experimental structure measurement of molten UO_2 had been reported. While physical property measurements and molecular dynamics models did exist for molten UO_2 , they were often parameterised from solid-state properties and exhibited large differences in their melt structures. This structural uncertainty resulted in molten UO_2 models that exhibited differing characterisations of physical properties such as viscosity and compressibility – properties that are significant in determining nuclear reactor safety.

‘Our synchrotron X-ray diffraction measurements, by contrast, find a precise value r_{UO} of $2.22 \pm 0.01 \text{ \AA}$ at 3270 K, providing a new tool to test the validity of liquid UO_2 models,’ the paper reports. Added Skinner, ‘This work finds relatively high U–U mobility in the melt, a key reference point against which structural models may now be tested.’

The scientists combined laser heating, sample levitation and synchrotron X-rays to obtain pair distribution function measurements – describing the probability of finding atom pairs with a given separation r – of hot solid and molten UO_2 .



Aerodynamic levitation set-up at the advanced photon source beamline 6-ID-D. The sample chamber in the foreground is lit from inside by the 3000 K laser heated sample inside.

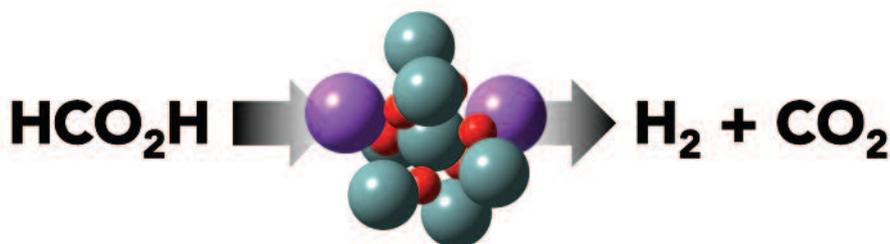
Levitation of the sample was crucial. Uranium dioxide melts around 3140 K, posing serious problems for traditional furnace heating methods. Most container materials (such as magnesium oxide, platinum and zirconium dioxide) melt or become chemically reactive at these extreme temperatures.

To avoid chemical reactions with the sample container, the researchers aerodynamically levitated the sample on a stream of argon gas while it was heated with a 400 W continuous CO_2 laser. The levitation negated any solid contact with the sample, maintaining high chemical purity.

‘In the future, we would like to investigate the atomic structure and properties of important U-containing compounds,’ Skinner said. ‘This includes eutectic U–Zr–O, which forms in extreme accidents as the UO_2 melts and reacts with its zirconium cladding.’

STONY BROOK UNIVERSITY

Hydrogen from formic acid without transition metals



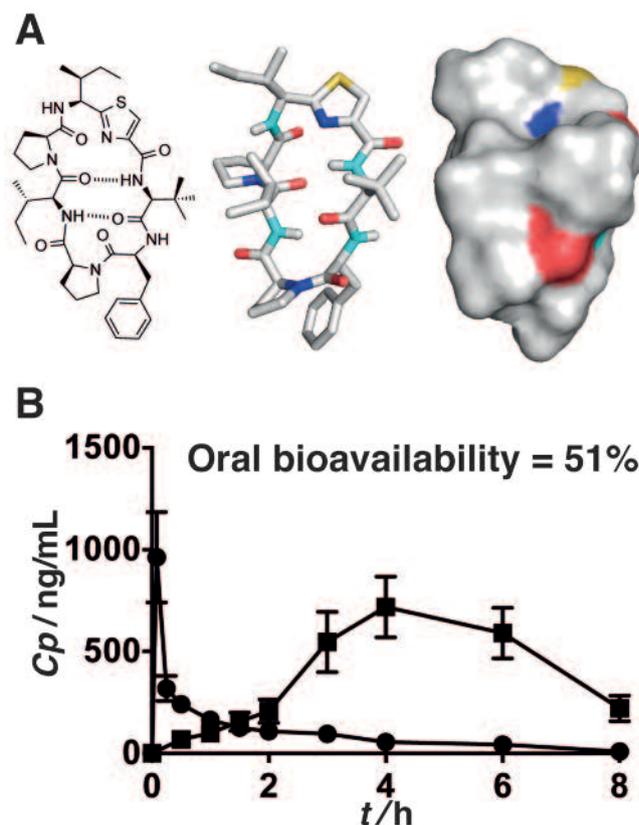
One of the major challenges of the 21st century is to ensure a sufficient and sustainable supply of energy. In this regard, hydrogen is a clean energy alternative carrier that can be generated from a range of renewable energy inputs. However, many impediments still need to be overcome prior to its widespread use,

one of the major difficulties being the identification of improved methods for hydrogen transport. In this context, formic acid represents a possible medium, not only for H₂ storage but also for H₂ transport. A joint computational and experimental study, led by Professors Leo Radom and Thomas Maschmeyer at the

University of Sydney, and Professor Chris Easton at the ANU, has developed a robust sodium-germanate-based catalyst for the selective dehydrogenation of formic acid to liberate hydrogen gas (Amos R.I.J., Heinroth F., Chan B., Zheng S., Haynes B.S., Easton C.J., Masters A.F., Radom L., Maschmeyer T. *Angew. Chem. Int. Ed.* 2014, **53**, 11275–79). This is the first such catalyst not based on transition metals, and it exhibits very encouraging performance. This study represents an important step towards the use of renewable formic acid as a hydrogen storage and transport vector in fuel and energy applications.

NMR spectroscopy guides PK enhancement of cyclic peptides

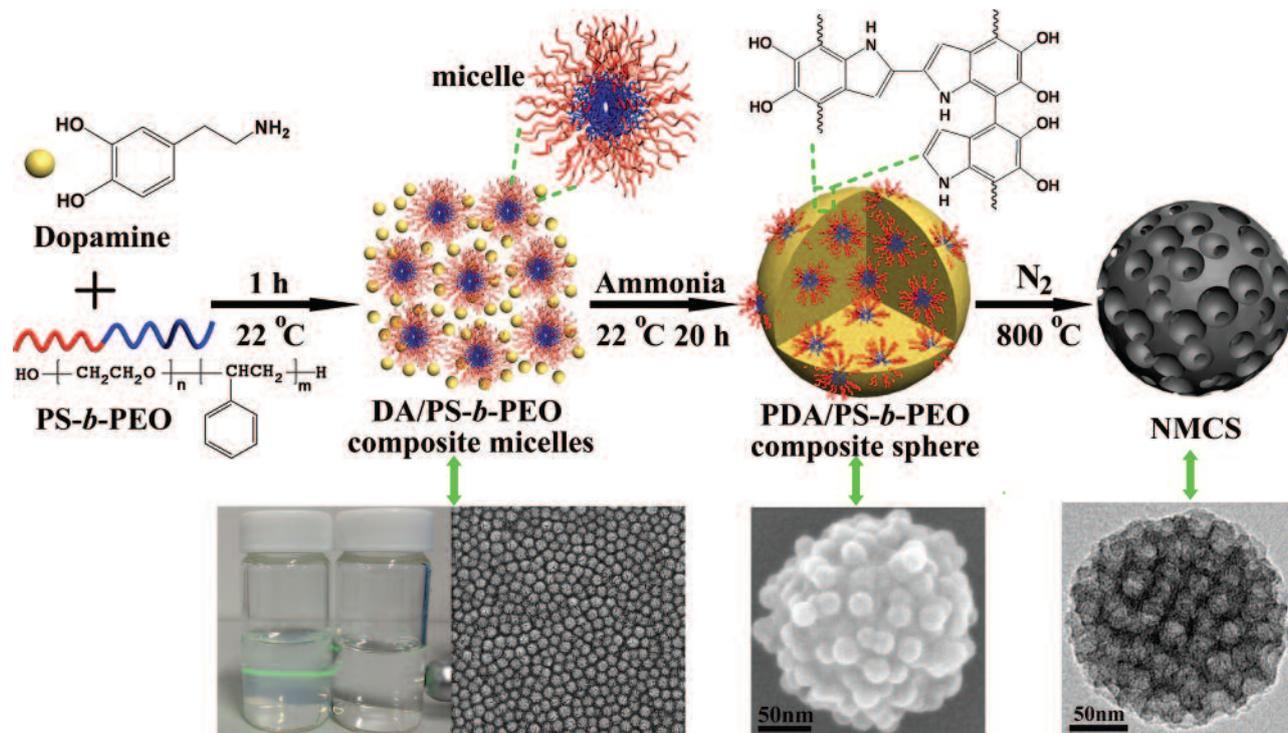
Researchers from the Institute of Molecular Bioscience, University of Queensland, in collaboration with Pfizer USA, have used a novel approach to make orally bioavailable analogues of a cyclic heptapeptide natural product derived from a nudibranch (Nielsen D.S., Hoang H.N., Lohman R.J., Hill T.A., Lucke A.J., Craik D.J., Edmonds D.J., Griffith D.A., Rotter C.J., Ruggeri R.B., Price D.A., Liras S., Fairlie D.P. *Angew. Chem. Int. Ed.* 2014, **45**, 12059–63). Traditional methods directed at optimising cell permeability – raising logP, and reducing total polar surface area – were unsuccessful. Solvent-accessible surfaces were predicted and identified from three-dimensional solution structures, hydrogen–deuterium exchange rates, and variable temperature–chemical shift coefficients, all derived from standard NMR experiments. This information guided subtle modifications that provided cyclic peptides with excellent pharmacokinetic properties. This is the first example solely using NMR spectroscopic analyses to design orally bioavailable peptides. The results highlight the failure of traditional dogmas used to guide development of orally bioavailable peptides and the work provides a combination of tools to overcome this problem.



N-Doped mesoporous carbon spheres

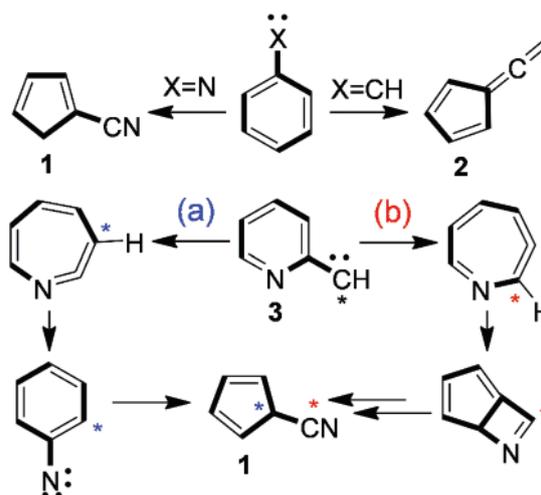
Carbon spheres have attracted a great deal of attention from scientists and engineers for their appealing structures, and tunable physical and chemical properties. However, synthesis of carbon spheres with large pores is still a great challenge. The group of Dr Jian Liu at Curtin University, in collaboration with Professor Yusuke Yamauchi at National Institute for Materials Science, Japan, and Professor Sheng Dai from University of Tennessee, US, have described a new method for the synthesis of N-doped

mesoporous carbon spheres with 16 nm pores, which are very effective catalysts of the oxygen reduction reaction (ORR), comparable with Pt/C (Tang J., Liu J., Li C.L., Li Y.Q., Tade M.O., Dai S., Yamauchi Y. *Angew. Chem. Int. Ed.* 2014, **54**, 588–93). The strong hydrogen-bonding interaction between the template (PS-*b*-PEO, see figure) and polydopamine (PDA) is thought to be the key to the synthesis, and can be tailored by varying the molecular weight of the block copolymer to vary pore size.



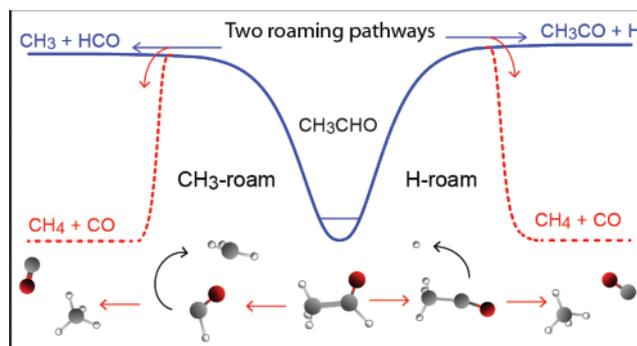
Mechanistic masterpiece

The mechanisms of ring contraction of phenylnitrene and the pyridylcarbenes to cyanocyclopentadiene (**1**), and of phenylcarbene to fulvenallene (**2**), have long been an enigma, and several conflicting proposals have been made. Now the group of Professor Curt Wentrup at the University of Queensland has solved the problem by means of ¹³C labelling studies, matrix isolation spectroscopy, and calculations, which reveal a unified mechanism involving ring expansion, transannular cyclisation, and ring-opening (Kvaskoff D., Lüerssen H., Bednarek P., Wentrup C. *J. Am. Chem. Soc.* 2014, **136**, 15203–14). In the case of 2-pyridylcarbene (**3**) there are two paths to cyanocyclopentadiene via ring expansion to the two isomeric azacycloheptatetraenes shown. In path (a) ring contraction affords the detectable phenylnitrene, which then suffers direct ring contraction to ring-labelled **1**; in path (b) a transannular cyclisation followed by cleavage of the four-membered ring leads to CN-labelled **1**.



Photochemical roaming

Professor Scott Kable (University of New South Wales) and Associate Professor Meredith Jordan (University of Sydney) have led a multinational team that has redefined the photochemistry of acetaldehyde in terms of two 'roaming' pathways instead of via the classical transition state (Lee K.-L.K., Quinn M.S., Maccarone A.T., Nauta K., Houston P.L., Reid S.A., Jordan M.J.T., Kable S.H. *Chem. Sci.* 2014, **5**, 4633–38). Transition state theory has served generations of chemists well. It posits that reactants must overcome an energy barrier to progress to products. Roaming reactions do not follow this paradigm. In a roaming reaction, a simple bond cleavage process is 'frustrated'; too much energy is retained in one of the fragments to allow them to separate. They orbit, or 'roam' about each other and undergo an intramolecular abstraction producing different chemical products. No specific transition state structure is identified. The authors demonstrate that there are two roaming pathways in CH_3CHO photodegradation – one associated with a CH_3 fragment roaming about an HCO core, and the other a hydrogen atom roaming around CH_3CO . No evidence for the



conventional transition state mechanism was found, even though this mechanism had been written about for many decades. Many atmospheric photochemical reactions involve a simple bond cleavage. This work suggests that all bond cleavage reactions will have a parallel roaming pathway and hence all these atmospheric photochemical degradation pathways might have to be re-visited and roaming pathways included.

Compiled by **Matthew Piggott** MRACI CChem (matthew.piggott@uwa.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 Matthew.

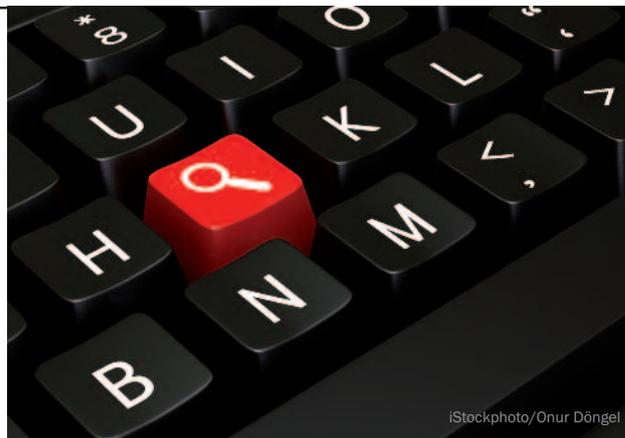
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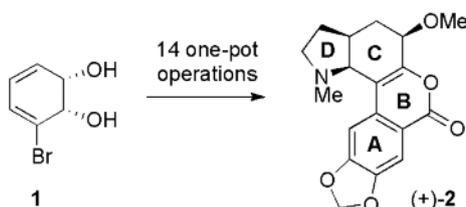


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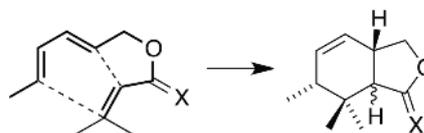
The February issue is dedicated to the memory of Desmond (Des) Joseph Brown, formerly of the John Curtin School of Medical Research (JCSMR), ANU, from where he retired as Head of the Medical Chemistry Group in 1985 to become a Visiting Fellow at the Research School of Chemistry until 2012 (see obituary in *Chemistry in Australia*, July 2014, p. 28). Des Brown was best known for his many books on heterocyclic chemistry, particularly pyrimidines, purines and pteridines (he was known as 'Mr Pyrimidine' in some circles), and for his contributions to the understanding of the Dimroth rearrangement. The collection of papers by his former students, collaborators and colleagues was assembled by Wilfred (Wilf) L.F. Armarego of JCSMR.

Martin Banwell and co-workers (ANU) describe a chemoenzymatic route to the (+)-form of the Amaryllidaceae alkaloid narseronine, (+)-2, which involves a 14-step synthesis starting with the pure enantiomer of 3-bromo-*cis*-1,2-dihydro-1,2-dihydroxybenzene **1**, itself prepared enzymatically from bromobenzene. This work complements an earlier chemical

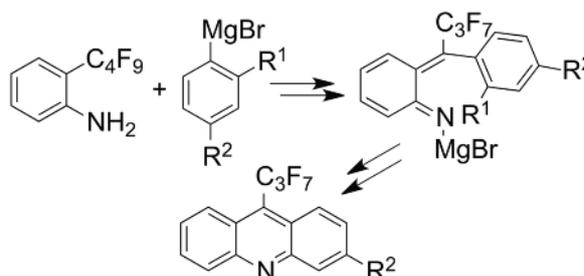


synthesis of the (-)-form of the alkaloid from the same starting material.

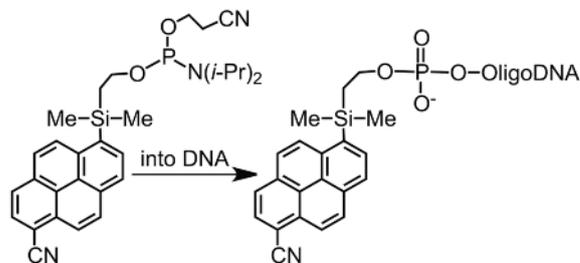
Michael Sherburn (ANU), Michael Paddon-Row (University of New South Wales) and co-workers report a combined computational and experimental study of the intramolecular Diels–Alder reactions of 6-oxanona-1,3,8-trienes to hexahydroisobenzofurans with evaluation of activation parameters and ^2H kinetic isotope effects, all leading to the conclusion that the triene cycloaddition is concerted but asynchronous.



Strekowski et al. (Georgia State University, US) have developed an intriguing synthesis of perfluoroalkyl-acridines by reaction of 2-(perfluoroalkyl)anilines with arylmagnesium bromides carrying a methyl or ethyl group (R^1) at the *ortho* position. Notably, the acridine product contains a shorter perfluoroalkyl group at position 9 and has lost the R^1 group. The aza-*ortho*-xylylene reactive intermediate shown was isolated for the first time.



Fluorescence labelling is an important method for detecting and quantifying biological substances. Shinozuka and co-workers (Gunma University, Japan) describe the synthesis of a suitably functionalised cyanopyrene with a high fluorescence quantum yield of 0.7 and its incorporation into DNA as a fluorescence label.



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

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A push start for hydrogen power

Hydrogen power should be afforded the same opportunity to shine as other renewable energy technologies, say the creators of a new fuel cell bicycle.

BY **KONDO-FRANCOIS AGUEY-ZINSOU**

The fuel cell provides electrical assistance with pedalling, enabling the rider to easily travel long distances or up hills.

Global demand for cleaner energy technologies is growing. For example, in 2013 the World Health Organization recognised air pollution as a grade 1 carcinogen (<http://tinyurl.com/m9oybbm>). With the large deployment of renewable energies such as wind and solar, the ability to store large amounts of energy in a clean and safe manner with hydrogen is more relevant than ever.

At the University of New South Wales School of Chemical Engineering, we have built an Australian-first bicycle that can take riders up to 125 kilometres on a single battery charge and \$2 of hydrogen. The Hy-Cycle's main innovation is the demonstration of hydrogen as a clean and safe energy.

The Hy-Cycle, created by a team including myself and technical officer Paul Brockbank, is powered by a hydrogen fuel cell. The fuel cell provides electrical assistance with pedalling, enabling the rider to easily travel long distances or up hills. This could make the Hy-Cycle a low-cost, sustainable transport option.

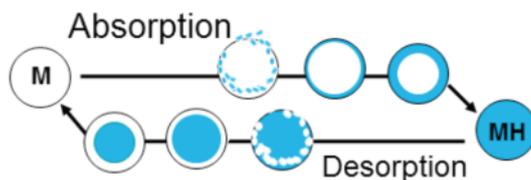
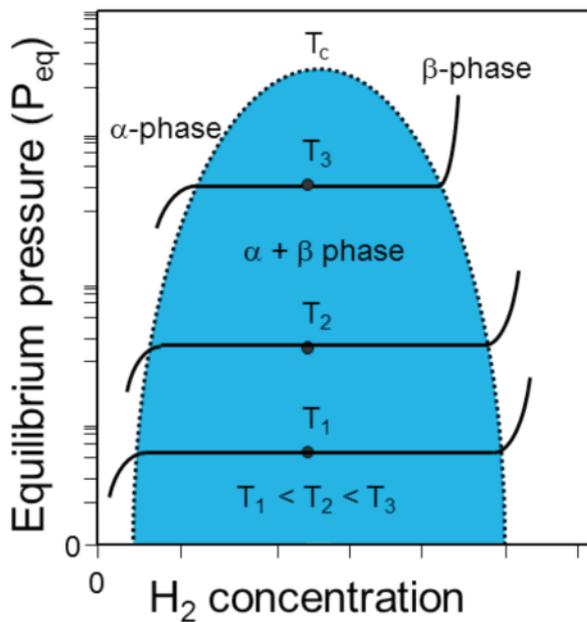
Hydrogen for the Hy-Cycle is carried in a 2.5-kilogram canister that sits adjacent to the pedals. The canister feeds the fuel cell, which is located under the seat and continuously recharges a lithium-ion battery.



The Hy-Cycle at the University of New South Wales Open day September 2013. The hydrogen canister contains a metal hydride, which stores hydrogen safely. Just above and behind the grid, a 100 W fuel cell provides power to run the electrical motor of the bike.

Catalysts make for a cheaper fuel cell future

A fuel cell is an electrochemical device that reacts hydrogen and oxygen to generate electricity from chemical energy. It can continuously provide electricity if there is a constant supply of hydrogen and oxygen. The first commercial use of fuel cells (alkaline based) was in the 1960s with the NASA space Apollo program. Since then, the cost of fuel cells has dramatically decreased through extensive research in the development of alternatives to platinum as a catalysts, reduction of the amount of platinum used, higher activities per catalytic sites and high surface area carbon electrodes (from \$275 per kilowatt in 2002 to \$4 per kilowatt in 2012 for PEM fuel cell; <http://1.usa.gov/1wxyWEM>). The future would be the effective design of biomimetics of enzymes such as hydrogenases capable of splitting hydrogen with high turnover rates and this indifferently of potential poisoning from impurities including CO.



Pressure composition isotherm showing the various phases: α (hydrogen solid-solution) and β (hydride) upon hydrogen absorption-desorption, and schematic representation of hydrogen absorption-desorption by materials. At the equilibrium plateau pressure, P_{eq} , α and β coexist.

In the future, riders could purchase replacement canisters from a network of distribution points, rather than needing to produce hydrogen or produce their own hydrogen at home with a personal electrolyser.

A standard metal hydride inside the canister enables safe, user-friendly storage of the hydrogen. One kilogram of the standard metal hydride is capable of storing 100 litres of hydrogen, but at the Material Energy Research Laboratory in nanoscale (MERLin), we are developing borohydrides that could store the same amount of hydrogen using just 50 grams of storage material.

Hydrogen for the Hy-Cycle can be produced with as little as 100 millilitres of water. The water is split into oxygen and hydrogen and the fuel cell recombines the hydrogen with oxygen to produce electricity. In the future, riders could purchase replacement canisters from a network of distribution points, rather than needing to produce hydrogen or produce their own hydrogen at home with an personal electrolyser.

In the Hy-Cycle, a 100 W proton exchange membrane fuel cell (PEM; see box) is used to power the 200 W electrical motor. The fuel cell runs on a hydrogen source provided by a metal hydride. The technology is extremely safe because the release rate of

About the Hy-Cycle

- Range → 125 km at 20 km/h
- Maximum speed → 35 km/h
- Battery → 518 Wh lithium-ion battery continuously recharged by fuel cell and hydrogen canister. Battery can be recharged in six hours on mains power.
- Fuel cell power → 100 W
- Canister → 738 Wh capacity; can be exchanged for a new canister in 30 seconds



Kondo-Francois Aguey-Zinsou and the Hy-Cycle.

hydrogen is intrinsically controlled by properties of the metal hydride. Furthermore, excessive build-up of hydrogen pressure is not possible: the material will safely regulate the amount of hydrogen released to remain under 'equilibrium conditions' around the plateau pressure P_{eq} .

Hydrides are beautiful self-regulating materials that make hydrogen technology extremely simple to use. When hydrogen storage materials are exposed to hydrogen, molecular hydrogen is first dissociated at the surface before absorption. The host material initially dissolves the hydrogen as a solid solution (α -phase) and as the hydrogen pressure and hydrogen concentration within the material increases, the growth of the hydride (β) phase occurs. While the two phases coexist, the isotherms show a flat plateau (equilibrium plateau P_{eq}) (see graph page 18), the length of which determines how much H_2 can be stored reversibly with small pressure variations. Hence, at a given temperature and pressures above P_{eq} , the material will fully absorb and store hydrogen. At pressures below P_{eq} ,

hydrogen will be automatically released from the material. The Hy-Cycle contains a room temperature metal hydride (storage capacity up to 1.2 mass% H_2 and $>100 \text{ g H}_2 \text{ L}^{-1}$), the P_{eq} of which is slightly above atmospheric pressure and thus the fuel cell can be fed at a constant pressure.

Many materials are capable of storing hydrogen; the ultimate goal is to enable the reversible storage of hydrogen with light elements, i.e. common inorganic compounds such as borohydrides (e.g. LiBH_4 , MgBH_4) and alanates (LiAlH_4) or amino boranes (NH_3BH_2) holding more than 18 mass% of hydrogen. In this respect, the Australian community has been very active and our research group has demonstrated the potential of novel core-shell approaches to enable the control of the hydrogen properties of borohydrides through particle size effects.

The Hy-Cycle demonstrates the potential of hydrogen-based technologies. With the increasing penetration of renewable energies worldwide, effective storage is a pressing issue. Hydrogen provides a

unique and clean way to do this. The ability to effectively store hydrogen holds great promise in developing sustainable technologies. Cities such as London and Paris are trying to provide fleets of bicycles that people can hire for a few hours a day to commute to and from work. This is a key market for the Hy-Cycle.

Australia has been missing a lot of great opportunities because of its focus on solar energy, when we have a lot of other renewable opportunities. With the right R&D support, Australia could leverage on its leading role in solar and energy storage research to create new businesses in clean energy technologies.

The Hy-Cycle is also a showcase for the potential practical applications of a chemical engineering degree: we wanted to build something to show students that chemical engineering is not only about building big plants to synthesise chemicals.

The Hy-Cycle was publicly launched at a UNSW Open Day last September.

Associate Professor Kondo-Francois Aguey-Zinsou
MRACI is at the Materials Energy Research Laboratory (MERLin), UNSW Australia (www.merlin.unsw.edu.au).

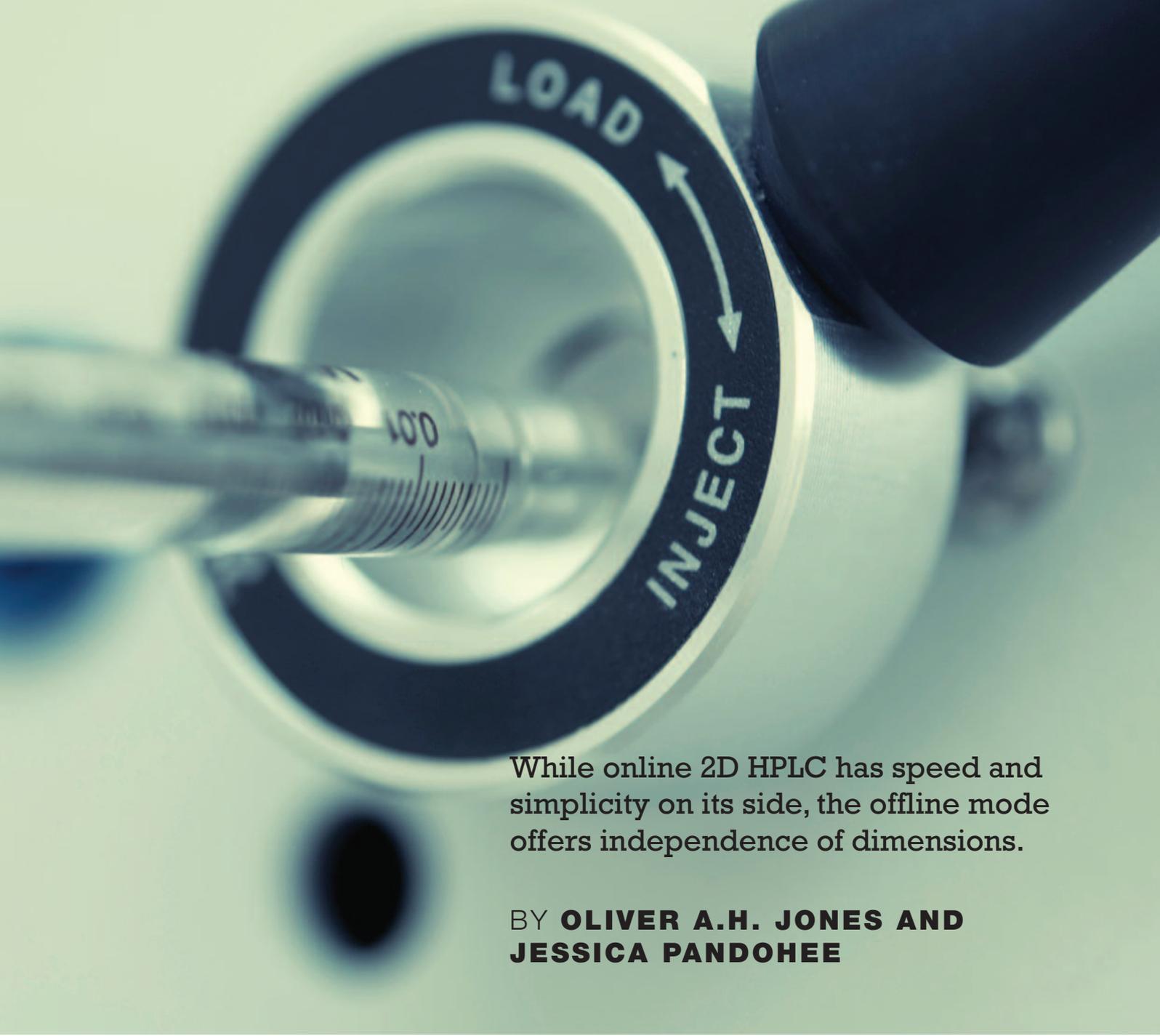
HPLC and the power of two

Water contaminants, food nutrients, peptides and proteins in blood, illicit substances – in these and many other areas of industrial and academic research, separation science is crucial. Such applications require chromatographic techniques that can separate as many compounds as possible in every sample run. As such, a lot of innovative technology and chemistry is currently being developed that could profitably be

employed in many different fields of research.

A particular problem for chromatographers is that isomeric molecules tend to co-elute (see box on page 22). This results in overlapping peaks in the chromatogram and associated poor resolution of compounds of interest, and the potential masking of target compounds of low concentration under peaks of other compounds.

One answer to this problem is to



While online 2D HPLC has speed and simplicity on its side, the offline mode offers independence of dimensions.

BY **OLIVER A.H. JONES AND JESSICA PANDOHEE**

increase the available resolution power by using multidimensional chromatography. This technique involves coupling two columns (dimensions), with uncorrelated retention mechanisms, in series. During the analysis, effluent from the first dimension is reinjected onto the second and the resulting data are then plotted in either two- or three-dimensional space. The total peak capacity of the system is the product of peak capacities of each individual

dimension, and far exceeds the peak capacity of standard, one-dimensional systems.

It is also possible to perform what is known as 'heart-cutting' and only inject specific fractions of interest onto the second column, for example from a section of a chromatogram where peaks from isomeric compounds of interest are overlapping.

Both liquid chromatography (LC) and gas chromatography (GC) can be undertaken in multidimensional mode

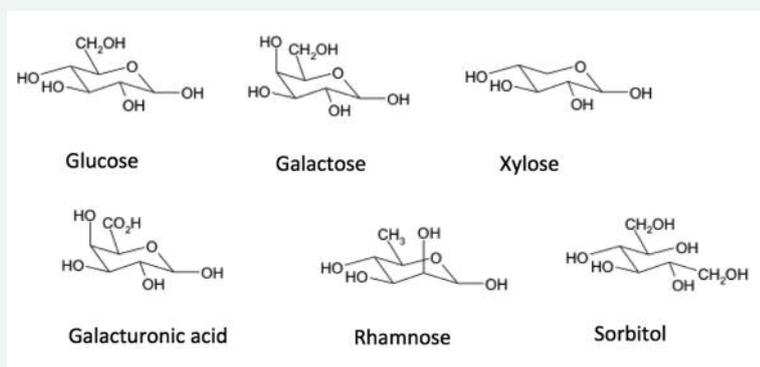
and both have found a variety of applications including in food, fragrance and forensic chemistry as well as in biological, environmental, geochemical and materials sciences. Comprehensive two-dimensional chromatography (LCxLC), a focus of recent efforts in our labs at RMIT University, can be performed offline and online (automated). Each brings its own challenges and benefits.

Offline LCxLC has been around for over 30 years but has recently

A challenge of complexity

Chromatographic separation is a challenging task. Samples often consist of thousands of substances differing in, for example, class, concentration, stability, mass or polarity. Some samples contain many compounds that are very similar but still need to be separated effectively. A further complication is that the constituents of many compound classes are often isomers.

A pertinent case is fatty acids (where the difference between molecules can be the position of a single double bond) and sugars (the bane of many an analytical biochemist). Glucose and galactose, for example, are isomeric aldohexoses, while arabinose and xylose are aldopentoses; the uronic acids are the 6-carboxyl derivatives of glucose and galactose; rhamnose and fucose are the 6-deoxy derivatives of mannose and galactose, respectively and sorbitol is the aldehyde-reduced derivative of glucose.



Structure of selected sugar isomers, whose similarity poses a problem in separation science.

... modern online LCxLC today is greatly facilitated by advances in software and is essentially 'walk up and use' with the added benefit of not having to count all the peaks yourself.

undergone something of a resurgence. Such a set-up can be achieved with a standard HPLC unit with a fraction collector at the end of the first column to collect fixed aliquots of the eluent from multiple samples into chromatography vials. The column of the instrument can then be changed and each of the combined fractions is then run as a 'new' sample. This method is relatively simple and cheap to set up since all that is required is a standard one-dimensional HPLC system, a fraction collector and appropriate data-processing software (a paper describing this technique can be seen at bit.ly/1C56cYx). It is also possible to chemically modify the samples between dimensions if needed. However, since collecting and running multiple aliquots from multiple samples can add up to hundreds, if not thousands, of individual runs, the total

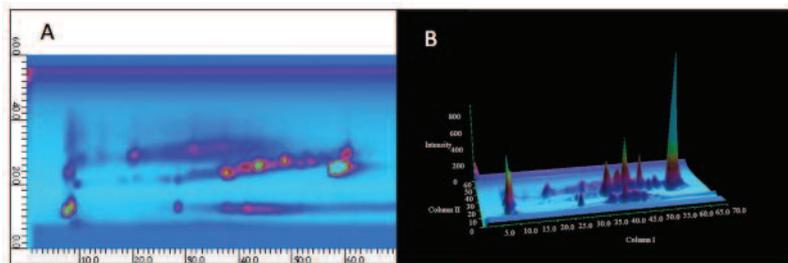
run time for offline LCxLC is often several days or even weeks. It is, therefore, time, resource and operator intensive. Integrating the two resulting datasets can also be challenging and require specialist knowledge.

Fully automated LCxLC is a relatively new technique currently only really offered by the Agilent 1290 Infinity, the Shimadzu Nexera-e and Waters Acquity instruments. Such systems still make use of multiple HPLC columns but benefit from the use of a switching valve in conjunction with advanced software (that controls both the valve and the solvent pumps) to automatically move aliquot eluent from the first column to the second.

Many potential users of two-dimensional technology are put off by its apparent complexity, but modern online LCxLC today is greatly facilitated by advances in software and

is essentially 'walk up and use' with the added benefit of not having to count all the peaks yourself. The equipment is relatively easy to use and the high-pressure capability of modern instrumentation allows high flow rates and correspondingly high-speed analysis. Disadvantages include the increased price of these systems compared to single-dimension systems and the fact that short second-dimension columns are required in an online LCxLC system. The latter are needed because such instruments require the separation of a sub-sample in the second dimension to be completed before the subsequent sub-sample from the first dimension is injected so as to avoid the potential mixing of sequential sample aliquots.

Although fully automated online LC-LC is very useful, the offline mode can be more suitable in some cases. For



Comprehensive 2D LC analysis of black tea. Data are shown as a contour plot (panel A) and a three-dimensional chromatogram (panel B), generated by using GC Image software (bit.ly/17G1ebQ). Others may use custom-written code in Mathematica MATLAB or the R programming language to plot the data.

One of the most important factors to consider for any two-dimensional LC method development is the choice of phases in the two columns.

example in the offline mode, optimisation of factors such as the length of the second dimension and sampling frequency from the first dimension is less time-consuming, which can often provide better efficiency. Additionally, the second dimension is independent of the first (as the separation of the second does not have to be completed before the next sampling is injected). Moreover, as the two columns are not directly connected, longer columns can be used as the second dimension results in a larger total peak capacity than is possible using short columns. It should be noted though that the use of longer columns as the second dimension often causes samples to become diluted because they have further to travel, so overloading of the first column is usually necessary. This tends to result in unsymmetrical, broad peaks in the first dimension that must be resolved in the second.

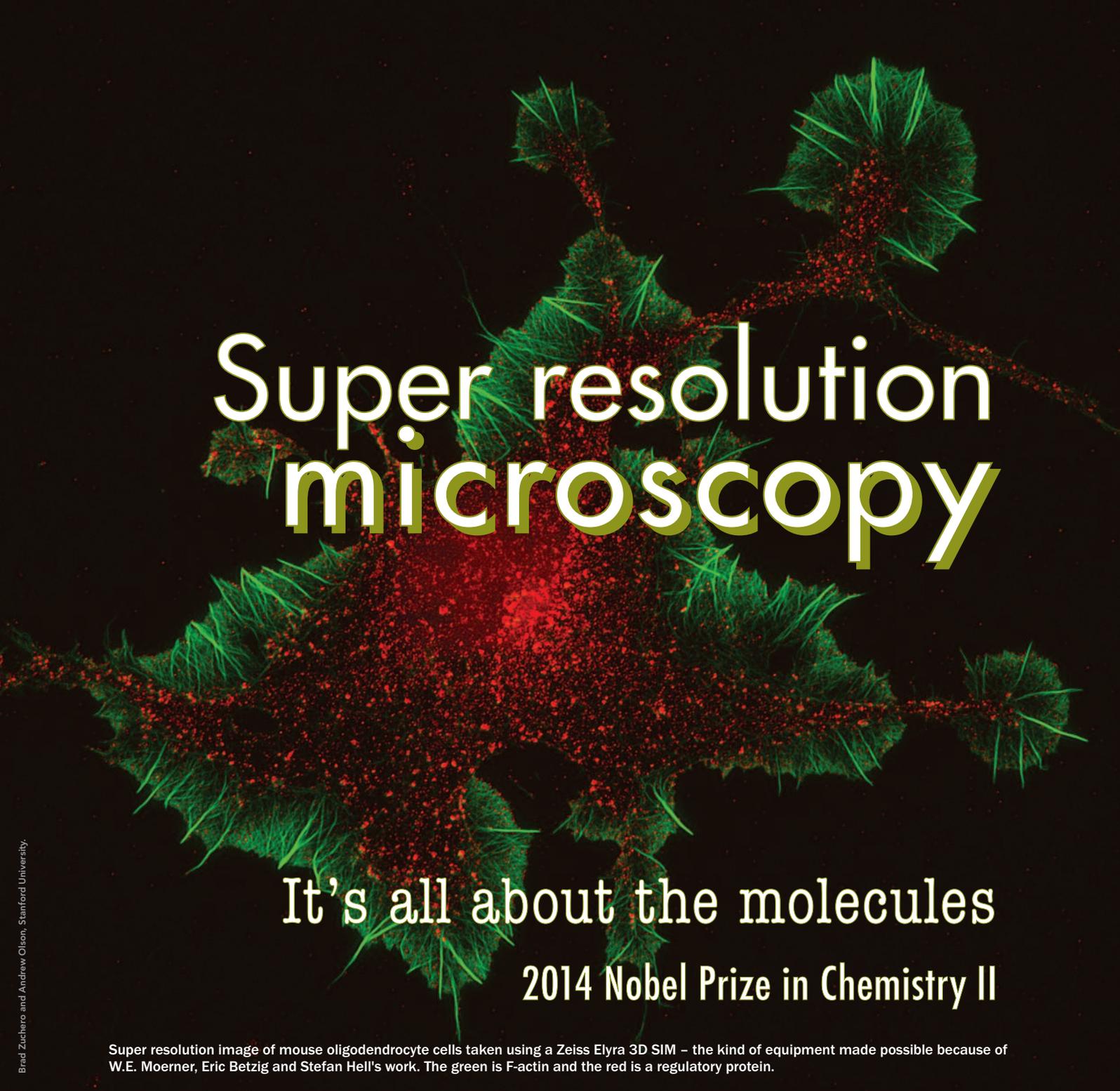
One of the most important factors to consider for any two-dimensional LC method development is the choice of phases in the two columns. To ensure

high-resolution separation, the columns should consist of different phases so that the peaks are spread across the maximum separation area. Chromatographers often refer to the difference between column phases in LCxLC as the columns being 'orthogonal' to each other. Reference to such orthogonal columns does not mean one needs to literally connect them perpendicularly to each other (although you could if you felt so inclined), but merely that the column chemistries are diverse (and unrelated). The choice of which two columns to use for a given separation is usually decided by using selectivity studies – running samples on multiple column types to generate knowledge as to which two phases offer the most different chromatograms and thus the greatest separation for the sample type in question. A detailed knowledge of column phase chemistry can help in this process and the final separation can be maximised via adjustments in solvent composition, flow rate, temperature etc., just as in standard LC.

Although not yet widespread, two-dimensional chromatography and its better separation power has great potential, particularly for compounds that are too sensitive for mass spectrometry but are contained in matrices too complex for standard LC analysis. The combinations of new column chemistries that could be used are many and varied and the use of size exclusion and chiral columns in the first dimension offers many further opportunities for novel applications.

Looking further ahead, it is likely that we will see many more interesting developments in separation science and technology. There are already a number of groups working on, for example, two-dimensional electrophoresis (bit.ly/14BkJAi) as well as various hybrid LC-GC systems (bit.ly/1FXRGIp). So, to our mind, the future of separation science in Australia looks very bright indeed.

Oliver Jones MRACI CChem is a senior lecturer and **Jessica Pandohee** MRACI is a PhD student in Analytical Chemistry at the Australian Centre for Research on Separation Science (ACROSS), at RMIT University in Melbourne. Despite working in 'separation science' they get on pretty well with the rest of the department.



Super resolution microscopy

It's all about the molecules
2014 Nobel Prize in Chemistry II

Super resolution image of mouse oligodendrocyte cells taken using a Zeiss Elyra 3D SIM – the kind of equipment made possible because of W.E. Moerner, Eric Betzig and Stefan Hell's work. The green is F-actin and the red is a regulatory protein.

BY **PETER KARUSO**

Thanks to the properties of certain fluorophores, biological systems can be viewed at resolutions far beyond those theoretically possible with light microscopy. The challenge of obtaining real-time images of cellular events lies in design and synthesis of the right probes.

On 10 December 2014, the Nobel Prize in Chemistry was given to Stefan Hell (Max Planck Heidelberg),

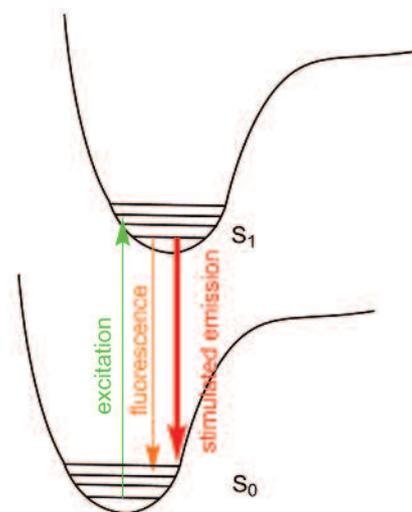
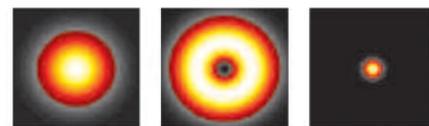
William E. Moerner (Stanford University) and Eric Betzig (Howard Hughes Jenalia Research Farm) 'for the development of super-resolved fluorescence microscopy'. In the February issue (p. 14), we looked at the development of the light microscope and the contribution of **W.E. Moerner**, who was the first person (1989) to show that it was possible to detect single molecules. W.E.'s research has spanned the areas of spectral hole-burning for optical storage, mechanisms of photorefractivity in organic materials, single-molecule spectroscopy and super-resolution microscopy.

Stefan Hell

At the same time W.E. was doing his Nobel Prize-winning research at IBM in the late 1980s, **Stefan Hell** was doing his Masters and PhD at the University of Heidelberg under **Siegfried Huncklinger** ('Imaging transparent microstructures in confocal microscopy'). Stefan Hell is a Banat Swabian – Banat Swabians are ethnic Germans who emigrated to what is today Romania in the 18th century, when it was part of the Austrian Empire. While most Banat Swabians were forcibly expelled by the Russians after World War II, some remained. Hell was born in Arad (Romania) and lived there with his father (an engineer) and mother (a teacher) until 1978 when they emigrated to Germany. He studied physics as an undergraduate and after his PhD, he worked at EMBL (Heidelberg, 1990–3) and successfully demonstrated the 4-Pi microscope, which reduced the axial (z-dimension) of the confocal spot from 700 nm to <200 nm. This is significant because for more than 100 years light microscopy was believed to be confined to a resolution of less than 200–400 nm due to Abbe's 1873 diffraction limit ($d = \lambda/2\sin\theta$), which

dictates that an optical microscope cannot resolve two objects closer than about half the wavelength of the light used for detection. After his success with the 4-Pi microscope, Hell was obsessed with breaking Abbe's diffraction limit for far-field microscopy, but he struggled to obtain funding and drifted from one postdoc to another because his ideas seemed just too absurd. Unable to get a position in Germany, he left for Finland and took up another postdoc at the University of Turku (Medical Physics, 1993–6). He thought that there had been a lot of new physics invented since 1873 and there must be something out there to overcome Abbe's diffraction limits and push optical microscopy into the nanometre range. One Saturday afternoon in the autumn of 1993, while reading a textbook on quantum physics (Loudon's *The quantum theory of light*), he came across a chapter on 'stimulated emission' and realised that this was what he was looking for, a way to make molecules excited to fluoresce, turn off.

Fluorescence is the emission of light by a substance at a longer wavelength than it has absorbed and forms the basis for confocal microscopy. **Stimulated emission** is the process by which an excited state of a fluorescent molecule interacting with an electromagnetic wave of a certain frequency may drop to a lower energy level, transferring its energy to that field. A new photon created in this manner has the same phase, frequency, polarisation and direction of travel as the photons of the incident beam. This is in contrast to spontaneous emission (fluorescence), which occurs without regard to any electromagnetic field and is propagated in every direction. Stefan Hell's idea was to use a confocal microscope to excite a volume in the sample, labelled with fluorescent molecules, and then to quench (by **ST**imulated **E**mission **D**epletion; **STED**) the excited state for most of the molecules with a donut shaped laser



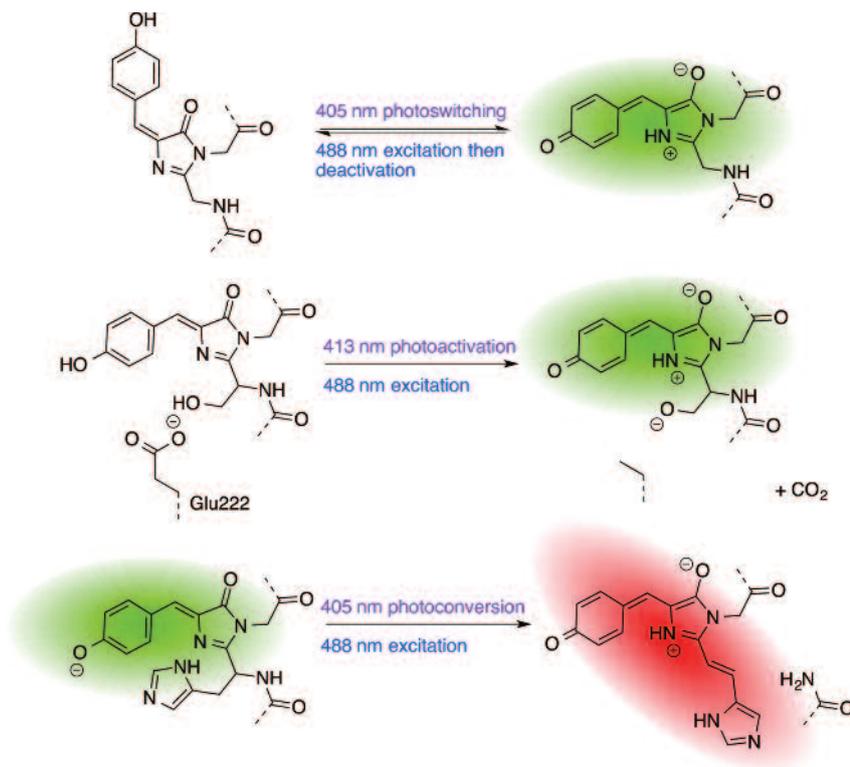
The principle of STED microscopy is to generate a focused excitation pulse (green arrow) that obeys Abbe's diffraction limit and then use a stimulated emission pulse (red arrow) immediately thereafter to knock down the excited state back to the ground state for most of the excited molecules. The size of the hole is proportional to the power of the STED pulse (I) and could theoretically be as small as one molecule.

(see figure). Only the difference between the excitation (I_e) and STED (I) beams is registered as a fluorescence image and if this is swept across a sample it is possible to get a comprehensive image at a resolution much better than the Abbe diffraction limit.

The donut-shaped STED pulse is easy to generate by placing a phase plate in the STED beam. The effect is to turn off most the fluorophores except a small volume in the middle, thus breaking Abbe's diffraction limit through a sleight of hand. The volume of fluorophores that remain in the excited state and thus able to emit fluorescence is now given by:

$$d = \frac{\lambda}{2n \cdot \sin\alpha \sqrt{1 + I/I_s}}$$

Very large values of I/I_s allow the resolution to be reduced essentially to



Green fluorescent protein (GFP) mutants that can be switched on and off.

the size of the molecule emitting fluorescence. Hell published a theoretical paper on this idea (S.W. Hell and J. Wichmann, *Opt. Lett.* vol. 19, pp. 780–2) in 1994 with no experimental details. The paper received no citations until 1997 and only six (mostly self-citations) between 1994 and 2000, but the idea was interesting enough for Hell to be offered a job at the Max Planck Institute for Biophysics and Chemistry in Göttingen, Germany. In 2000, at the Max Planck Institute, the proof of principle was achieved with a working prototype of a STED microscope. Hell's theoretical paper now has well over 800 citations, and this is increasing rapidly.

Robert Eric Betzig

After seven years away from science (see February issue, p. 14), Eric Betzig had learnt two things: (1) he was a lousy salesman and (2) while he disliked many aspects of academia, he

missed science itself. He knew that if he were to get back into science he would have to come in with a big splash. Initially he did not want to do microscopy and was looking for other opportunities. After countless hours of reconnecting with the scientific literature and contemplation in his cottage near Hiland Lake, Michigan, in 2003, Eric Betzig came across some papers on green fluorescent protein (GFP) and immediately called up **Harald Hess**.

Hess was a long-time friend and colleague from Bell Labs. While at Bell, Hess was interested in Hutchie's 1931 idea, scan probe microscopy, which really only worked at very low temperatures. Hess saw that scan probe microscopy was reaching the end of its limits so he left for California to work for PhaseMetrics in 1998 and use his scanning technology for real-world applications such as checking information-storage devices. PhaseMetrics was acquired by KLA-

Tencor in 2001 and while he was there he came up with the idea of the REBL (Reflective Electron Beam Lithography) Nanowriter that uses an electron beam to write data to silicone wafers at nanometre resolution. This idea eventually got off the ground but without Hess, who decided he also wanted to get back into research. As part of the search for a job, Hess (and Betzig) visited Tallahassee, Florida (Florida State University), in 2003 and were introduced to **Mike Davidson** by the director (**Greg Boebinger**). Boebinger was thinking about hiring them and thought that Davidson's interest in GFP would be of help. Due to a lack of funding, Davidson was not in a position to help but he did introduce them to the curious photoactivatable GFPs (PA-GFP), known as 'optical highlighters'. As they left Tallahassee, waiting at the airport, they realised that this was it. This was the missing link to make Betzig's 1995 theoretical paper a reality.

PA-GFP is one of a group of proteins first described by Moerner and Tsien, where they stated:

... these GFP mutants provide the first example of a room-temperature optical switch in which each molecule is individually addressable ...

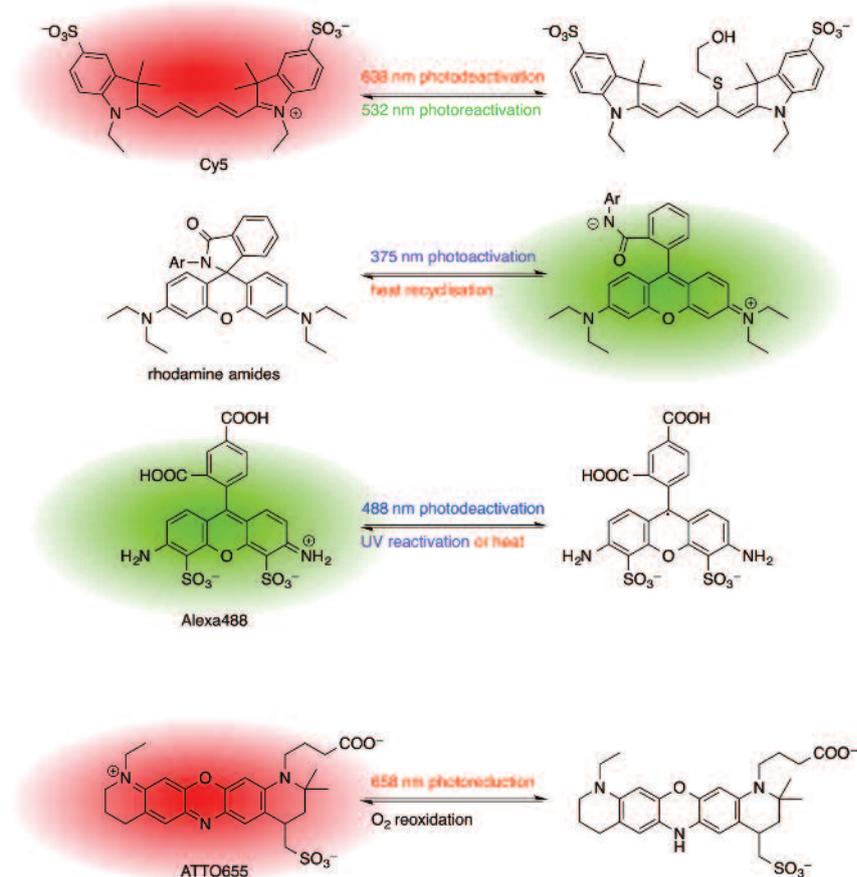
In the simplest form, the S65C/S72A/T203F mutant used by Moerner switched from *cis*- to *trans*- and back again in response to blue and violet light respectively (see diagram). The one that got Betzig and Hess really excited was the T203H mutant that upon irradiation with 413 nm (or 405 nm) light, decarboxylated E222 to yield a fluorescent version. More recently, the S65H mutants have been shown to undergo photoconversion to orange or red fluorescent proteins in a similar mechanism to photomaturational of the kaede proteins.

Betzig's idea was simple; if you use very weak 405 nm light, you can switch/activate/convert just a few molecules of GFP in a heavily labelled sample. Only the few converted

molecules will then respond to an intense 488 nm excitation pulse, resulting in a very sparse field of single molecule fluorescence. As long as not too many of the activated fluorophores are overlapping, the exact centre of the fuzzy ball of fluorescence can be mathematically determined as a point source.

If the 488 nm read laser is pulsed long enough to completely bleach the sample, another set of well-separated fluorophores can be turned on with a weak 405 nm pulse and the process repeated until all the fluorophores are turned on, read and bleached. Each point source can be deconvoluted and added together to make an image far exceeding Abbe's diffraction limit in resolution.

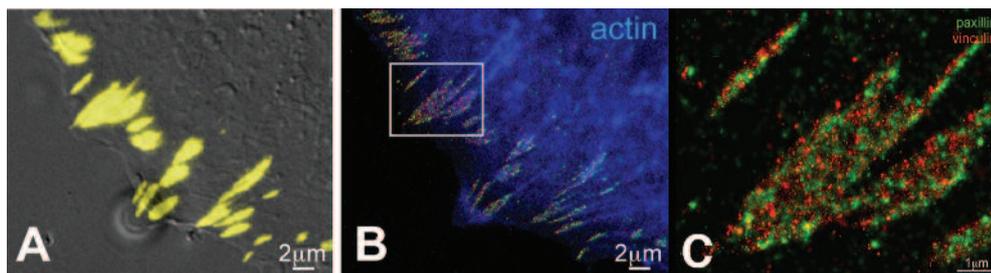
Excited by the prospects, Betzig and Hess took off to somewhere quiet – Sedona, Arizona – and wrote up a patent (WO2006127692). As Hess was single, they set up shop in his living room, which was eminently more comfortable than working in a garage, like Jobs and Wozniak, and there was no one to tell them to clean up their mess. Using parts left over from their time at Bell labs, and with another \$25 000 apiece, they quickly assembled a prototype, about the size of a lounge chair. But there was still one piece missing – the fluorescent protein – and as two physicists, they had no idea how to do any real biology or chemistry. As Betzig was about to go for a job interview at the National Institute of Health (NIH) in Bethesda, Maryland, he wangled the opportunity to visit **Jennifer Lippincott-Schwartz** and **George Patterson**, who invented the PA-GFP that **Mike Davidson** had introduced the pair to, at the same time. Betzig took the pair to lunch, swore them to secrecy, and then told them of his idea and begged for help. Not only was **Lippincott-Schwartz** willing to help, she gave Betzig and Hess some space in a windowless ex-dark room in her lab and some equipment money to finish off the microscope that was quickly



Some examples of switchable fluorescent dyes used in STORM and FPALM.

transported from Hess' living room to the NIH. After a few short months, with their home-built microscope, they managed to get 10–20 nm resolution images of fixed cells and now all they needed was a name. They decided on **PhotoActivated Localisation Microscopy (PALM)** and this provided the big splash Hess and Betzig needed. Both got jobs at the Howard Hughes Medical Institute's Janelia Farm Research Campus, thanks to the foresight of Jerry Rubin. The results were reported in their Nobel Prize winning paper published online on 10 August 2006 (E. Betzig, G.H. Patterson, R. Sougrat, O. Wolf Lindwasser, S. Olenych, J.S. Bonifacino, M.W. Davidson, J. Lippincott-Schwartz, H.F. Hess *Science* 2006, vol. 313, 1642), which was just as well because Betzig and Hess were not the only ones with the same idea.

At Harvard, in 2005, **Xiaowei Zhuang** had noticed that the fluorescent cyanine dye (Cy5) could be switched off with a red laser and switched back on with a green laser. To get this to work required the absence of oxygen, the presence of millimolar concentrations of a thiol, such as β -mercaptoethanol, and the proximity of another dye (Cy3). This molecular 'switch' could be cycled hundreds of times before permanent photobleaching occurred. Two postdocs in Zhuang's lab, **Mark Bates** and **Michael Rust**, then completely independently came up with the idea of using this switching phenomenon to obtain super-resolution microscopic images using exactly the same procedure Betzig was employing. They published their results, one day before Betzig, in *Nature Methods* with a paper entitled 'Sub-diffraction-limit imaging



Comparison of regular confocal image (A) and a PALM image (B) of a human cell stained for actin (blue), paxillin (green) and vinculin (red). (C) is an expansion of the boxed region in B.

Eric Betzig

by stochastic optical reconstruction microscopy (STORM)' (M.J. Rust, M. Bates, X. Zhuang (2006) *Nat. Methods* 2006, vol. 3, 793). **Xiaowei Zhuang** has gone on to develop STORM applications for other fluorescent dyes. As it turns out, many common microscopic stains can be turned on and off using light or chemistry and there has been a concerted effort in recent years to find new switchable probes with unique properties.

The 2014 Nobel Prize in Chemistry recognised **W.E. Moerner** for being the first to observe single molecules in condensed matter. This discovery had broad interdisciplinary impact and led directly to the development of super-resolution microscopy that depends on being able to turn the fluorescence of single molecules on and off and then observe these individually. This possibility was predicted by **Eric Betzig** and shown in practice by Betzig using fluorescent proteins and **Xiaowei Zhuang** using switchable small molecules virtually simultaneously. However, the research that got everyone thinking that breaking Abbe's diffraction limit was even possible came from **Stefan Hell**. He used stimulated emission to shrink the size of the excitation volume of the confocal microscope to (theoretically) the size of one molecule. However, the light intensity required (up to 10^9 W/cm^2) is immense and you have to wonder what this is doing to a biological system. As life evolved under $\sim 0.1 \text{ W/cm}^2$, the promise of 'live cell imaging' using super-resolution microscopy is still just that, a promise.

Sure, there have been technical demonstrations of real-time imaging of live cells using various techniques but there has been very little new biology learned so far. Challenges still remain in introducing the time dimension to unlock the secrets of high-speed cellular events.

STED, STORM and PALM have become mainstays of super-resolution microscopy and have led to other forms such as SR-SIM, SPRAI-PAINT and FPALM for example. Traditional chemists might also be wondering why the Nobel Committee, in their wisdom, decided to award the Nobel Prize to three physicists. However, this question really misses the point that modern chemistry cannot be so easily differentiated from physics or biology and for our discipline to not only survive but prosper, we need to recognise that great chemistry can be done in molecular biology labs as well as physics labs. This year's Nobel Prize does highlight the crossing of a traditional field of biology (microscopy) into our domain.

In a telephone interview with Adam Smith (nobel.org), Betzig said:

I ... trained as a physicist, when I was a young man I would look down on chemists. And then as I started to get into super-resolution, which is really all about the probes, I came to realise that it was my karma, because instead I was on my knees begging the chemists to come up with better probes for me all the time. So, it's just poetic justice ...

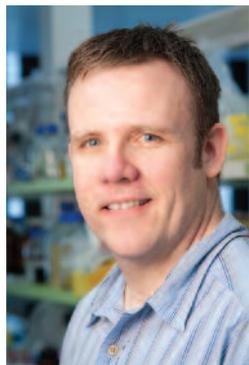
As Stephan Hell also noted, for microscopy in the 20th century, if you wanted the best pictures you went to the lens makers; in the 21st century it

is now the chemists who make the best pictures. It really is all about the molecules.

Finally, many young people read these articles in a hope of finding some advice on how to, perhaps, some day achieve a Nobel Prize in Chemistry for Australia (there has only ever been one). This story, especially the experience of Betzig and Hess contains salient lessons for the aspiring laureate: (1) Avoid jumping on someone else's bandwagon, forge your own path, (2) ignore what you have been told and (3) nothing worthwhile is ever done without passion.

Eric Betzig dedicated the 2014 Nobel Prize to 'those that struggled, took risks and failed'.

Peter Karuso FRACI CChem (peter.karuso@mq.edu.au) is Professor of Chemistry at Macquarie University, Sydney.



Conor F. Hogan received his BSc in 1994 from the Cork Institute of Technology and a PhD in 2000 from Dublin City University (Ireland).

Following a postdoctoral position under Professor Alan Bond at Monash University, he accepted an academic position at La Trobe University in 2003. Hogan's research spans electrochemistry, analytical

chemistry, inorganic chemistry and photophysics, including explorations of the fundamental processes of electrochemiluminescence, novel luminescent materials and the immobilisation of electrochemically active luminescent materials on electrode surfaces, for a variety of sensing applications, in particular; paper microfluidics and mobile phone based sensing.

He served as chair of the RACI Electrochemistry Division from 2011 to 2013 and he is currently Australian regional representative for the International Society of Electrochemistry.

Phil Gale was born in Liverpool and grew up in Woolton. He then moved to the University of Oxford where he received a BA(Hons) in 1992 and a MA and DPhil in 1995. In 1995, he moved to the University of Texas at Austin where he spent two years as a Fulbright Scholar before returning to Oxford in 1997 as a Royal Society University Research Fellow. In 1999 he moved as a Lecturer to the University of Southampton and was promoted through the ranks to a personal chair in supramolecular chemistry in 2007. Since 2010, Gale has been the Head of Chemistry at Southampton. In 2014 he was awarded a DSc by the University of Oxford and was listed by Thomson Reuters as a Highly Cited Researcher in chemistry.

Gale's research interests focus on the supramolecular chemistry of anionic species and in particular the molecular recognition, sensing and lipid bilayer transport of anions. He has worked on a number of collaborative projects with colleagues in Australia, including squaramide-based anion receptors and transporters and transmembrane sulfate transport with Professor Kate Jolliffe at the University of Sydney, and pyrrole, thiophene and furan-based ligands with interesting photophysical properties with Professor Mark Ogden at Curtin University.

Gale has won a number of research prizes including the RSC 2014 Supramolecular Chemistry Award, a Royal Society Wolfson Research Merit Award and the RSC Corday Morgan medal and prize.

He currently serves as the chair of *Chemical Society Reviews* editorial board and is a member of the Advisory Board of *Chemical Science*. He is also the co-editor of *Supramolecular Chemistry*. In 2012, he was elected chair of the RSC Macrocyclic and Supramolecular Chemistry Group.



National Awards

2015

The RACI National Awards recognise and promote the contributions and achievements of our members.

The awards cover a broad range of areas and are aimed at the full membership demographics.

They are open to all members of the RACI. Some can be applied for by the candidate; others have to be nominated by third parties.

- Academia:** Applied Research Award
Cornforth Award
HG Smith Memorial Award
- Distinction:** Citation
Distinguished Contribution to Economic Advancement (Weickhardt) Award
Distinguished Fellowship
Leighton Memorial Award
- Education:** Centenary of Federation – Primary and Secondary Teaching Award (Branch/National Award)
Fensham Award for Outstanding Contribution to Chemical Education
Pearson Education/RACI Chemistry Educator of the Year Award
- Young Chemists:** Masson Memorial Award

MRACI Post Graduate Student Travel Bursary

An amount of \$2000 to assist Post Graduate Student members of the RACI to travel professionally from their home institution, to collaborate with a research group, at another Australian university or overseas, or to make use of specialised research facilities (e.g. an advanced light source), or to deliver a paper at a meeting overseas.

Full details of the awards and the requirement criteria can be found on the RACI website at: www.raci.org.au/events-awards/national-awards-2015

Congress and community spirit

Family, colleagues and the chemistry community were the order of the evening at the 2014 National Awards Dinner held in December. As the function room filled at Adelaide's Hotel Grand Chancellor, acquaintances were formed or renewed; old colleagues and friends debated and reminisced.

Awards were presented during the formal part of the event (see December issue pp. 27–30 for details). The Cornforth Medal has been an early part of many promising careers. The 2014 recipient, Anya (Ganna) Gryn'ova, was unable to attend, but I remember clearly a previous (beaming) winner attending with his entire family.

The awardees expressed their gratitude to family, students, mentors and the wider chemistry community. The importance of students (Honours, PhD and postdoc) was a strong theme – the satisfaction in teaching them and what their teachers could learn from them, how hard they worked and the sense of fun they bring.

Professor Simon Pyke (Fensham Medal for Outstanding Contribution to Chemical Education) walks into a classroom to have fun, and pushing boundaries is what gets him up in the morning. He noted the importance of families for support and in 'walking the journey'.

Many awardees talked about their partners and their support/endurance. Others spoke of what their families would be doing at the moment – partners attending other functions and teenagers living it up while the cat's away.

The awardees thanked the RACI, as you would expect at an RACI award presentation. More than that, though, many chose to explain what the RACI had done for them. Dr Brian Smith (Citation – for Contributions to Chemistry and the Chemical Profession) explained that being an RACI member had given him 'opportunities that I could have never imagined'. Informally during the evening and at the RACI National Congress 2014 that followed, I heard about the flexibility of some employers to



Past Chief Scientist of South Australia Don Bursill speaking at the National Awards dinner.



Delegates at the Congress exhibitor stands.

accommodate the demands of being an office bearer within the RACI.

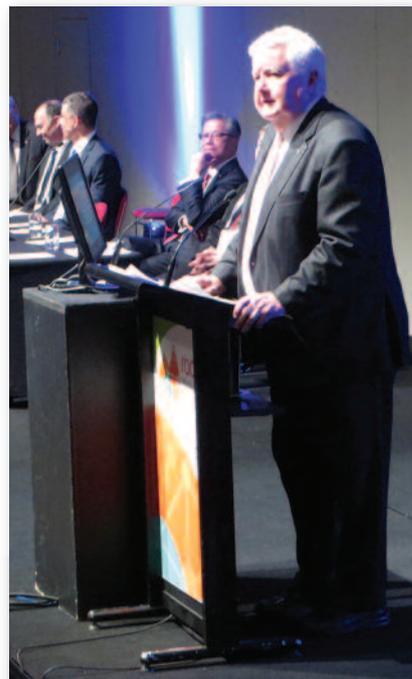
All of these examples of people and organisations show that chemists can, as Martin Banwell (H.G. Smith Memorial Medal) put it, 'do things by virtue of being embedded in the community'.

The invited dinner speaker was Professor Don Bursill, past Chief Scientist of South Australia. Reflecting on some of his own past experiences in the Australian water industry, he talked

about the difficulties in interfacing with industry, the frustrations of losing IP, generated with the help of grants, to other countries. State bodies keep insisting on the potential for international investment, he said. How can we usefully transfer our STEM capabilities? Why do we have no national objectives or strategies? We have lost our sense of adventure, he noted, and we need to restore national confidence, have more faith in our abilities.



H.G. Smith Memorial Medal recipient Martin Banwell (right) and Immediate Past-President Mark Buntine (left) sharing a joke at the Awards dinner.



Australian Chief Scientist Ian Chubb addressing the Congress.

Congress plenary lectures: the President's overview

The Congress featured many excellent lectures across a wide range of themes and symposia. In addition, we were treated to nine superb plenary lectures.

Stacie Canan (Celgene Global Health) spoke about drug discovery and its impact on diseases endemic in the developing world. A case study on Celgene's recent development of a potential antimalarial drug was presented.

Greg Scholes (Princeton) delivered a lecture on how ultra-fast (time-resolved) spectroscopy has brought deeper understanding to the mechanisms of light harvesting in photosynthesis.

David Leigh (Manchester) presented a highly entertaining and absorbing lecture on designing compounds that function as molecular motors or machines mimicking highly sophisticated processes in nature. His lecture was punctuated by a selection of magic tricks to the delight of the audience.

Phil Baran (Scripps Research Institute) illustrated his lab's radical approach to natural product synthesis.

Katharina Landfester (Max Planck Institute for Polymer Research) showed the diversity of applications that can emerge from the use of microemulsions in, for example, photonics and drug delivery.

Makoto Fujita (Tokyo) showcased a new methodology to use crystalline coordination polymers as hosts for organic guest molecules leading to the crystal structure of the encapsulated guest molecule. This revolutionary method provides a way of determining crystal structures of small molecules in the absence of crystals of the isolated compound.

Alán Aspuru-Guzik (Harvard) showed how computational chemistry is contributing to our understanding of and prediction of novel material properties and also how shared (personal) computing resources can be utilised to tackle large-scale problems of this kind.

Daniel Nocera (Harvard) gave a lecture focusing on research that has led to a device (an 'artificial leaf') that can split water into hydrogen and oxygen using visible light as the only energy source. His system is inspired by the principles of photosynthesis requiring catalytic centres to achieve coupled multi-electron redox reactions.

Hubert Girault (Lausanne) illustrated how cutting-edge highly sensitive mass spectrometry methods are transforming bioanalytical chemistry.

Paul Bernhardt FRACI CChem, RACI President



Part of the foyer display at the Congress.

Interfaces were also on Australian Chief Scientist Professor Ian Chubb's mind as he spoke at the opening of the Congress. Quoting Andrew Holmes at *The Conversation* (reprinted in our May 2014 edition, p. 34), he said 'most major advances take place at the interface of two or more disciplines and chemistry sits at the core of trans-disciplinary research'. It's more than a discipline, said Chubb, it's a way of thinking. Perhaps therein lies the problem with 'interfacing' with people outside of science – the thinking is along different lines. Because of the vitality of these interfaces, neglecting one science diminishes them all, Chubb continued.

And yet again we come back to relationships, beginning and growing at these interfaces, professional and personal.

During his Welcome to Country, Karl 'Winda' Telfer, senior cultural custodian for Kurna Meyunna, distinguished between observing the environment, as scientists do, and being part of it. He complemented his words with the rich tones of a didgeridoo, a gift to him from the Yolngu people.

In his address at the Congress opening, newly minted President Professor Paul Bernhardt greeted his 'RACI family', asking for a show of hands to indicate RACI membership. There was strong RACI attendance at the Congress, including about 300 students. He encouraged attendees to see the Congress as an opportunity to meet people outside their area of expertise.

Professor Paul Mulvaney, chair of the National Committee for Chemistry working group for the Australian Decadal Plan for Chemistry, discussed the group's plans and efforts so far to put together a grassroots document based on national surveys, meetings and submissions. Visit <http://chemistrydecadalplan.org.au> for more details. Web submissions are expected to open in May and a White Paper be released later this year. This will contribute to their goal to understand the role and future of chemistry in Australian society. Mulvaney says part of this will explore 'what it means to be a chemist', and I'm confident that the Congress offered new and positive inputs to the committee's findings.

Sally Woollett

Milton Hearn to receive ACS award

Professor Milton Hearn FRACI CChem will be the recipient of the American Chemical Society 2015 Alan S. Michaels Award. The award itself will be conferred at the 2015 Spring National Meeting of the American Chemical Society, in Denver, Colorado, 22–26 March 2015.



Credit: Steve Morton

The Award is in recognition of outstanding research and practice contributions toward the advancement of science and technology for the recovery of biological products that has exceptionally significant impact. This is the second ACS 2015 Award that Hearn has received; he also received the 2015 ACS Chromatography Award (see October 2014 issue, p. 30).

Curt Wentrup wins Birch Medal

Emeritus Professor Curt Wentrup FAA, FRACI CChem from the School of Chemistry & Molecular Biosciences at the University of Queensland has won the 2014 A.J. Birch Medal for excellence in organic chemistry research.

The A.J. Birch Medal is the premier award of the RACI Organic Chemistry Division.

Wentrup earned his PhD at the ANU in 1969, and after a career in Europe returned to Australia as Professor and Head of Organic Chemistry at the University of Queensland (1985–2008). Since 2008 he has continued intensive collaborative research, and published prolifically as emeritus professor. He is a Fellow of the Australian Academy of Science (elected 2000) and since 2008 has been editor-in-chief of the *Australian Journal of Chemistry*. He has also served as Chair of the National Committee for Chemistry (Australian Academy of Science).

Wentrup has authored over 300 journal publications, plus several reviews, book chapters and two textbooks. His research interests embrace both experimental and computational chemistry of reactive intermediates and highly unusual molecules using photochemistry, flash vacuum thermolysis and low temperature matrix/isolation photochemistry to investigate reaction mechanisms and the reactivity of novel and/or transient molecular species.



Presentation of the Birch Medal to Emeritus Professor Curt Wentrup by Professor Kate Jolliffe, Chair of the RACI Organic Division, at the RACI Congress in Adelaide, December, 2014.

Wentrup presented a paper and accepted the A.J Birch accolade at the RACI Congress in Adelaide on 11 December 2014.

In addition, Wentrup received an honorary doctorate from the University of Pau (France) as well as the David Craig Medal of the Australian Academy of Science in 2014.

Kliti Grice wins AOGC Medal

John Curtin Distinguished Professor and Discovery Outstanding Research Awardee Kliti Grice FRACI CChem, and Fellow of the Geochemical Society and European Association Geochemistry, has been awarded the prestigious Australian Organic Geochemistry (AOGC) Medal.

The Medal is awarded biennially to a distinguished member of the scientific community for lifetime achievement in the field of organic geochemistry. It was presented at the Australian Organic Geochemistry Conference in Adelaide on 1 December.

Grice is the first-ever female recipient of the AOGC Medal. She is an internationally recognised and widely published organic and stable isotope geochemist and is especially well known for identifying a geological and environmental basis for the largest mass extinction in Earth's history, which happened at the end of the Permian period, about 252 million years ago. She has also studied three of the big five events using molecular fossils and stable isotopes and has worked on modern to ancient environments, including those associated with Global Anoxic Events with applications to petroleum and mineral exploration. She has published about 130 papers including *Science* and *Nature*.

Her outstanding research reputation has attracted many national and international PhD and postdoctoral earth sciences scholars to Curtin.

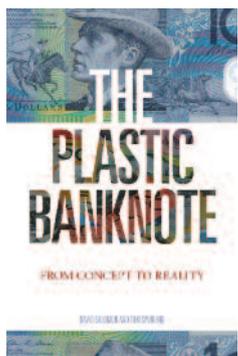
Curtin Deputy Vice-Chancellor Research and Development, Professor Graeme Wright, said the award was due recognition from the scientific community for the quality and depth of Grice's research and her determination to discover new knowledge.

'Kliti works exceedingly hard at her research and is a highly productive scientist. She is prolific and well connected to a global network of collaborators.'

Grice completed an honours degree in Applied Chemistry 1991, before studying under Professor James Maxwell in the Organic Geochemistry Unit at Bristol University. She finished her PhD in 1995 and went on to a research fellowship at the Royal Netherlands Institute for Sea Research before joining Curtin in 1998, where she has successfully established the Western Australian Organic and Isotope Chemistry Centre, which is part of The Institute for Geoscience Research.

CURTIN UNIVERSITY





The plastic banknote: from concept to reality

Solomon D., Spurling T., CSIRO Publishing, 2014, paperback, 240 pp., ISBN 9780643094277, \$39.95

After 20 years (1968–88) of collaboration and research and development between CSIRO and the Reserve Bank of Australia (RBA), the world's first polymer banknote was issued in 1988. It coincided with the 200th anniversary of the arrival of the First Fleet. In this book, David

Solomon, who made a significant research contribution, and Tom Spurling give an interesting chronological account in 13 chapters of 'from rags to polymers' in banknote technology, punctuated by the constant challenges arising from the meeting of different minds and the evolution of research commercialisation practices.

From the outset, producing plastic currency was a top-secret project. It was not so much the secrecy surrounding the science but a response to the problem of counterfeiting posed by colour photocopiers and technology. Currency security dominated bankers' minds, and initiated the search for more secure banknotes.

The early chapters provide a brief history of how Australian banknotes were produced, and the prototype plastic notes. The account of the second meeting of scientists and RBA officials on 16 June 1968 at a ski resort highlights the initial tensions, agendas and differences between the participants. Not surprisingly, to make progress, many letters of agreements and meetings were needed.

Chapters 7 and 8 recount the events from Solomon's CSIRO team's three-day think-tank meeting on 2 October 1974 to develop its research direction. The RBA had no scientific expertise; it imagined itself as a printer and issuer of banknotes and was in need of a plastic banknote with security devices. Solomon's scientists devised a strategy to produce four plastic prototype banknotes, each with security devices of increasing complexity, thereby allowing maximum flexibility for the graphic designers to work on.

Further chapters detail the constant trials and tribulations surrounding security device technologies, the Currency Notes Research and Development Committee and its responsibility for the development of banknote pilot production and evaluation. Commitment to the banknote project was sustained by off-site conferences and the Bank's forward planning group, an external high-level project review oversight committee known as the Fink Committee. Its members were Professor P.T. Fink, CBE (Chairman; Professor of Mechanical Engineering, UNSW); H.M. Morgan (Executive Director, WMC and part-time Member of CSIRO Executive); E.E. Peacock (Chairman and Managing Director, Crooks, Michell, Peacock, Stewart, Consulting Engineers); Ralph Tobias (First Assistant Secretary, Productivity Development Division, Department of Productivity); H.W. Worner (Director, Institute of Industrial Technology, CSIRO); D.R. Parr (Advisor and Chief Manager, Accounting, Operations and Services, RBA); and J.S.

Pearson (Manager, Currency and Banking Operations and Services, RBA, Secretary to the Group.). This committee played an important part in assessing/reviewing the project, helping to ensure that both the RBA and CSIRO moved towards commercial production.

The book unequivocally confirms how the search for innovative banknote security technology, which could not be photographed, remained a constant challenge for two decades. However, later events confirmed that the plastic substrate banknote as well as the inclusion of a transparent zone provided excellent security. Together these two features were the key innovations that made the plastic banknote far superior to its paper counterpart.

The final two chapters detail the profound influence Governor Johnston's remodelling of the RBA had on bringing the project to a successful finale. Johnston was the catalyst for the bank's modernisation and revamping of its technical capacity, changes essential to the success of this collaborative project. Consequently, the RBA was able to purchase the CSIRO manufacturing technology and produce plastic banknotes for circulation on 26 January 1988. Since then, the plastic banknote has proven more durable than its paper-based counterparts and has been widely adopted by other countries.

The plastic banknote provides an insightful historical account of the commercialisation of how leading Australian technology was commercialised and represents excellent reading for all.

Helmut Hügel FRACI CChem

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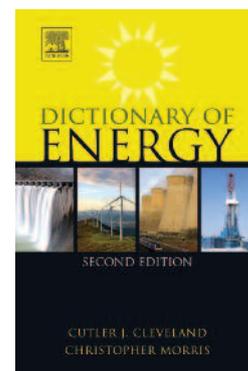
Dictionary of energy

Cleveland C.J., Morris C. (eds), Elsevier, 2014, hardcover, pp. 680, ISBN 9780080968117, \$130

This dictionary describes itself as a comprehensive and authoritative reference on all aspects of energy, and I can agree with the 'comprehensive' part. References cover all major areas of energy, from sources and usage, power generation methods and location of power stations, to pioneering researchers in various areas of energy, greenhouse gases and climate change, manufacturing industry, as well as more obscure topics.

The editors have clearly put in a lot of effort to make a good reference source; however, readers with an in-depth knowledge of energy-related topics may find the brief references lack enough detail. Therefore, rather than a defining referencing source, I suggest the dictionary be used for quick definition checks, especially of industry jargon and terminology.

To break up the dictionary style, the editors include what they call 'window essays' on a range of energy topics, written by some high-profile people, such as Howard Herzog from MIT, Enrico Sciubba from the University of Rome and, for an Australian connection, Naj Aziz from the University of



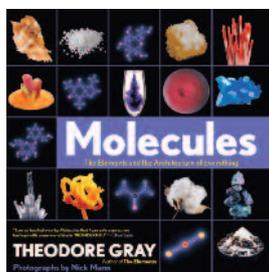
Wollongong. Topics covered by these essays cover wind farms, temperature scales, strip mining and the Otto cycle. The essays are an excellent idea, as they provide more information and details about important areas of energy than you would otherwise appreciate from the reference entries alone.

One major drawback with this dictionary is the editors' choice to pad it out with references I believe aren't related to energy topics. For example, under 'G', there are entries on Gaia hypothesis, game theory, Bill Gates, GATT trade agreement, geocentric theory and gray economy, to highlight a few. Though all have descriptive, informative entries that describe the subject matter, there's a very weak link to energy at best.

I would recommend the *Dictionary of energy* to those whose employment or interests exposes them to a wide range of energy fields, since it's an excellent reference source to help elucidate and understand the technical terminology and industry speak.

Colin Scholes FRACI CChem

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Molecules: the elements and the architecture of everything

Gray T., Mann N., Black Dog and Leventhal, 2014, hardcover, 240 pp., ISBN 13:9781579129712, \$35

You will absolutely love this book, which is, in a sense, a companion volume to

Theodore Gray's book *The elements* (see review April 2014 issue, p. 32). It's relatively inexpensive (\$25–35), full of wonderful photographs (by Nick Mann), and full to the brim with lots of solid, but eminently palatable, chemistry.

Everybody between the ages of nine and 99 will enjoy *Molecules*. In a way, it is a large format (250 × 250 mm approx.), annotated picture book. So you can just look at the photographs, or also read their captions (which are generally interesting and sometimes wryly amusing), or launch into the more detailed text. Hence, it suits all ages and everyone will take away some interesting chemistry from its perusal.

And it's fun! For example, from my perspective as a dog owner, I'm continually astonished at the amount of hair that's shed (usually in the house and, dare I admit, sometimes on the forbidden couches!). I've often mused over possibilities for a canine analogue of the merino and possum (strictly New Zealand of course) yarn, which is used to make high-quality knitted garments. Imagine my excitement, indeed satisfaction,

when the book revealed a photograph of a pair of knitted socks ... made solely of dog hair! All very quirky, but neatly embedded in discussion of the molecular architecture of fibres.

Perhaps chemistry's most enlightening contribution to our everyday lives lies in the framework it provides us to view and make sense of our physical world. An understanding of the structure of molecules is essential to understanding the properties and behaviour of the macroscopic world. That's why we became chemists in the first place – to make sense of our world! It's why we're so fond of referring to our discipline as the 'core molecular science'. And that's why this book's so good; it's essentially structure–property relationships in a palatable, user-friendly form. If you were looking to write a book designed to inspire the neophyte towards chemistry and rejuvenate the jaded to chemistry's delights, then you've left your run too late. *Molecules* does it superbly.

The book is organised along 14 themes, which range from an explanation of how atoms bond to form molecules and compounds, through a discussion of what constitutes 'organic' and 'inorganic', to an exploration of a wide selection of the materials made from molecules. The latter selection includes, inter alia, soaps and solvents; ropes and fibres; ores and rocks; painkillers and opiates; sugars and sweeteners; perfumes and aromas; and colours and pigments.

Chemistry's been compared with sex – it can be stimulating, fun and occasionally creative, but even when it's none of these things, it's better than nothing. There are enough books in the 'better than nothing' category. In my view *Molecules* is definitely sexy!

R. John Casey FRACI CChem

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Characterising competitive advantage

In October 2013, the Grangemouth petrochemical facility in Scotland was threatened by closure over an industrial dispute. This resulted in a high level of commentary in both Scotland and the UK in general, exacerbated by the imminent 2014 referendum on Scottish independence. Concern was expressed that the closure of Grangemouth would have the knock-on effect of closure of Scotland's only refinery, which would raise fuel security issues for an independent Scotland. The political pressure resulted in settlement of the dispute in favour of the company and for now the operation and jobs appear saved. Since that time, Ineos (the owners) have announced plans to make major investments in trans-Atlantic shipment of low-cost ethane from the US to Europe, which should further improve the profitability of the operation and help its future.

In Australia, the contrast in attitude to the hydrocarbon processing industries is stark. In early 2014, Shell announced the sale of the Geelong refinery and its closure if it could not be sold. This followed earlier announcements of the closure of the Shell refinery at Clyde in Sydney and Caltex's Kurnell refinery. In March, BP announced the closure of their refinery operation at Bulwer Island near Brisbane. These announcements have been greeted with relatively little interest with few commentators expressing a concern that such closures would compromise Australia's fuel security.

An impact of refinery closure will be the closure of chemical processing operations juxtaposed to it. One effect will be on the availability of propylene for the production of polypropylene in Sydney. For now, the Geelong refinery seems secure after the announcement of its purchase by Vitol, so that polypropylene production in Victoria may be safe for now. Closure of the Geelong refinery would also undermine the profitability of ExxonMobil's Footscray refinery, which would in turn adversely impact on Qenos' ethane cracking operation at Altona.

Because of export LNG projects coming on-stream in Gladstone, there is increasing concern for the future price and supply of natural gas (see statements by PACIA in *Chemistry in Australia* July 2013, p. 5; September 2013, p. 9). Originally, these were to be supplied from coal seam gas (CSG), but political issues with rolling out CSG developments and the high cost of these developments has changed the gas source to include conventional gas sources currently supplying Australian industry. Consequently, gas suppliers are reluctant to supply gas that does not meet the high value for LNG exports, which could result in gas prices being set to double or triple over the next few years.

Because ethane could be incorporated into export LNG, these changes in the feedstock supply chain will affect the supply and price of ethane for cracking operations in Australia. This ethane price is far higher than ethane feedstock for cracking operations in other parts of the world, so retrofitting back to liquid feedstock would require considerable expenditure in re-building downstream liquids handling facilities.

The rise in gas price would also have a major impact on the

The rise in price of gas would also have a major impact on the cost of production of other chemicals, most notably the production of ammonia and fertiliser on the eastern seaboard. The result would be a major contraction in the chemical and allied industries in Australia ...



cost of production of other chemicals, most notably the production of ammonia and fertiliser on the eastern seaboard. The result would be a major contraction in the chemical and allied industries in Australia, which would have significant ramifications for the future employment of chemists and engineers.

The agricultural products industry is often touted as Australia's future. As a trustee of a self-managed super-fund, I must say the investment opportunities in this sector have been historically poor and I do not see any prospect of change. We spread the idea that 20% of manufacturing is in the wine industry, but this could be a lifestyle choice for many rather than a future export industry. From my observations, the leader in agricultural produce in our region is New Zealand; it dominates overseas wine lists from our region with their Sauvignon Blanc and Pinot Noir and have very low production costs for dairy and downstream industries. Furthermore,

Cabernets from Chile and Argentinean Malbec lead the pack in bigger reds. Australia seems happy to play in the second division or supply boutique wines such as Grange to be drunk by politicians and their ilk.

In today's global village economy, industries grow by having a competitive advantage. This competitive advantage is often local in character and can be quite specific. Industries without a competitive advantage go into decline unless supported by government regulation or finance. For instance, trade to the EU results in import tariffs to 'protect' European industry but as recent history shows when some industries have a production cost more than the trade barrier, then decline is inevitable. Industry protection can take other forms; for example, production of ammonia for fertiliser is seen by many countries as a strategic necessity and is highly regulated.

Given the caveat on trade barriers, what are Australia's competitive advantages? The answer clearly (as we all know!) is basic minerals (iron ore, coal, gold etc.) and basic agricultural products (wheat, cotton, wool etc.), which can be exported to the major economies at prices that cannot be matched by local production. For example, Australian coal landed in the UK will be of lower cost than UK-produced coal.

In the past, Australia had a competitive advantage in energy in the form of low-cost natural gas and electricity (generated from the abundant supply of low-cost coal). However, over the past decade, this competitive advantage has disappeared. Domestic gas is being priced relative to the high-value north Pacific LNG market and electricity prices have significantly increased from regulation, carbon taxes, renewable energy schemes and infrastructure investment. These changes in the price of energy have major implications for adding value to Australia's minerals, in fact destroying many industries and increasing barriers to new ventures. Most value-added industries are fundamentally chemical process industries, so that these

changes have major implications for industrial chemistry and chemical engineering in Australia.

To understand the position of the chemical industry in Australia, in subsequent issues, I will generate some thoughts on the competitive situation of the Australian chemical industry relative to its peers and in particular against its peers in South-East Asia as well as those in Europe and the US.

I will limit the process descriptions to the parts with significant impacts on the

underlying process economics. Full detailed descriptions are available in industry handbooks. The economic analysis was developed by ICI and has been published elsewhere.*

Duncan Seddon FRACI CChem is a consultant to coal, oil, gas and chemicals industries specialising in adding value to natural resources.

*D. Seddon, *Petrochemical economics – technology selection in a carbon constrained world*, Imperial College Press, 2010, which describes the economic methodology based on A. Stratton 'Simplified method for calculating product cost', *Technical Note 3*, Economic Assessment Service, IEA Coal Research, London 1982).

Science with Focus



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Why students should study STEM

Students who do not intend to have a science-related career often ask why they should study STEM (science, technology, engineering and mathematics) subjects. This is strongly linked to the decline in the numbers of students studying the science-based subjects (see March 2012 issue, p. 40). In the 20 years between 1992 and 2012, the number of Australian year 12 students increased by 30 800, but the numbers of year 12 chemistry, physics and biology students declined by 4000, 8000 and 12 000 respectively.



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.

A 2014 report, *Science, Technology, Engineering and Mathematics: Australia's Future*, from the Office of the Chief Scientist,* highlights why students should study STEM. Internationally, 75% of the fastest growing occupations now require STEM skills and knowledge. In 2009, US President Obama stated that a world-class STEM workforce is essential to virtually every goal the US has as a nation. More recently, Prime Minister Tony Abbott stated that STEM is at the heart of a country's competitiveness. According to the Office of the Chief Scientist,

* The full report is available at www.chiefscientist.gov.au/2014/09

the five most significant societal challenges that Australia presently faces are:

- living in a changing environment
- promoting population health and wellbeing
- managing our food and water assets
- securing Australia's place in a changing world
- lifting productivity and economic growth.

School leavers and graduates with a background in the STEM disciplines are well placed to meet these challenges. We should learn from the US experience, where there are many opportunities for STEM-trained graduates to move into non-STEM industries and this migration of skills away from science to enrich other sectors is not seen as failure.

The big national and international picture is good for strategic planning, but that does not necessarily motivate students, who are keeping their options open and choosing school subjects that will maximise their Australian Tertiary Admissions Rank (ATAR) or tertiary education subjects that will apparently enhance their employment prospects. 'What's in it for me? Not for the national interest, but for me as an individual?' How would non-STEM students benefit from studying chemistry as an elective?

As chemists, we know that chemistry knowledge is important for everyday life, and that the skills gained as part of an education in chemistry enable us to analyse and solve problems. For example, chemistry knowledge is useful in analysing advertising claims and understanding nutritional information on food packaging. However, chemistry education is not just about knowledge content in the curriculum, but also about developing important skills and abilities (see March 2013 issue, p. 35). These skills are useful in many careers, not just in STEM. For example, chemistry graduates have applied their analysis skills to the analysis and modelling of financial systems in the banking industry. Graphs and numerical information are also part of everyday life. We see them in advertising, in supermarkets, and in news and weather reports. 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. Studying chemistry also instils a culture of workplace and individual safety and fosters the ability to assess risk and minimise hazards: work health and safety (WHS) is important in all workplaces, not just in STEM industries.

The next time a young person asks you 'Why should I study chemistry?', you can answer that studying chemistry will develop important life and career skills.



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iStockphoto/Nomadsoul1

Volatile sulfur compounds and unpleasant wine aroma

When winemakers and oenologists speak of 'reductive characters', they are usually referring to compounds that impart an unpleasant aroma or nose to the wine. The Australian Wine Research Institute (AWRI) web page that refers to these aromas is entitled simply 'What's that horrible smell?' (bit.ly/17yisrI). Hydrogen sulfide and various mercaptans or thiols and disulfides have been identified as compounds contributing to the off-aroma.

H₂S has been one of, if not the most, notorious of these sulfide compounds and it still remains the subject of active research. With a pK_{a1} around 7, the proportion of H₂S existing in the molecular form will be close to 100% in the wine pH range of 3.0–3.6. It is also readily volatile and while it appears that the Henry's law constant is not available for wine, the value for wastewater suggests that the concentration in the vapour above the liquid surface is about 10 times that in the wine. The aroma threshold for H₂S in wine has been recently evaluated at the AWRI. Using the ASTM method for standard practice for the determination of odour and taste thresholds (Method E679-04), the aroma threshold was found to be 1.6 µg/L in white wine (28 judges) and 1.1 µg/L in red wine (30 judges). The standard error in both cases was relatively high at 1.3 µg/L, reflecting individual variation. For white wine, seven of the 28 judges had thresholds above 10 µg/L, although for red wine, only two of the 30 judges had threshold values above 10 µg/L. More detail can be found in the *AWRI Technical Review 183* (December 2009).

Common aroma descriptors for H₂S include *rotten egg* and *sewage-like* – far from favourable. The descriptors for thiols and disulfides are even less favourable. Methanethiol might add *rotten cabbage* and *burnt rubber* characters, while ethanethiol's aroma has been described as *rubbery*, *burnt match* and *earthy*. The aroma of dimethyl sulfide has been described as *blackcurrant* (perhaps positive, if one appreciates cordial), *cooked cabbage*, *asparagus*, *canned corn* and *molasses*, while that for dimethyl disulfide is *vegetal* or *cabbage*. For those who think that wine research must be fun, just think of the researchers who are required to spend months training and assessing characters for these thiols and disulfides. I can assure you that it is painful.

Stress during the fermentation, especially yeast stress, is one of the most common causes for the formation of H₂S. Lack of readily available nitrogen, sometimes referred to as 'yeast-assimilable nitrogen', or YAN, is a major contributor to yeast stress. Winemakers may decide to add diammonium phosphate to the fermenting system to improve the level of YAN in the hope that the yeasts will be happy and not reach stress levels that result in H₂S formation. There are, however, multiple factors that contribute to the formation of these sulfide compounds in wine and I will discuss these in a subsequent column.

If H₂S is detected in wine, the standard practice is to use copper finings – the addition of incremental amounts of a copper(II) solution, usually its sulfate or citrate, to the wine. Then the concentration of added copper(II) at which the wine smells 'clean' is selected. The chemistry underlying this strategy is relatively simple. The solubility product for copper(II) sulfide in water is 6.3×10^{-36} (mol/L)², implying that essentially complete removal of sulfide should occur after the addition of a stoichiometric amount of copper(II). Once the determined amount of copper(II) is added to the bulk wine in barrel or tank, it is assumed that the precipitate will settle out or be removed by filtration.

This copper finings procedure is a good example of reality not matching theory. In practice, the amount of copper(II) determined in the fining process is generally in considerable molar excess of the amount of sulfide. Methanethiol and ethanethiol will also react with copper(II), but irrespective, the amount of added copper(II) is in excess of the 1 : 1 molar ratio. Residual copper(II) in wine, especially white wine, can lead to oxidative spoilage, adding a different quality defect to the initial 'off-odour' defect. To add to winemaker frustration, there is increasing evidence that the H₂S aroma may return during storage.

In a project led by my colleague, Dr Andrew Clark of the National Wine and Grape Industry Centre in Wagga Wagga, we set out to re-examine some of the issues surrounding the chemistry of copper fining (see doi: 10.1111/ajgw.12114). Fourteen white wines with variable copper concentrations were selected. First, sulfide was added and after equilibration, the copper concentration adjusted to 1 mg/L, giving the H₂S to Cu ratio of 1 : 1 in all samples. After one day, a portion of each sample was decanted, equivalent to wine industry racking. Separate samples were also filtered through either 0.45 µm or 0.2 µm filters and the copper concentration in all samples was measured by flame AAS. Little or no copper was actually removed, yet the H₂S aroma was no longer apparent suggesting that copper sulfide was being formed, but the particle size was too small to be captured by settling or filtration.

While initially surprised by this result, I was transported back in time to second year chemistry and the barium sulfate gravimetric analysis experiment and the frustrations of trying to coagulate the precipitate. Maybe there are some answers in classical precipitation chemistry, about which I will write in my next column.

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.



It's time to prepare for peak phosphorus

A looming global shortage of an important fertiliser necessitates the development of phosphorus-efficient crops, recycling of phosphorus from sewage and even separating it from urine.

Australians should be very concerned and New Zealanders alarmed by their dependence on phosphorus. Why? On a per person assessment, Australians and New Zealanders use 5.3 and 15.4 times more phosphorus than the world average, which is 2.4 kg per person per year.

The reason for the high usage per person is the small populations of these countries relative to their production of exported products – mainly cereals from Australia and milk and meat from New Zealand. As our populations increase, more food will be consumed locally relative to the amount of food exported, but the demand for imported phosphorus fertiliser will remain high.

The food security of nations is highly dependent on phosphorus. The need for continual inputs of phosphorus fertiliser for food production cannot be taken for granted. Crop yields would immediately decline on average by an estimated 20% and by 30–40% within five years if phosphorus fertilisers

became unavailable. This would be disastrous. The world population increases by about 75 million people annually and crop yields must increase by about 1.2% each year to keep pace.

Furthermore, the availability of phosphorus for food production cannot be taken for granted. The major reserves of the world are now concentrated in the US and North Africa, but the latter will become the dominant provider in only 50 years from now. Supply could be limited at short notice due to economic, political or military events. Australia has small reserves of phosphorus but these should be preserved until imports become unavailable or prohibitively expensive.

Increases in fossil fuel costs will lead to increases in transportation costs, and these will flow on to the price of fertiliser at the farm gate in Australia and New Zealand. An illustration of the volatility in the cost of phosphorus occurred about eight years ago. The price of triple superphosphate, a fertiliser containing about 19% phosphorus, rose from \$207/tonne in January 2007 to more than \$1100/tonne in August 2008. Within a year, the price collapsed to \$220, but since then it has been increasing progressively.

Both Australia and New Zealand must prepare for life with less affordable phosphorus. This scenario must be seen as a community challenge and not simply the responsibility of the agricultural sector.

Worthy goals in Australian and New Zealand should be to reduce the export and promote the recycling of phosphorus. Some studies estimate that the amounts of phosphorus exported in wheat and rice grains can be reduced by 10–15% in the short term by switching to phosphorus-efficient cultivars. The saving in fertiliser-equivalents would be some \$30 million annually for the wheat industry and \$750 000 annually for the rice industry – more than enough to fund a serious R&D program dedicated to reducing our dependence on imported phosphorus.

The phosphorus efficiency of every genotype in every crop-breeding program should be known. While traditional analytical methods are accurate, they are costly in terms of time, chemicals and technical skills. However, the rapid, chemical-free technology of near-infrared spectroscopy is able to assess phosphorus in plant and grain samples, and with little effort could be used to identify and utilise phosphorus-efficient lines in plant breeding programs.

To reduce our dependence on imported phosphorus, we must change the one-way phosphorus path to a closed phosphorus cycle. This would include reducing dependence on some products, increased recycling of phosphorus in waste products such as sewage, and separating phosphorus in urine.

This is a worthy challenge for all citizens.

Graeme Batten is Honorary Professor in the Department of Plant and Food Sciences at the University of Sydney and Editor-in-Chief of the *Journal of Near Infrared Spectroscopy*. **Lindsay Campbell** is a senior lecturer in the Department of Plant and Food Sciences at the University of Sydney. First published in *Australasian Science* (www.australasianscience.com.au).

Crop yields would immediately decline on average by an estimated 20% and by 30–40% within five years if phosphorus fertilisers became unavailable.



Prickly pear

The story of the infestation of prickly pear, *Opuntia* spp., in southern Queensland and northern New South Wales is well known because it includes a major success of biological control – the destruction of most of the pest species by the *Cactoblastis* beetle. What is not so well known is the pre-beetle history of attempts to destroy the prickly pear by treatment with arsenic, and even less well known are the efforts to use the plant as stock food and ... now I get to the point ... for the treatment of diabetes.

In 1921, Frederick Banting and Charles Best, working in Toronto and following hints from earlier studies by European physiologists, showed that a pancreatic factor could reduce blood glucose levels in diabetic dogs (and later humans). This was the peptide hormone insulin that was soon shown to regulate glucose levels by formation and depolymerisation of the polysaccharide glycogen. Insulin therapy was quickly adopted by physicians in other countries, including Australia, but folk remedies lingered on for quite a while, as the following story reveals.

In 1925, Dr W.G. Shellshear of Wallsend (now a suburb of Newcastle, NSW) reported that he had a patient ('Mrs B') who was resistant to insulin but had been told by a school-teacher friend (J.R.) that he kept his blood sugar under control by taking regular draughts of a solution prepared by boiling the 'leaves' of prickly pear with water. Shellshear had some success by treating Mrs B jointly with insulin and prickly pear extract, the combination being more effective than either medication alone. A year later, Shellshear reported continued success and gave details of the preparation of the decoction. Prickles were removed from 1 pound of tissue of *Opuntia inermis*, after which it was shredded with a fork, mixed with a tablespoonful of bicarbonate of soda, covered with a quart of cold water and allowed to stand overnight. The liquid was filtered and the patient drank a wineglass full three times a day before meals. 'This mixture is unpleasant', wrote Shellshear, 'and slimy to take', but certainly effective and worthy of further scientific investigation.

Some years passed before a further report appeared from the Parke Pope Research Laboratory of the Sydney Technical College where A.R. Penfold and F.R. Morrison, both members of the Australian Chemical Institute (FACI and AACI, respectively) and Fellows of the Chemical Society of London, had taken up Shellshear's challenge. The slimy nature of the extract they attributed to the presence of the polysaccharide arabin, which the government analyst, W.M. Hamlet, agreed was probably present in the aqueous extract. Since arabin is insoluble in alcohol, it was suggested that it could be precipitated from the solution, but a better procedure was to make an alcoholic extract in the first place. Administered in the ratio of one teaspoonful to a wineglass of water, three times a day, this proved so effective that 'between thirty and forty persons who have used the concentrated extract during the past five or six



years speak very highly of it'. No blood sugar tests were performed and Penfold and Morrison raised the possibility that unknown constituents of the extract might be responsible for what they called a tonic effect. A Dr Morrison had done blood tests for Shellshear at the Wallsend Hospital but I can't be sure it was the same chemist.

Hamlet also investigated the nutrient properties of prickly pear, which he compared favourably with those of melon or cabbage. Some farmers found it was valuable as stock fodder in times of drought because of its high water content.

I recently browsed in a book about the social history of the prickly pear(s) in the Eastern Cape region of South Africa, where a number of uses were reported. Of the several *Opuntia* species in the area, two were important – a prickly one and a non-prickly one. Efforts to clear land of the prickly one using biological controls – *Cactoblastis* (as in Australia) and cochineal – met resistance from those who grew the non-prickly type as stock food since it was also vulnerable to beetle predation. Fruit from the prickly type were hard to harvest, for obvious reasons, and they are covered in fine, irritant hairs that need to be removed before any handling was possible. They were cheap food for black people, who also collected them for sale along the roadsides and at markets, and used them as fresh fruit, in jam and for brewing beer. Following the fermentation, it was also possible to manufacture a distilled spirit known locally as 'Witblits'. This industry has been strongly discouraged but Witblits is still produced legally at the annual Prickly Pear Heritage Festival held at the historical museum in Uitenhage, near Port Elizabeth. Production of beers and spirits from prickly pear is reported for a number of northern hemisphere countries, too.

Although prickly pear is no longer a scourge because the most invasive species have been all-but eliminated in Australia, there are some very large clumps near Chinchilla in southern Queensland. The fruit are available in some shops in Melbourne; in my limited experience they could be considered 'interesting', but on historical rather than gustatory grounds.

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.



35th Australasian Polymer Symposium

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

IUPAC 2015

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

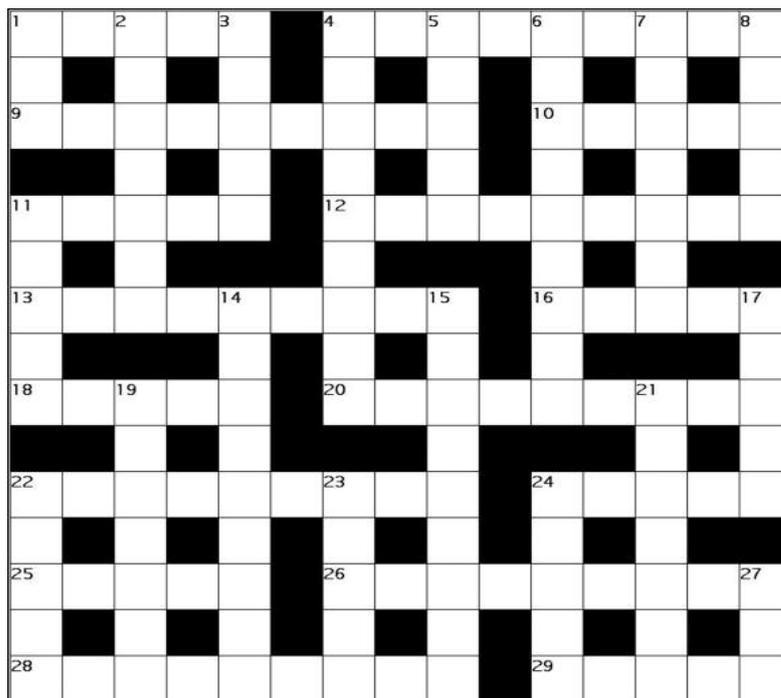
2015 Sustainable Industrial Processing Summit and Exhibition

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

Pacifichem 2015

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

FRACI events are shown in blue.



Across

- 1 Crow sound for Australian-born Nobel Prize winner. (5)
- 4 Paint comic sets. Spill! (9)
- 9 $E_{120} = 27\chi_{1013}$. (9)
- 10 A metal on? Negative. (5)
- 11 A little way and . . . Get up! (5)
- 12 One form of an element to alter loop design. (9)
- 13 Objection anomaly. (9)
- 16 Concentration of Spooner's base spoil. (5)
- 18 Burning about volume. (5)
- 20 Broken arm. In clue, it's about the numbers. (9)
- 22 H_2NO^- made by adding iodine to messy anode mix. (9)
- 24 Sharp radical in a group of investigators. (5)
- 25 The fourth incremental change in the variable. (5)
- 26 Nitrene's manufacture from MgI_2 nodes. (9)
- 28 Regent got knocked over by the odour of H_2S . (6,3)
- 29 Let it rest in the container to determine a concentration. (5)

Down

- 1 Combination of three light elements serves as a protective group in solid phase peptide synthesis. (3)
- 2 Obsolete use of flavoured tea in a flash. (7)
- 3 Pulverise the treadmill. (5)
- 4 Leach into debris binding metal ions. (9)
- 5 Backing inclusion of propranolol as one would phenyl salicylate. (5)
- 6 Centres delay brainstorming isomerism of rubber-like material. (9)
- 7 $RC(NR')-$ made over molybdenum, dysprosium and lithium iodide. (7)
- 8 Perhaps hearing 34734. (5)
- 11 Way fish alloy. (5)
- 14 $C_6H_5O^-$ and phosphorus layer with oxygen departed. (9)
- 15 Making a count of bromine, indium, germanium, uranium and manganese reactions. (9)
- 17 Governed with lines. (5)
- 19 Three lines or one of three. (7)
- 21 Appropriate discipline. (7)
- 22 Summer snake. (5)
- 23 I dig $RN=CR_2$. (5)
- 24 Around a round. (5)
- 27 Reference electrode made up of two elements. (3)

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

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Coming up

- Chlorophyll, carotenoids and other autumnal pigments
- More on marine conservation chemistry
- The past lives of our Sun



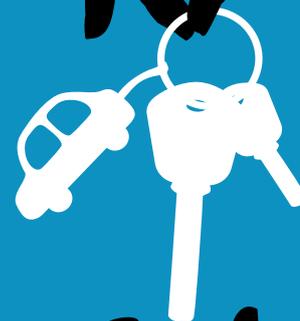
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