

chemistry

April 2017

in Australia

The chemistry of a century ago

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- Detecting drugs on the road
- What's on at the Centenary Congress
- Fool's gold and plate tectonics

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From the President

The RACI is 100 years old and the Board recognises the need to continue strongly for the next 100 years, at least. The RACI needs to strengthen itself to ensure that the hard (and voluntary) work of our predecessors to make the Institution what it is now is not wasted. To truly understand how far and wide the tentacles of the RACI reach, one has to become involved in its activities, and we urge all members to be active so they can get the maximum benefit from the RACI's activities.

Recently, the Board has been working towards ensuring the RACI continues the success of the work of previous Boards. We have recruited a non-member of the RACI to the Board who has marketing and communication skills, but who also has a non-chemist's point of view. This will help the broaden the Institute's appeal and therefore membership. We have also started work on a strategic plan to work towards for the next five years. The five areas proposed as part of this plan are:

- (i) *Membership attraction and retention.* This has been an area of concern for several years as membership numbers have declined. It is the most important item to pursue here, and all other areas feed into this. We intend to create a framework for executing member retention and attraction strategies consistently on a national level, so the RACI continues to exist with strength, have an impact and meet our vision and mission.
- (ii) *External relevance.* We intend to increase RACI's profile and the impact we are having on the community. Initial plans are to create and embed a media and government relationship strategy and to have RACI spokespeople prepared to communicate RACI's position/opinion.
- (iii) *Review internal structure.* To maximise the effective operational performance of all RACI entities, we need to ensure Groups, Branches and Divisions (entities) are conducting meaningful activity aligned to the strategy. We will ensure each entity has a framework for how to set up and run a successful entity (operational user guide and charter of expectations).

The RACI needs to strengthen itself to ensure that the hard (and voluntary) work of our predecessors to make the Institution what it is now is not wasted.

- (iv) *Seek strategic partners.* This should increase member value through the establishment of mutually beneficial partnerships. Initially, we will identify a framework and criteria for target strategic relationships to ensure we are creating value for members.
- (v) *Marketing and communications.* By establishing a marketing group or committee, we will increase the reputation, brand awareness and effectiveness of communications between all stakeholders. We have engaged marketing expertise into RACI and will devise a marketing strategy towards the future.

As part of this strategic plan, we will be encouraging all members to be part of this. Your help will ensure the future success of the Institute. A strategic plan will not be successful unless it is actively implemented. This is a crucial time for all members to get involved, so I urge you to contact your Branch, Division or Group representatives to help ensure the success of the RACI for the next century and beyond.



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What to expect from big pharma in 2017

In the US last year, the Food and Drug Administration approved just 22 new therapeutic drugs, which is less than half the number approved in 2015. The cover story in January's *Chemical & Engineering News* explains why 2016 was such a lacklustre year for new medicines, and whether it was an anomaly or the start of a longer term pharmaceutical slow-down.

Lisa M. Jarvis, a senior correspondent for *C&EN*, reports that the dip in approvals was partly due to delays. Some pharmaceutical manufacturing plants weren't in compliance with current standards and needed to be brought up to the required standard. Also, the number of new cancer drugs, which often account for several drug approvals a year, suffered a cut. Only four drugs targeting cancer got the green light in 2016 whereas during the previous year, 14 did.

Ultimately, seven big pharma companies didn't get a single product to market in 2016. Forecasters expect numbers to turn around next year and return to the average of 30, including a boost in cancer drug approvals, but some industry watchers interpret last year's poor showing as a sign of uncertain times ahead.

American Chemical Society

STEM mentoring network appoints inaugural executive director

The Australian Academy of Technology and Engineering (ATSE) has appointed Dr Marguerite Evans-Galea as the inaugural Executive Director of the Academy's Industry Mentoring Network in STEM (IMNIS) program.

IMNIS is a mentoring program that links PhD students in science, technology, engineering and mathematics with individual industry-based mentors, who act as role models and provide advice on industry-based STEM careers. Evans-Galea will manage the program as it expands nationally, following successful pilots in Victoria and Western Australia.

Evans-Galea has degrees in science and music from the University of Queensland, and a PhD in molecular biology from the University of New South Wales. She has over 15 years' experience leading translational medical research programs in the US and Australia, and her work has been internationally recognised with numerous awards. Strongly committed to empowering early career researchers, Evans-Galea mentors students, postdoctoral fellows and faculty, and has developed graduate mentoring programs in the US. She was the founding Chair of the Early-Mid Career Researcher (EMCR) Forum with the Australian Academy of Science, and is currently a member of the Science in Australia Gender Equity (SAGE) Expert Advisory Group, Chair of the Australian Science and Innovation Forum, and Co-Founder of Women in STEM Australia.

Australian Academy of Technological Sciences and Engineering

2016 may serve as a reminder to sponsors that all of their manufacturing facilities must be in compliance with cGMP regulations if they wish to ensure approval of their application.

John Jenkins, then director of FDA's Office of New Drugs

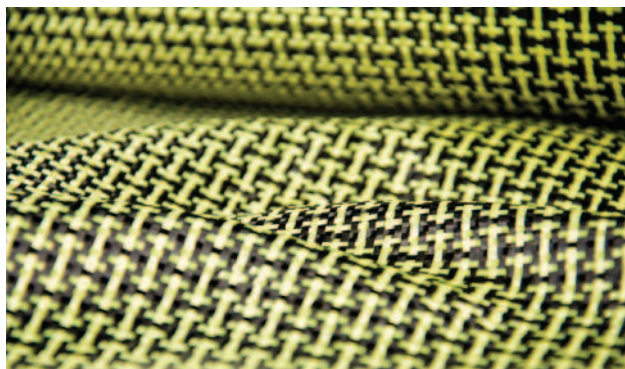


By connecting young researchers with industry leaders, IMNIS will foster a cultural shift, upskill and educate our future leaders in STEM and extend their professional networks in academia, industry and beyond. IMNIS will also expose young researchers to the suite of career opportunities that lie beyond academia.

Dr Marguerite Evans-Galea, Executive Director, Industry Mentoring Network in STEM



Chemists tie tightest-ever knot



Interwoven polymer strands have the potential to be more flexible than materials such as carbon fibre composite (shown).

iStockphoto/PragasitLalao

Scientists at the University of Manchester have produced the most tightly knotted physical structure ever known – a scientific achievement that has the potential to create a new generation of advanced materials.

The researchers, led by Professor David Leigh in Manchester's School of Chemistry, have developed a way of braiding multiple molecular strands, enabling tighter and more complex knots to be made than has previously been possible.

The breakthrough knot has eight crossings in a 192-atom closed loop – which is about 20 nanometres long.

Being able to make different types of molecular knots means that scientists should be able to probe how knotting affects strength and elasticity of materials, which will enable them to weave polymer strands to generate new types of materials.

Leigh said: 'Tying knots is a similar process to weaving so the techniques being developed to tie knots in molecules should also be applicable to the weaving of molecular strands.'

'For example, bulletproof vests and body armour are made of Kevlar, a plastic that consists of rigid molecular rods aligned in a parallel structure – however, interweaving polymer strands have the potential to create much tougher, lighter and more flexible materials in the same way that weaving threads does in our everyday world.'

'Some polymers, such as spider silk, can be twice as strong as steel so braiding polymer strands may lead to new generations of light, super-strong and flexible materials for fabrication and construction.'

Leigh explained that they 'tied' the molecular knot using a technique called 'self-assembly', in which molecular strands are woven around metal ions, forming crossing points in the right places just like in knitting – and the ends of the strands were then fused together by a chemical catalyst to close the loop and form the complete knot.

The research was published in *Science* (doi: 10.1126/science.aal1619)

University of Manchester

Report underlines the impact of risk on society's decisions

We live in a risky world. Risks from antibiotic resistance, environmental impacts and international security are hot issues in research, but delaying action until the science is settled isn't always feasible.

The Australian Academy of Science has released a think tank report discussing how risk and uncertainty affect the decisions we make as a society.

The report addresses specific risks from antibiotic resistance, environmental challenges, international security, and the challenges of making decisions when data is uncertain.

'Risks are part of life, and we need to learn how to make decisions when the data is uncertain,' said Professor Hugh Possingham, from the University of Queensland, who chaired the think tank steering committee.

'Some uncertainty is not worth resolving; it's better to act sooner than wait until you are absolutely certain. Australians, as big gamblers, already love to embrace that uncertainty.'

The report recommended changes to antibiotic prescription and usage, and proposed that antibiotic usage in foods be included on labels to inform and empower consumers.

The group also identified areas needing further study, such as the role of environmental pollution, including human and animal waste in the development of antimicrobial resistance.

The difficulty of adequately costing environmental impacts and factoring them into cost-benefit analyses when allocating resources for environmental projects was also discussed at the think tank.

The group flagged risks that unfold or change over long time periods as particularly difficult to grapple with.

They recommended that policy-makers and scientists jointly develop a set of guidelines for cost-benefit analysis, and that tools used by scientists for sequential decision-making could be simplified and adopted for policy-makers.

'More data is not always better,' said Dr Kirsty Kitto from Queensland University of Technology. 'But sometimes uncertainty is misinterpreted as a lack of evidence by decision-makers.'

The group found that even their own discussion of uncertainty was hampered by the differing language used between research fields. So they recommended the development of a common set of terminology to clarify communication between scientists and policy-makers.

Uncertainty plays a large role in the risks inherent in negotiating international security concerns. The think tank also covered and offered recommendations on a broad range of international security issues such as global migration flows, Australia's compliance with international legal obligations, environmental change and disruptive technologies.

The full report is available at www.science.org.au/think-tanks/risky-world.

Australian Academy of Science

How bacteria exploit a chink in the body's armour

Scientists have determined how a unique bacterial enzyme can blunt the body's key weapons in its fight against infection.

Researchers at the University of Illinois at Urbana-Champaign, US, and Newcastle University in the UK are investigating how infectious microbes can survive attacks by the body's immune system. By better understanding the bacteria's defences, new strategies can be developed to cure infections that are currently resistant to treatments, the researchers said.

The study, reported in *PLOS Pathogens* (doi: 10.1371/journal.ppat.1006125), focused on the bacterium *Staphylococcus aureus*, which is found on approximately half of the population. While it usually safely coexists with healthy individuals, *S. aureus* has the ability to infect nearly the entire body; in its most pathogenic form, the bacterium is the so-called 'superbug' methicillin-resistant *S. aureus*, or MRSA.

The human body uses a diverse array of weapons to fight off bacteria like *S. aureus*. 'Our immune system is very effective and prevents the majority of microbes we encounter from causing infections,' said University of Illinois microbiology professor Thomas Kehl-Fie, who led the study with Kevin Waldron, of Newcastle University. 'But pathogens such as *S. aureus* have developed ways to subvert the immune response.'

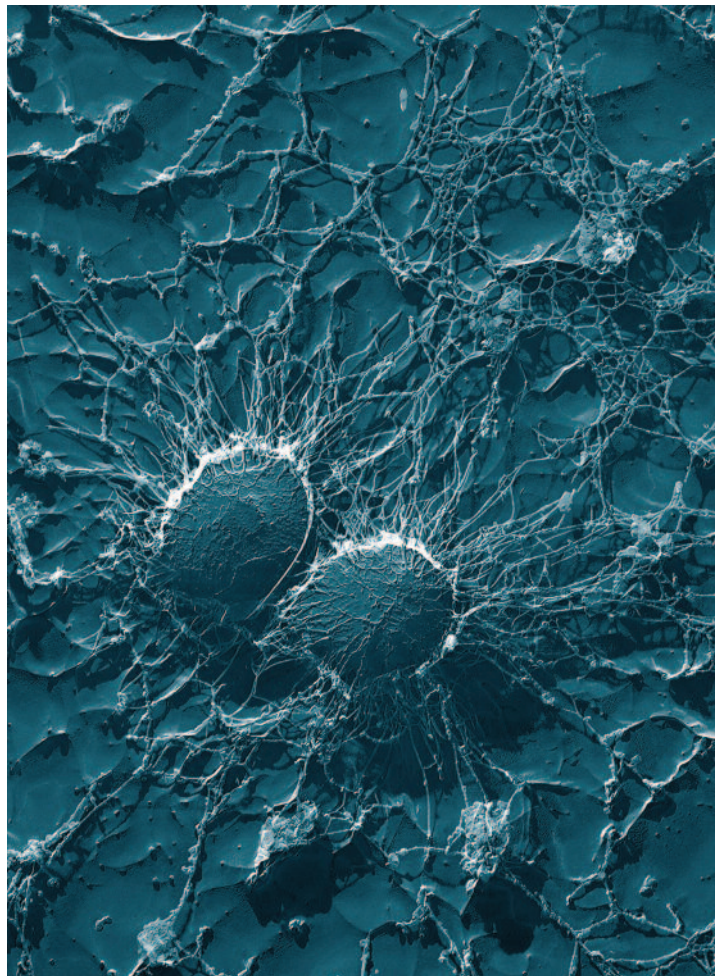
S. aureus can overcome one of the body's key defences, nutritional immunity, which prevents bacteria from obtaining critical nutrients. It starves *S. aureus* of manganese, which is needed by the bacterial enzyme superoxide dismutase, or SOD. This enzyme functions as a shield, minimising the damage from another weapon in the body's arsenal, the oxidative burst. Together, the two host weapons usually function as a one-two punch, with nutritional immunity weakening the bacteria's shields, enabling the oxidative burst to kill the bacterium.

S. aureus is particularly adept at causing devastating infections. Differing from other closely related species, *S. aureus* possesses two SOD enzymes. The team discovered that the second SOD enhances the ability of *S. aureus* to resist nutritional immunity and cause disease.

'This realisation was both exciting and perplexing, as both SODs were thought to utilise manganese and therefore should be inactivated by manganese starvation,' Kehl-Fie said.

The most prevalent family of SODs, to which both of the *S. aureus* enzymes belong, has long been thought to come in two varieties: those that are dependent on manganese for function and those that use iron.

In light of their findings, the team tested whether the second staphylococcal SOD was dependent on iron. To their surprise, they discovered that the enzyme was able to use either metal. While the existence of these cambialistic SODs (capable of using both iron and manganese) was proposed decades ago, the existence of this type of enzyme was largely dismissed as a quirk of chemistry, unimportant in real biological systems. The team's findings dispel this notion, demonstrating that cambialistic SODs critically contribute to infection.



***Staphylococcus aureus* is one of the causal agents of mastitis in dairy cows. These capsules contain the bacterial cells and protect them from the cows' immunological defences.** Agricultural Research Service/Wikimedia

The group found that, when starved of manganese by the body, *S. aureus* activated the cambialistic SOD with iron instead of manganese, ensuring its critical bacterial defensive barrier was maintained.

'The cambialistic SOD plays a key role in this bacterium's ability to evade the immune defence,' Waldron said. 'Importantly, we suspect similar enzymes may be present in other pathogenic bacteria. Therefore, it could be possible to target this system with drugs for future antibacterial therapies.'

The emergence and spread of antibiotic-resistant bacteria, such as MRSA, make such infections increasingly difficult, if not impossible, to treat.

This has prompted leading health organisations, such as the Centers for Disease Control and Prevention and the World Health Organization, to issue an urgent call for new approaches to combat the threat of antibiotic resistance.

University of Illinois at Urbana-Champaign

Breathing molecule identified: vital to treating respiratory conditions

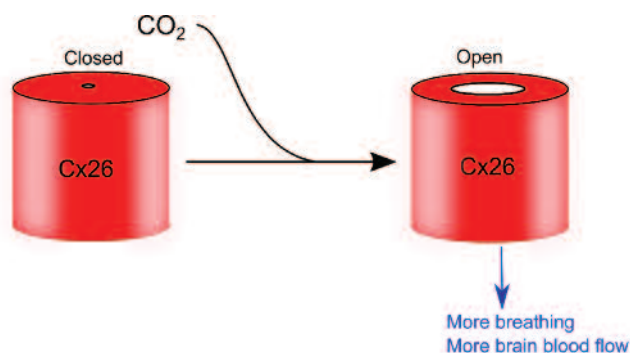
Respiratory conditions could be better targeted and treated, thanks to the identification of the vital molecule that regulates breathing.

Professor Nicholas Dale at the University of Warwick, UK, has identified Connexin26 (Cx26) as a key molecule that reacts to CO_2 in our bodies and activates breathing.

Cx26 molecules detect levels of CO_2 in the bloodstream and, when levels reach a certain point, the molecules tell our bodies to excrete the CO_2 and take in oxygen. Without this essential molecular function, harmful levels of CO_2 would remain in the bloodstream, making breathing difficult or impossible.

Mutations in Cx26 are directly connected to a number of serious conditions – ranging from congenital deafness, to respiratory conditions, and serious syndromes that affect skin, vision and hearing. As Cx26 is vital to breathing well, people carrying these mutations may be at risk of sleep apnoea.

Identifying these mutations and working out how to restore the molecule to its normal function could lead to effective, targeted, personalised treatments to mitigate these risks and improve quality of life.



Different animals have varying levels of sensitivity to CO_2 . Dale's group exploited this idea to see whether the properties of Cx26 matched the physiological requirements of birds, which fly at high altitude and can tolerate low levels of CO_2 ; humans and rats which are broadly similar at an intermediate level; and mole rats, which live exclusively underground and tolerate very high levels of CO_2 .

The researchers found that the CO_2 binding properties matched the sensitivities of these different animals. Evolutionary natural selection has thus modified the CO_2 -binding properties of Cx26 – showing that this molecule is a universally important sensor of CO_2 in warm-blooded animals.

The research is published in the *Proceedings of the Royal Society B* (doi: 10.1098/rspb.2016.2723).

University of Warwick

Physicists map the atomic structure of an alloy

Virtually all materials have defects on the atomic level. These imperfections – missing atoms, atoms of one type swapped for another, and misaligned atoms – can uniquely determine a material's properties and function. Now, University of California, Los Angeles scientists have mapped the coordinates of more than 23 000 individual atoms in an iron–platinum nanoparticle to reveal the material's defects.

The results demonstrate that the positions of tens of thousands of atoms can be precisely identified and then fed into quantum mechanics calculations to correlate imperfections and defects with material properties at the single-atom level. This research was published in the 2 February issue of *Nature*.

Professor Jianwei 'John' Miao and his team focused on an iron–platinum alloy, a very promising material for next-generation magnetic storage media and permanent magnet applications.

By taking multiple images of the iron–platinum nanoparticle with an advanced electron microscope and using powerful reconstruction algorithms, the researchers determined the precise three-dimensional arrangement of atoms in the nanoparticle.

The team identified and located more than 6500 iron and 16 600 platinum atoms and showed how the atoms are arranged in nine grains, each of which contains different ratios of iron and platinum atoms. Miao and his colleagues showed that atoms closer to the interior of the grains are more regularly arranged than those near the surfaces. Also, interfaces between grains, called grain boundaries, are more disordered.

The researchers then used the three-dimensional coordinates of the atoms as inputs into quantum mechanics calculations to determine the magnetic properties of the iron–platinum nanoparticle. They observed abrupt changes in magnetic properties at the grain boundaries.

In the future, as the researchers continue to determine the three-dimensional atomic coordinates of more materials, they plan to establish an online databank for the physical sciences, analogous to protein databanks for the biological and life sciences.

Miao and his team also look forward to applying their method called GENFIRE (GENeralized Fourier Iterative Reconstruction) to biological and medical applications.

UCLA



Future STEM leaders

It is estimated that by 2030, 40% of current Australian jobs probably won't exist as we know them and that the pathway to the careers of the future will mostly come from a STEM education.

Twenty-six Australian teenagers (pictured), selected as finalists in the BHP Billiton Science and Engineering Awards, have proven themselves to be STEM leaders of the future by producing work that has solved real-world problems with innovative inventions and ambitious scientific investigations.

A beach-side rip warning system, a laser system to keep cyclists safe on roads, and research into treatments for diabetes and antibiotic-resistant bacteria are just some of the projects that have been chosen for the finals of the 2017 BHP Billiton Science and Engineering Awards.

The winners of the 2017 BHP Billiton Science and Engineering Awards are Justin Mitchell (Vic., 1st Place Engineering Award), Jade Moxey (NSW, 1st Place Investigations Award), Amber Krackowska (SA, Innovation to Market Award), Hamish Gibson (WA, Teacher Award), Callum and Declan Predavec (NSW, 2nd Place Engineering Award), Amy Zhou (Qld, 2nd Place Investigations Award), Dylan Sanusi-Goh (Vic., 3rd Place Engineering Award) and Rebekah Kang (NSW, 3rd Place Investigations Award).


Selected finalists will represent Australia at the Intel International Science and Engineering Fair (Intel ISEF) in the US in May 2017.

A winner with a chemistry interest is Amy Zhou, of the Queensland Academy of Health Science. After a friend's father

died from a bacterial infection that failed to respond to antibiotics, Zhou decided to put her interest in molecular chemistry to work by finding a way to fight antibiotic resistance. The World Health Organization warns that antibiotic resistance is a major global health threat to the effective prevention and treatment of an ever-increasing range of infections caused by bacteria. Amy found that when the protein structure of fructose-6-phosphate aminotransferase is disrupted, it is more difficult for bacteria to mutate and there is a lower likelihood of the bacteria developing resistance.

The Awards, which have been running since 1981, reward young people who have undertaken practical research projects that demonstrate innovative approaches and thorough scientific or engineering procedures.

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news

Teabags as a climate change tool



Mangroves are carbon-storing coastal wetlands. CC BY-SA 3.0/Wikimedia

A group of scientists from Deakin University's Blue Carbon Lab has launched a project that will use Lipton teabags as a tool to measure how well global wetlands are storing carbon.

According to Dr Peter Macreadie, lab director and senior lecturer in Deakin's School of Life and Environmental Sciences, by monitoring how quickly the teabags decompose, scientists will be able to determine the carbon-sink capacity of wetlands.

'If the buried teabag is quickly munched up by microbes living within the wetlands, we know it's not an ideal spot, but if the teabag stays relatively intact it means the wetland is a nice stable environment perfect for storing carbon,' Macreadie said.

'Our inland wetlands, coastal marshes, mangroves and seagrass meadows are some of our most effective carbon sinks, removing atmospheric CO₂ and locking it away in the ground more than twice as effectively as the world's rainforests.

Dr Macreadie and his team hope to engage climate change researchers, NGOs, citizen scientists and environmental groups across the world to bury a Lipton teabag at their local wetlands.

'Certain teabags have a uniform decomposition rate within wetlands, allowing scientists to easily study variability in rates of carbon breakdown – a critical determinant of the carbon-sink capacity of an ecosystem,' Macreadie said.

'Right now we have different countries using a variety of ways to measure the carbon storage capabilities of their wetlands and coming up with results that are difficult to compare.

The project is an extension of a global initiative that started on land – called TeaComposition – which has run successfully in all continents except Antarctica.

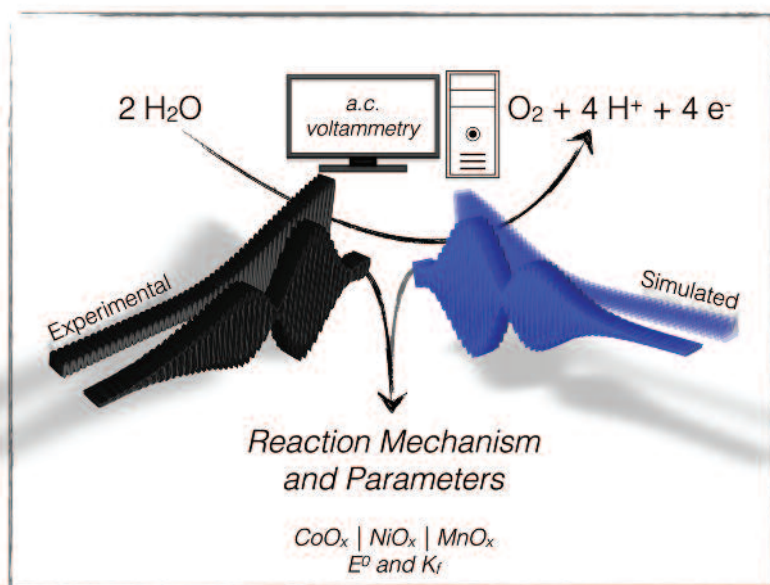
Once the data is gathered, the scientists hope that they will be able to confidently compare global CO₂ emissions from wetlands around the world.

For more information, visit bluecarbonlab.org/teacomposition-h2o.

Deakin University

This month's Research column is dedicated to the memory of Professor Leone Spicca FRACI CChem, who passed away on 18 December 2016 (see obituary page 31), and who was a regular contributor to this column. One of Professor Spiccia's recent articles features in this edition.

New insight into water oxidation electrocatalysis



Conversion of solar energy into fuels depends on endothermic redox reactions. Fuel formation is a reductive process, and so an electron source of a suitable scale is required. The ideal reactant is water, with O_2 released as the by-product, making water oxidation a fundamental

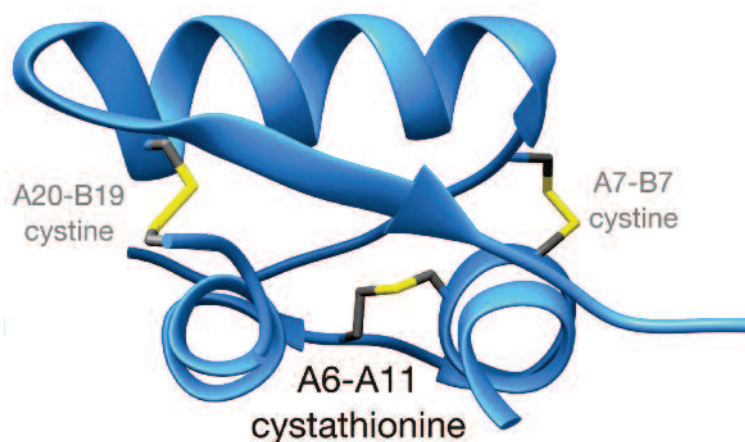
step in solar fuel synthesis. Researchers in the ARC Centre of Excellence for Electromaterials Science at Monash University have gained important new insight into the mechanism of electrocatalytic water oxidation using large-amplitude Fourier-transformed

alternating-current voltammetry (Bonke S.A., Bond A.M., Spiccia L., Simonov A.N. *J. Am. Chem. Soc.* 2016, **138**, 16 095–104). In contrast to conventional DC voltammetry, the AC technique filters out the water oxidation current and allows redox transformations of metal oxide electrocatalysts directly involved in the catalytic cycle to be resolved. The team also developed a general reaction model that couples these surface-confined redox transformations to a catalytic reaction with a substrate in solution. The model emphasises the role of the Brønsted base in proton abstraction from the electrode surface, which is critical for efficient catalysis. By comparing experimental data and model simulations, the researchers were able to quantify thermodynamic (reversible potentials) and kinetic (electron transfer and catalytic rate constants) parameters for this highly technologically important process for the first time.

Insulin analogue can take the heat

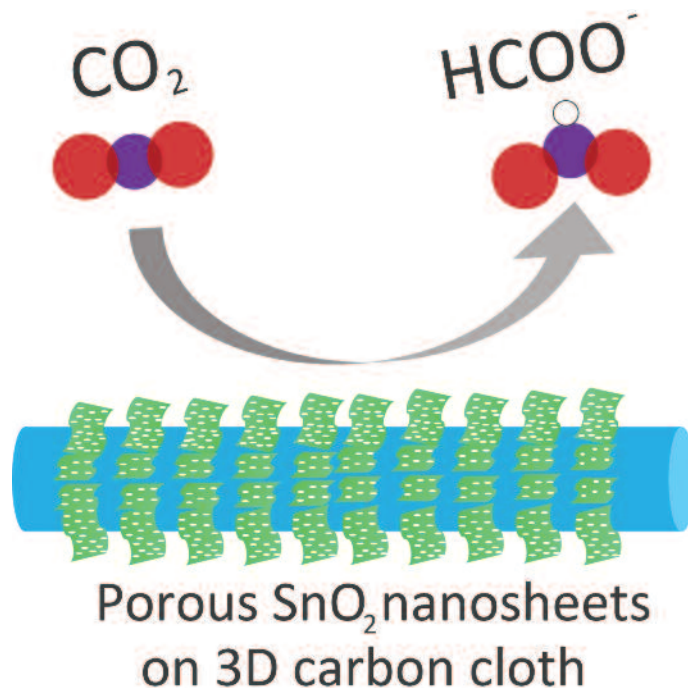
Despite recent advances in the treatment of type 1 diabetes mellitus, storage of insulin therapeutics at 4°C is still necessary to minimise degradation and to preserve biological activity. This can be problematic in poor tropical regions where reliable refrigeration is often not ubiquitous. To address this issue, a team of medicinal chemists led by Dr Mohammed Akhter Hossain of the Insulin Peptides Laboratory at the Florey Institute of Neuroscience and Mental Health has developed a novel insulin molecule that possesses enhanced thermal stability (Karas J.A., Patil N.A., Tailhades J., Sani M.A., Scanlon D.B., Forbes B.E., Gardiner J., Separovic F., Wade J.D., Hossain M.A. *Angew. Chem. Int. Ed.* 2016, **55**, 14 743–47). Dr John Karas, the lead author of the paper, replaced A6-A11 cystine in insulin with a stable isostere, cystathionine. This modified analogue was synthesised efficiently and found to be structurally similar to the native hormone. Importantly, both the native binding affinity for the insulin receptor and stability in human serum were maintained. This thermostable insulin has potential as a next-generation therapeutic for type 1 diabetes mellitus.

thermostable human insulin



Renewable liquid fuels from CO₂ on a 3D electrode

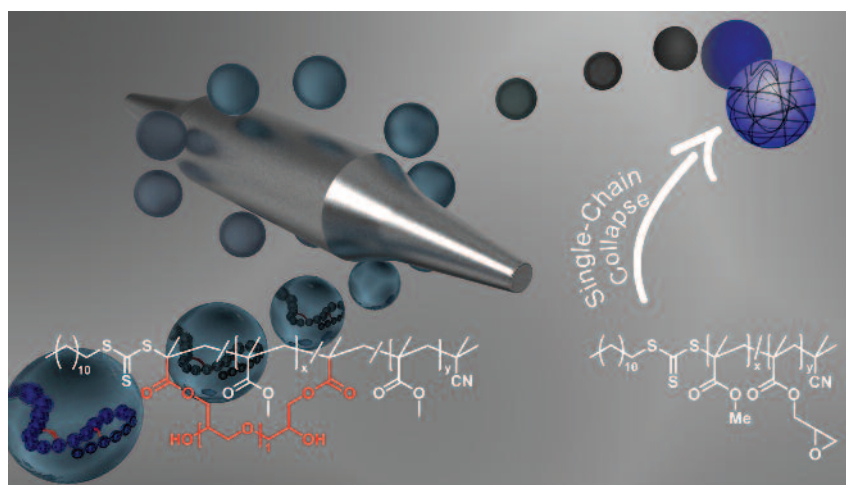
Producing liquid fuels from CO₂, one of our largest sources of carbon, is an attractive way to achieve a carbon-neutral energy cycle. Electrochemical reduction of CO₂ (ERC) is potentially a 'green' method of producing fuels on a large scale, especially when coupled with electricity from renewable energy sources such as solar or wind. Unfortunately, even state-of-the-art ERC catalysts show insufficient activity to allow an economically sustainable production cycle. Most significantly, the current densities allowed by catalysts available today are usually low (below 10 mA cm⁻²). Thus, in order to efficiently implement ERC in an 'artificial photosynthesis' process, it is imperative to boost the activity of the electrode material. To address this challenge, the groups of Dr Jie Zhang and Professor Doug MacFarlane in the ARC Centre of Excellence for Electromaterials Science at Monash University have recently developed a 3D electrode composed of electroactive porous SnO₂ nanosheets grown on conductive carbon cloth (Li F., Chen L., Knowles G.P., MacFarlane D.R., Zhang J. *Angew. Chem. Int. Ed.*, 2017, **56**, 505–9). Thanks to the porous and hierarchical features, this 3D electrode exhibits an unprecedented current density (~50 mA cm⁻²) in the electroreduction of CO₂ to formate, which can be used to generate electricity directly from fuel cells. This study opens up exciting new avenues to design other forms of active 3D electrodes for practical devices.



Following single-chain folding

The team of Professor Christopher Barner-Kowollik at the Queensland University of Technology and the Karlsruhe Institute of Technology has recently pioneered a novel and advanced technology for imaging the folding of linear polymer chains into single-chain nanoparticles (SCNPs) via high-resolution electrospray ionisation mass spectrometry (ESI MS) (Steinkoenig J., Rothfuss H., Lauer A., Tuten B.T., Barner-Kowollik C. *J. Am. Chem. Soc.* 2017, **139**, 51–4).

As biomolecule mimetics, SCNPs find applications in drug delivery, self-reporting nano-containers and catalysis. Standard techniques for characterising SCNPs, such as dynamic light scattering, diffusion-oriented spectroscopy or small-angle X-ray scattering, provide information about nanoparticle morphology. But high-resolution ESI MS goes a step further by

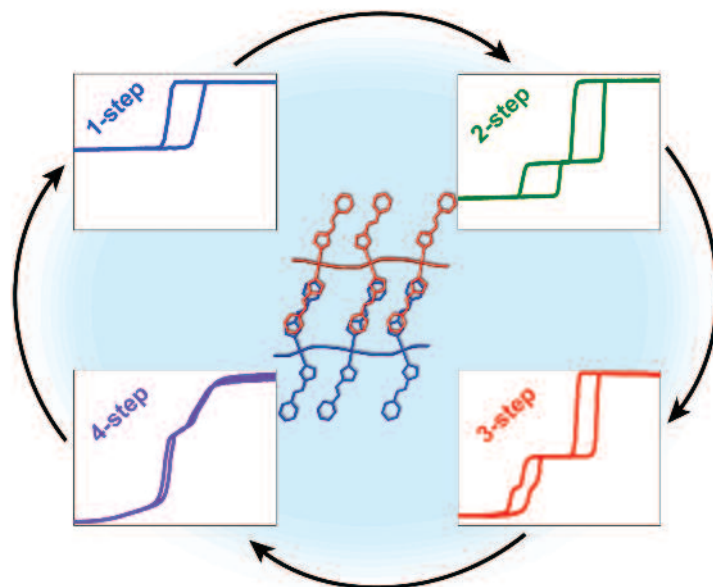


allowing single chains and the transformations they undergo while forming the nanoparticle to be imaged. The team showed that the characteristic mass changes in the studied system allow two mechanistic modes of chain collapse – propagation and bimolecular coupling of the intra-chain crosslinking units – to be differentiated

unambiguously. Confirmed by isotopic pattern simulations, bimolecular coupling (the entropically favoured scenario) is the dominant pathway of single-chain collapse. The novel characterisation platform can be employed for all SCNP systems that ionise well and provides critical molecular information regarding the folding process.

Taking the next step

Molecule-based switching materials are actively pursued in data storage, sensory and optical device technologies. Exemplifying such materials are spin crossover (SCO) complexes, which can switch between high-spin (HS) and low-spin (LS) states with external stimulus (e.g. temperature, pressure, light). Mechanically, the SCO process is mediated by elastic interactions, which when strong can result in abrupt and hysteretic transitions (i.e. bistability). When such interactions are frustrated, such as through the presence of antagonistic lattice interactions, the reversible HS to LS transition can occur via multiple steps that proceed through various stable fractional spin states (HS^nLS^{1-n}). Aside from fundamental interest, multi-step switching materials are desirable because they lead to higher order data storage possibilities, such as ternary and quaternary processing. Researchers at the University of Sydney have discovered a rare example of a four-step SCO process and confirmed that elastic frustration underlies the spin-state cascade (Sciortino N.F., Zenere K.A., Corrigan M.E., Halder G.J., Chastanet G., Létard J.-F., Kepert C.J., Neville S.M. *Chem. Sci.* 2017, **8**, 701–7). Alongside this, the same group has shown that multi-step switching can be manipulated by more



subtle means than predicted, showing that weak host-guest interactions can tune one-, two- and three-step SCO characters in a single porous framework material (Murphy M.J., Zenere K.A., Ragon F., Southon P.D., Kepert C.J., Neville S.M. *J. Am. Chem. Soc.* 2017, **139**, 1330–5). These works open new avenues for strategically producing higher-order multi-step spin transitions through structural design that exploits antagonistic interactions and host-guest chemistry.

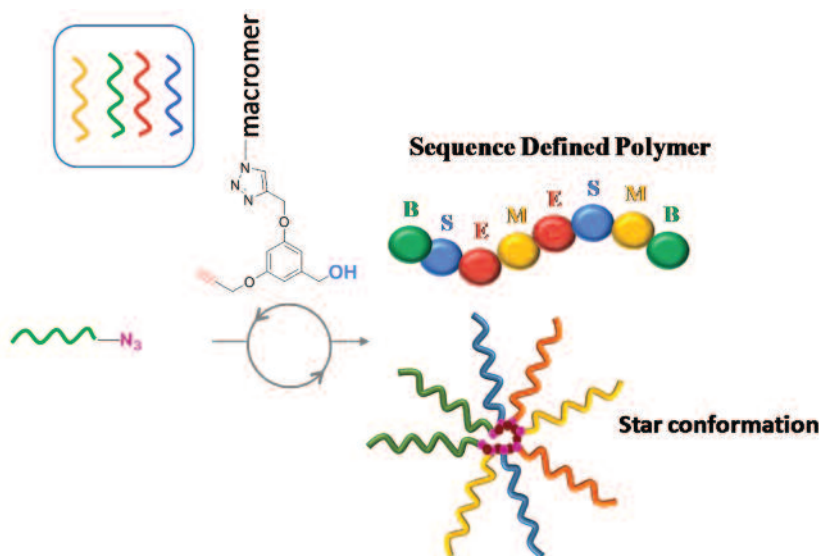
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Sequence-controlled polymers with complex architectures

The quest for polymers with new and predictable solution and bulk properties has driven the creation of complex polymer architectures. Incorporating sequence control into these architectures through the judicious choice of monomers or macromers could produce advanced polymer materials with unique properties and functions commonly found in biological proteins. A team at the University of Queensland led by Professor Michael Monteiro has developed a general, direct and one-pot synthetic strategy to build polymers from the sequential addition of low-molecular-weight macromers with diverse chemical composition (Amir F., Jia Z., Monteiro M.J. *J. Am. Chem. Soc.* 2016, **138**, 16 600–3). The chemistry is highly efficient, allowing compositionally different macromers to be coupled together in close proximity. The synthesis employs the near-quantitative azidation

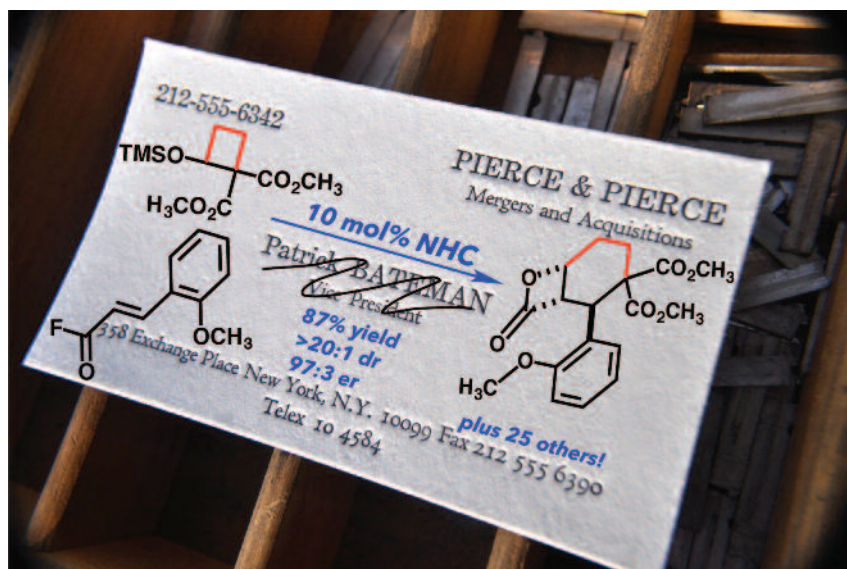


of benzyl alcohol via the DPPA/DBU method. The next polymer can then be coupled using the CuAAC 'click' reaction. Four different low-molecular-weight building blocks were coupled in sequence to produce spherical polymer miktoarm

stars of 50 000 molecular weight with a narrow molecular weight distribution. Interestingly, the coil diameter depended on the sequence of macromer addition, opening a way to design materials with advanced and predictable properties.

Hip to be square

Release of ring strain is a potent driving force for novel chemical transformations. This is clearly demonstrated by the numerous reactions enabled by the ring-opening of donor–acceptor cyclopropanes. Remarkably, despite similar strain energy, related donor–acceptor cyclobutanes have received significantly less attention. This is most striking in the context of enantioselective catalysis, with only a single example of Lewis acid catalysis reported. Recently, studies by Alison Levens, Adam Ametovski and David Lupton at Monash University have led to the discovery of the first organocatalytic enantioselective reaction of donor–acceptor cyclobutanes (Levens A., Ametovski A., Lupton D.W. *Angew. Chem. Int. Ed.* 2016, **55**, 16 136–40). The transformation provides 26 examples of



densely functionalised β -lactone cyclohexanes with excellent yields (75–100%) and stereochemical integrity (all >20:1 diastereometric ratio, most >97:3 enantiometric ratio). In addition

to rapidly producing molecular complexity (three steps from commercial materials), the reaction is scalable, providing a platform to enable studies in total synthesis and medicinal chemistry.

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

Seventh Heron Island Conference

This month's issue highlights the 7th Heron Island Conference on Reactive Intermediates and Unusual Molecules – Synthesis and Mechanism, which was held 9–15 July 2016 at the Heron Island Resort on the Great Barrier Reef.

The practice of leaving part of the day available for island pursuits makes attendance at the meeting very enjoyable. However, the science is what the meeting is all about and having a reaction named after it, the conference is testament to that! Stephen Glover, University of New England, has written an account of the reaction that he has studied for over 20 years, HETEROATOM REARRANGEMENTS ON NITROGEN. This reaction describes an unusual rearrangement of bisheteroatom-substituted amides $RCON(X)(Y)$ where the more electron-deficient group, X, migrates from nitrogen to the carbonyl carbon, giving acyl, $RC(O)X$, and Y-stabilised nitrenes.

The 'Unusual Molecules' tag opened attendance up to a broader church of participants. John Gladysz and his team from Texas A&M University, US, showed how macrocycles can be prepared by the Williamson ether synthesis and appending a coordinating functionality, such as phenanthroline, results in the formation of copper complexes with CuI.

Michelle Coote and Ganna Gryn'ova, ANU, use accurate quantum-chemical calculations to analyse the effects of charges on the kinetics and thermodynamics of radical reactions, with specific attention given to the origin and directionality of the effects.

Goetz Bucher, University of Glasgow, uses calculations to investigate the intramolecular interaction of ketone triplet excited states with nucleophilic substituents by studying the electronic properties of phenalene and a range of functionalised phenalenes. The presence of nucleophilic substituents neighbouring a ketone functional group switches the character of the lowest triplet excited states from (π, π^*) or (n, π^*) to (σ^*, π^*) .

Philip Chan, Monash University, described the synthesis of a versatile building block in organic synthesis, aziridines. These are prepared from reaction of 2-alkyl-substituted-1,3-dicarbonyl compounds and 2-acyl-substituted-1,4-dicarbonyl compounds with arylsulfonyliminoiodinanes ($PhI=NSO_2Ar$) under base-mediated conditions. The reaction mechanism involves the formal oxidation of the substrate followed by the key step of aziridination of the intermediate by the hypervalent iodine(III) reagent.

Rainer Streubel's team, Rheinische Friedrich-Wilhelms-Universität Bonn, Germany, described the acid-induced ring-expansion of a tungsten oxaphosphorane complex with an electron-withdrawing C-substituent. They use Brønsted acids to give stereoselectively pure 1,3,4-dioxaphospholane complexes.

The meeting has an excellent international reputation, which allows for the building of on-going relationships between Australian researchers and researchers from Europe, North America and the Asia-Pacific region.

George Koutsantonis FRACI CChem and John D. Wade FRACI CChem, Co-Editors-in-Chief, *Australian Journal of Chemistry*

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Should you wish to know more about the program or to determine if your company may qualify, please contact:



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Looking back Chemistry in 1917

BY **IAN D. RAE**

A century ago, amongst military conflict and political change, chemistry in Australia and around the world was making its mark.

Glimpses of chemistry in Australia

In 1917, Australia was still at war. The conflict that major protagonists had expected to be over by Christmas 1914 was dragging on.

Prime Minister W.M. (Billy) Hughes, re-elected in May as the head of the new coalition Nationalist Party, was preparing a second conscription referendum. In December, it was defeated. Life went on, however, and the Trans-Continental Railway linking Melbourne and Fremantle was finally completed.

To all this we can add the formation of the Australian Chemical Institute as perhaps the greatest chemical event of the year. At that time, many Australian chemists were in Britain, toiling in the

munitions industry, and perhaps some of their output was included in the 454 tonnes of ammonal (a combination of ammonium nitrate and aluminium powder) that was exploded under German lines at Messines Ridge in June.

Import replacement in Australia had begun with the establishment of a wood distillation plant near Melbourne, where methanol and acetic acid were produced from *Eucalyptus regnans*. Acetone, produced by dry distillation of calcium acetate, was then used in the production of cordite, a combination of nitroglycerine and nitrocellulose. Shmith and Nicholas, having worked out the process for the manufacture of acetylsalicylic acid, were marketing Aspro as a replacement for Bayer's Aspirin.

The Commonwealth Advisory Council on Science and Industry (a forerunner of CSIR) had considered the need for the chemical industry to produce other chemicals formerly imported from enemy countries, with emphasis on potash for use in fertilisers and on industrial alcohol. Rain-spoiled wheat from Victoria and South Australia was suggested as a source of alcohol, and the Society of Chemical Industry of Victoria heard a lecture about alcohol as a future substitute fuel.

It could not have been evident at the time, but major contributions to chemistry were to be made by three Australians born in 1917, all of whom later graduated from the University of Sydney. John Cornforth (1917–2013), an organic chemist, completed his doctorate at Oxford in 1941 and pursued his career in Britain. In 1977, he shared the Nobel Prize with Vladimir Prelog for their studies of the stereochemistry of enzyme actions. Ronald Nyholm (1917–71), an inorganic chemist, already had substantial research experience before he went to University College London (UCL) for PhD studies. After a couple of years at the University of New South Wales, he returned to UCL. Ernest Ritchie (1917–76) remained at the University of Sydney where he earned the DSc for his research on Australian plant products

Possibly Australia's first school chemistry book was published in 1917. It was *Australasian text book of chemistry*. Part 1, written by W.R. Jamieson, the senior chemistry master at Scotch College, Melbourne. Known to his pupils as 'Tort' (for 'retort'), Jamieson wrote that his book 'covers a two-years' course for boys (and girls, too, for that matter) from the age of 14 to that of 16'.

Possibly Australia's first school chemistry book was published in 1917.

New York Times (via ProQuest)

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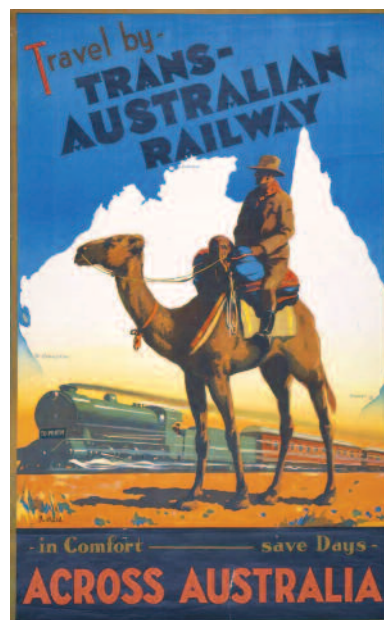
The trade-mark "Aspirin" (Reg. U.S. Pat. Office) is a guarantee that the mononuclear ester of salicylic acid in these tablets is of the reliable Bayer manufacture.

One of the first advertisements for Bayer Aspirin aimed at American consumers, published in February 1917, just before the US patent for aspirin was to expire. Following the patent expiry, Australian company Nicholas Pty Ltd built Aspro into a global brand, competing successfully with Bayer after German pharmaceuticals became available again after the war.

Glimpses of the year's research

For research in chemistry, I turned to the *Annual Reports on the Progress of Chemistry* published by the Chemical Society of London. This series began in 1904 with the aim of summarising and commenting on work published during the calendar year. The things that caught my eye were mostly those that were to become icons of chemistry during the next century.

The 1917 reviews included reports of shortages of material such as glycerol (no doubt for the manufacture of glyceryl trinitrate aka nitroglycerine), platinum (leading to



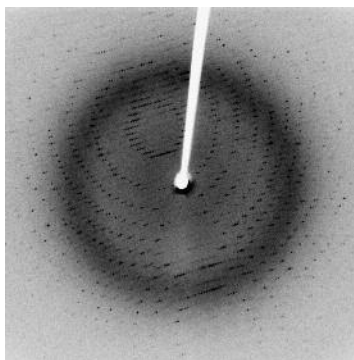
The Trans-Continental Railway was five years in the making. This advertising poster was circulated in the 1930s.

Copyright the James Northfield Art Heritage Trust

the use of gold and palladium in chemical apparatus) and microbalances of European make. Horse chestnuts and acorns were reportedly being used for food in Germany. Although the *Zeitschrift für physikalische Chemie* had ceased publication because suitable paper was unavailable, other journals were received from Germany and the publications were referenced as often as those from Britain and America.

A good deal of space in the General and Physical Chemistry section was devoted to X-ray crystallography and there was a Crystallography and Mineralogy section as well. The highlight was the introduction by P. Debye and P. Scherrer of a method for recording data for crystals of 'microscopic or submicroscopic dimensions'. The crystalline powder was placed on the axis of the cylindrically arranged film and irradiated with X-rays. Debye and Scherrer used this technique to study graphite and amorphous carbon and to show that they have the same (trigonal) structure. I remember using their method, half a century later, in a third-year experiment in which the X-ray pattern was used to show that a spinel had been formed from two oxides that I had sintered together. A little petroleum jelly was used to stick the powdered product to a glass fibre that was mounted in the X-ray beam.

At about this time, the Russian crystallographer Evgraf Stepanovich Fedorov (1853–1919) was publishing criticism of the Braggs' work, but inability to read Russian meant that the reviewer, H.M. Dawson, was unable to assess Fedorov's contentions. The Braggs had been awarded the Nobel Prize in Physics for 1915 but X-ray crystallography was still very new. A mini-(literally)-highlight was the report of its use by a former student of Fedorov, T.V. Barker at the University of Oxford, in his examination of a 'minute crystal' of 'intestinal' origin that was provided by a Belgian medical researcher. Consulting a table of unit



An X-ray diffraction pattern of a crystallised enzyme. The pattern of spots (reflections) and the relative strength of each spot (intensities) can be used to determine the structure of the enzyme. Jeff Dahl/CC BY-SA 3.0

cell dimensions published by Fedorov, Barker thought the 229-milligram crystal was either potassium niobate, methyl di-isopropyl sulfine hexachloroplatinate or phenyl salicylate (Salol), and the last of these was confirmed by measuring the melting point (43°C) of a 'tiny splinter' (<0.1 milligram) of the crystal. Why was it in the intestine? Well, it's not very soluble in water and was in use as an analgesic and anti-rheumatic, but Barker didn't say.

The X-ray boom had re-opened

X-ray methods were showing atomic lattices but the molecule concept was hard to put aside and one researcher quipped that rock salt could just as easily be regarded as consisting of $[\text{NaCl}_6]$ and $[\text{ClNa}_6]$...

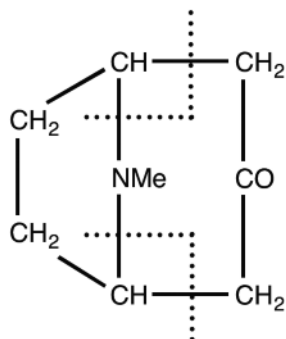
older questions of structure, such as whether there were molecules in crystalline inorganic solids. X-ray methods were showing atomic lattices but the molecule concept was hard to put aside and one researcher quipped that rock salt could just as easily be regarded as consisting of $[\text{NaCl}_6]$ and $[\text{ClNa}_6]$, but the reviewer observed that 'other practicing X-ray analysts leave such questions severely alone'.

The reviewer of *Inorganic Chemistry*, E.C.C. Bayly, felt that he was going beyond chemistry in covering the physical phenomenon of the phosphorescence of zinc sulfide, which was widely thought to be due to the presence of various impurities. A Glasgow research group led by A.W. Stewart (before he started writing detective stories as 'J.J. Connington') had reported that pure zinc sulfide does phosphoresce but only if it has been heated for long periods at 650–900°C to induce the formation of a semicrystalline state. Other researchers had demonstrated that the phenomenon could only be observed in this and other solids when impurities like manganese were present, and by mentioning their work, I think Bayly was begging the question 'Was Stewart's material really pure?'.

In the Organic Chemistry section, the synthesis by German chemists of lead tetra-alkyls containing four primary alkyl groups caught my eye. Starting with tetramethyl lead, a methyl group was removed by reaction with halogen at low temperature, and this substance was treated with a Grignard reagent to attach a new alkyl group. Two more halogenations, each removing a methyl group, and successive use of other Grignards, gave methylethyl-*n*-propyl-*n*-butyl lead.

There was, of course, a fair bit of natural product chemistry. From an aqueous extract of the fruit of the 'avocado pear' (*Persea gratissima*), American researchers isolated a seven-carbon sugar, a mannoketoheptose. Its reduction

product, a heptahydroxy alcohol, had been isolated from the same source by Emil Fischer in 1890. My award for the best paper of 1917 goes to Robert Robinson, who published his biomimetic synthesis of the alkaloid tropinone, and generalised the concept of phytochemical syntheses by suggesting how a series of simple reactions could effect the syntheses of a range of alkaloids. 'Without exaggeration', the reviewers said, 'it may be said that this paper marks an epoch in the consideration of alkaloid syntheses'. Robinson had only recently returned to England to take up the chair in Liverpool after three years in Sydney as foundation professor of organic chemistry there.



Structure of the alkaloid tropinone, synthesised by Robert Robinson. 'By imaginary hydrolysis at the points indicated by the dotted lines', said Robinson in his paper, 'the substance may be resolved into succinaldehyde, methylamine, and acetone, and this observation suggested a line of attack of the problem which has resulted in a direct synthesis'.

Reviewing *Analytical Chemistry*, C. Ainsworth Mitchell wrote that 'the influence of the war on chemistry in general is reflected in the utilitarian character of many of the recent contributions to analytical chemistry', dealing with 'industrial by-products or substances to take the place of those no longer available'. For example, with the best micro-analytical balances unobtainable, an ordinary balance had to be used and the quantity of substance necessary for analysis had to be increased to 11–22 milligrams. A tube packed with soda-lime was used

in place of the potash absorption bulb for capture of carbon dioxide.

In the section on Agricultural Chemistry and Vegetable Physiology, E.J. Russell reported that 'enormous quantities of ammonia and of nitric acid are now being synthesized on the Continent' but went on to write about British work with calcium cyanamide. He did refer to a publication in the *Journal of the Society of Chemical Industry* in which the role of Haber was made explicit. I revert to Australia for a minute: the professor of chemistry at the University of Adelaide, Edward Rennie, in his Commemoration Address in December, described the development of chemistry in connection with the war, and referred coyly to 'a German chemist' who had mastered the art of making ammonia from atmospheric nitrogen. Like so many commentators before him, Rennie deplored the lack of support for science in Britain. A reporter for the *Advertiser* paraphrased him thus: while other countries were treating science as a sort of hobby, Germany was exploiting it for purposes, not merely with industry, alas, but of war'. Rennie went on to describe German chemistry as it applied to munitions, food, poisonous gases, manures, dyes and drugs. Was he a little bit envious of German progress?

Some work of the Australian biochemist Thorburn Brailsford Robertson (1884–1930) was mentioned in the section on Physiological Chemistry compiled by Frederick Gowland Hopkins. Robertson completed his BSc at the University of Adelaide and PhD at the University of California where he was appointed full professor in 1917. After a couple of years in Toronto, he returned to Adelaide but then in 1927 was appointed by CSIR to form their Division of Animal Nutrition. In 1917, he reported the isolation from the pituitary gland of a substance he called tethelin that promoted growth and healing. The molecule was said to

contain phosphorus and nitrogen atoms in the ratio 4:1, yielded *i*-inositol on hydrolysis, and gave a colour test for an imidazole group. Despite later investigations by Australian biochemists, its nature remains a mystery, although there has been extensive research on growth factors.

The 1917 prize for whimsy goes to B. Bloch who identified a black pigment formed by oxidation of 3,4-dihydroxyphenylalanine, to which he gave the name 'dopa'. It wasn't dopey at all, and despite Gowland's deprecation of it as an 'uneuphonious portmanteau name' that could lead to 'dopaoydase' for the enzyme, and 'dopamelanin' for the black pigment, the shorthand 'dopa' is widely used today for the amino acid.

But no Nobel

Given all the wonderful chemistry of the previous decade, I was surprised to find that the Nobel Prize in Chemistry was not awarded in 1917 (it wasn't in 1916, either). Among the names of the 11 unsuccessful nominees in 1917 were some recognisable ones like those of Walther Nernst and Fritz Pregl (Nobel laureates in 1920 and 1923, respectively) and Theodor Curtius, who never got a gong. It's possible that the selectors were wary of awarding the Prize to a German chemist but there were worthy nominees, I think, from other countries. Fritz Haber wrote later that 'I have no doubt that the political situation makes it impossible for a German nominated by Germans to be considered in Stockholm' but nonetheless, he was awarded the Nobel Prize in 1918. Not for gas warfare, of course, but for the ammonia synthesis, for which he was nominated by German engineer Ludwig Prandtl.

Ian D. Rae FRACI CChem is a veteran columnist, having begun his Letters in 1984. In addition to his regular Letters from Melbourne, Ian publishes longer articles about the history of chemistry and he is editor, together with Dr Sara Maroske, of the Australian Academy of Science journal *Historical Records of Australian Science*.



Drug detection *on the road*

BY **DAVE SAMMUT**

Despite numerous studies, our standards of evidence for drugs in relation to driver impairment still fall behind those for alcohol and fatigue.

Road safety is a significant issue worldwide. In Australia, we have been slowly reducing our road fatality statistics since the 1960s, but over recent years the pace of improvement has decreased. While education and enforcement have been relatively successful in changing behaviours in relation to alcohol and fatigue, the issue of the effect of drug impairment on driving has proved substantially more complex.

A problem of substance

NSW Government data indicates that from 2010 to 2013, alcohol (17%), fatigue (17%) and illicit drugs (13%) were all contributing factors in analysed road fatalities (bit.ly/2iSqSVa). Internationally, certain classes of licit drugs have also been identified as contributing to crashes, and evidence is growing that the risk of a crash increases significantly when mixing drugs and/or alcohol.

amphetamines, methamphetamines, opiates, cocaine and methadone) and licit drugs (such as benzodiazepines) have all been found to contribute to driver impairment, singly and, most particularly, in combination.

Drug detection

The detection of alcohol is relatively easy. Ethanol is a simple molecule, soluble in both aqueous and organic systems, and is volatile. It transfers easily from the blood to expired air, and is detectable in primary form rather than as metabolites.

Drug detection is significantly more complex. Most drugs do not transfer to expired air, requiring the analysis of fluid samples – blood, urine or oral fluid. Drugs are comparatively complex molecules, with multiple forms across multiple classes, and with a considerable spectrum of behaviour both between and within individuals over time.

The collection of blood or urine is impractical for random roadside screening, leaving only oral fluid, which is itself a complex combination of saliva, cells, blood and even food debris. It varies in pH between acid and alkaline (generally 6.0–7.9), viscosity and volume, and can vary with time of day, age of person, and other factors such as drug interactions. Several classes of drugs inhibit saliva production, making sampling more difficult, and samples can also be affected by extraneous factors. Inhaled cannabis smoke can transfer the active ingredient, tetrahydrocannabinol, directly to saliva.

So it is little wonder that it has taken nearly three decades of development to produce field screening methods that are practical, reliable and economic. In 2004, Victoria was the first jurisdiction worldwide to introduce mobile drug testing (MDT). Most other Australian states have since followed.

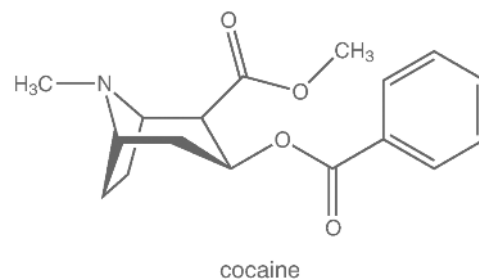
MDT methods use an immunochromatographic process. A sample (typically 10–1000 μL) is

collected on an absorbent collection pad, and transferred via capillary action or lateral diffusion. A buffer containing antibodies is used, where those antibodies are designed to be specific for the shape of the target molecule and/or structurally related class of molecules. An opiate immunoassay, for example, will detect morphine, codeine, heroin and related compounds. The methods indicate concentration, with different test manufacturers citing various accuracies.

If drugs are absent (or below detection limits), the unbound antibodies travel down the strip and bind to immobilised lines of the drug in the test region. If drugs are detected, the already-bound antibodies travel down the strip and pass by the immobilised lines. In the case of the instrument used in NSW, the test strip is then measured in a portable instrument for greater reproducibility and data storage.

These methods test directly for the target drug/drug class, as compared to other assay methods (most commonly LCMS on a blood and/or urine sample), which test for both the drug and the metabolites. Hence, the immunochromatographic approach gives less information about the timing of the drug use.

For drugs to pass from the bloodstream to saliva, the molecules must be lipid soluble, non-ionised and unbound to proteins. The pH of the saliva can significantly affect the drug transfer. An example from the road safety study in Ireland showed that the saliva to plasma ratio for cocaine varies from 273 to 0.44 between pH 5



A study by the Medical Bureau of Road Safety in Ireland found that in 2011 more than 75% of blood and urine samples taken from drivers suspected of intoxication contained at least one drug. Cannabis (>52%) and benzodiazepines (>40%) were the most common, but cocaine and opiates (including morphine, heroin and/or codeine) were each also encountered in more than 10% of samples (bit.ly/2jmJLvu). Nearly 50% of samples contained at least two drugs, and 9% contained four or more.

Illicit drugs (cannabis,



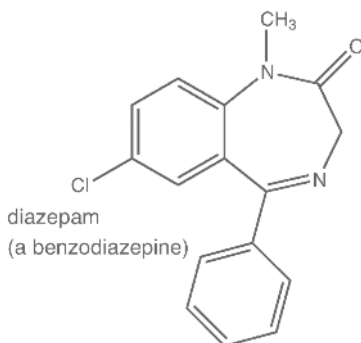
A multi-drug test strip.

and 7.8. Conversely, the ratios for benzodiazepines and cannabis are generally low.

This pH and volume of saliva varies with multiple factors. It has been observed that the sampling devices used in MDT can induce salivation, but the higher flow rate causes the pH to rise. Conversely, cannabis and ecstasy can reduce salivation, making it difficult to obtain sufficient sample from drug-affected drivers.

The MDT methods accommodate much of these variations.

The various test manufacturers then apply different threshold limits to alert the user to the presence or absence of the target drugs. The aim is to maximise sensitivity (the limit of detection, and ability to return a positive result when it should),



accuracy (agreement to other assay methods) and specificity (limitation of false negatives).

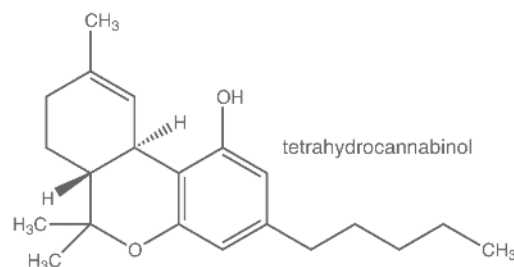
Perceptions of validity and risk

The development of fast, reliable and transportable (roadside) detection methods has been relatively slow. As late as 2006, Rosita-2, an extensive international field trial of nine commercially available MDT units found that all of them failed (to a greater or lesser extent) to meet the full set of criteria set down for the trial. However, with another ten years of development, subsequent studies, such as the DRUID project by the Federal Highway Research Institute in Germany (bit.ly/2k5MUR4), have concluded that the testing technologies are now becoming mature enough for field use.

Scientific data linking the timing of drug use and both the persistence of impairment and the ability to subsequently detect the drugs in certain samples remains relatively 'thin'.

In the absence of definitive science encompassing the whole field of MDT, there has been a lot of argument over the validity and 'fairness' of efforts to apply the technique in the field. Given that, by definition, illicit drug use is illegal, the most common approach in

Given that illicit drugs are already illegal, then until safe limits can be scientifically linked to impairment, zero tolerance is the logical precautionary approach.



many jurisdictions has been 'zero tolerance'. By contrast, less government attention has been paid to the even more complex issue of legal drugs, particularly benzodiazepines.

Opponents such as MP David Shoebridge of the Australian Greens have argued that this approach represents an 'ideological war' on illicit drugs, and that drug takers are being prosecuted for their use, rather than for any direct correlation to the users' actual impairment. Relying on anecdote rather than science, Shoebridge has emphasised cases where users *claim* to have taken the drugs up to four days before driving and still returned positive results. However, this is a clear example of where the precautionary principle must apply. There is enough evidence to demonstrate that driving under the influence of drugs is potentially unsafe, particularly when linking blood levels to driver impairment.

This points to a substantial dichotomy in the perception of risk for driving under the influence of drugs. A

Weary workers: urine test for fatigue could help prevent accidents

Doctors, pilots, air traffic controllers and bus drivers have at least one thing in common – if they're exhausted at work, they could be putting lives at risk. But the development of a new urine test, reported in *Analytical Chemistry* (doi: 10.1021/acs.analchem.6b03421), could help monitor just how weary they are. The results could potentially reduce fatigue-related mistakes by allowing workers to recognise when they should take a break.

The effects of fatigue have long been recognised and studied as a problem in the transportation and healthcare industries. In the early 2000s, studies published in scientific journals reported that fatigue-related mistakes were linked to thousands of vehicular crashes every year, and were a major concern in patient safety. Weariness can cause anyone on or off the job to lose motivation and focus, and become drowsy. Although very common, these symptoms come with biochemical changes that are not well understood. Zhenling Chen, Xianfa Xu and colleagues set out to determine whether a urine test could detect these changes.

The researchers analysed urine samples from dozens of air traffic controllers working in civil aviation before and after an eight-hour shift on the job. Out of the thousands of metabolites detected, the study identified three that could serve as indicators of fatigue. Further work is needed to validate what they found, the researchers say, but their initial results represent a new way to investigate and monitor fatigue – and help prevent worn-out workers from making potentially dangerous errors.

American Chemical Society

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survey by the Australian Drug Foundation (bit.ly/2jea5Kx) found that non-users and users had very similar perceptions that driving under the influence of alcohol was 'very risky' (94% vs 90%), but radically different perceptions for driving under the influence of cannabis (79% vs 30%) and even cocaine (83% vs 26%).

Arguments against the accuracy of MDT have to be acknowledged. However, there have been considerable improvements in the last decade. And just as a roadside breath test for alcohol is not directly used in prosecution, but is followed by more accurate confirmatory testing, then by exactly the same principles MDT is followed by more accurate blood and/or urine testing for those drivers identified as suspected of having threshold levels of key drugs in their system.

Most mine sites and many industrial facilities routinely use random drug

and alcohol testing, correctly arguing that this is a critical consideration to workplace safety when using heavy machinery. Yet we also know that even a relatively light vehicle is potentially hazardous, even before the potentially erratic and unpredictable behaviour of drug takers is taken to account.

A combined approach

Given that illicit drugs are already illegal, then until safe limits can be scientifically linked to impairment, zero tolerance is the logical precautionary approach.

At its current level of technical development, MDT appears to be suitable as a convenient roadside screening method when linked to subsequent confirmatory testing. Used in this way, the emphasis should be on accuracy and selectivity in the initial screening. Given the evidence of the substantive increase in risk through mixing drugs and alcohol, then a

combined approach to enforcement would also be a logical approach.

In the meantime, Victorian survey data cited in the Rosita-2 study is already showing that MDT has a substantive deterrent effect on driving under the influence of drugs (bit.ly/2je9dWk). Combined with education and other supporting initiatives, roadside drug enforcement can only improve the safety of our roads.

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

Choose your chemistry *at the* Centenary Congress

Early bird registration for the Centenary Congress closes on 23 April, so here's a taste of what each event has to offer.

The Centenary Congress program will run for five days from 23 July 2017. Each day will commence with a common Congress plenary speaker and then delegates can choose to attend any of the other major events.



RACI National Centenary Conference

The RACI National Centenary Conference will be planned alongside the 17th Asian Chemical Congress to cover any subject areas not covered by the international speciality partner meetings

to ensure the complete event will cover all the major areas of the chemical sciences.



17th Asian Chemical Congress and 19th General Assembly of Federation of Asian Chemical Societies

ACC is the major biannual congress organised by the members of FACS, the peak body representing chemistry in the Asia-Pacific region. FACS comprises 31 dynamic chemical societies from countries and territories in the Asia-Pacific.

17ACC at Melbourne will be an exciting, unprecedented opportunity for chemists to network with world leaders in chemistry, and to hear about the latest, increasingly boundary-spanning chemical research.

The indicative 17ACC scientific program topics have been chosen to illustrate the relevance and value of chemistry to modern society and commerce; however, papers from all aspects of chemistry are welcome.

6th Asian Conference on Coordination Chemistry



This biennial conference comes to the southern hemisphere for the first time, and will build on the success of the first five conferences in the series. The largest conference in the Asia-Pacific region focusing on coordination chemistry, the ACCC aims to provide a forum for inorganic and coordination chemists from all over the world to gather together and present their most recent research findings, and to offer a stimulating atmosphere to discuss and exchange ideas on frontier research topics in inorganic and coordination chemistry. The conference also serves to showcase the fast development of coordination chemistry in the Asia-Pacific region. The conference is devoted to recent advances and new trends in coordination chemistry, including electronic structure and bonding of metal complexes, supramolecular chemistry, organometallic chemistry, bioinorganic chemistry, catalysis, small molecule activation, functional coordination compounds for materials science, biomedical science and environmental science and energy, as well as other emerging topics in coordination chemistry.

Asia Hub for e-Drug Discovery Symposium 2017



AHeDD focuses on the computational drug design aspects of drug discovery and development. This field continues to increase in importance as it increasingly imparts greater efficiency to all aspects of drug discovery and development.

The history of AHeDD dates back almost 15 years, when Dr Akiyama and Dr No proposed and established a platform for exchange of electronic data in drug discovery. These same two individuals have been instrumental in facilitating several important symposia that have taken place since. A recent highlight was AHeDD 2014.

Building on the momentum established in 2014, a specific and high-impact program is currently being assembled, with significant interest already registered by prominent scientists in Korea, China, Japan and Australia. Although AHeDD 2017 will have a distinct profile, attendance at the symposium will be rewarded by access to a very large drug discovery program, as AHeDD 2017 has been chosen to dovetail with RACI centenary celebrations during July 2017, synergising in particular with AIMECS2017.



11th Asian Federation for Medicinal Chemistry's International Medicinal Chemistry Symposium

AIMECS2017 will run alongside the Centenary Congress because AIMECS2017 delegates will be interested in and will contribute to and enjoy the varied and rich chemistry on offer. The theme reflects this focus on chemistry: Chemistry in Drug Discovery, Design and Development.

AIMECS2017 will include sessions organised by the American Chemical Society (ACS) Division of Medicinal Chemistry, the European Federation of Medicinal Chemistry and the RACI Division of Medicinal Chemistry and Chemical Biology.



World Conference on Carbon

The World Conference on Carbon 2017 will bring together around 800 scientists, engineers and technologists from across academia and industry to learn about and debate the latest

advances in the carbon world. It is anticipated the program will be composed of five parallel sessions over five days, all kicked off by an outstanding set of plenary and keynote lectures focused on setting the scene in areas that span from the underpinning materials science and engineering through to advances in the characterisation of carbon and on to applications spanning from the traditional through to the more novel.



Industrial Chemistry/Chemical Engineering Annual Conference of Australia and New Zealand (Chemeca)

The theme for Chemeca 2017 is Innovation Through Science and Engineering and celebrates the pivotal role of chemical engineers and industrial chemists in creating new

knowledge and translating it into trailblazing technologies that enhance our quality of life.

As one of the largest ever gathering of scientists and engineers to be held in Australia, the RACI Centenary Congress aims to showcase innovative research and technology and to provide inspiration for creating new opportunities to address future challenges. As a platform to promote interdisciplinary thinking that is the core of creativity and innovation, it will facilitate professionals from diverse areas of chemical sciences and engineering to interact, collaborate and deliver innovative solutions for a sustainable world and way of life.

A world-class line up of invited speakers will share their high-impact works and interact with the delegates. Young researchers and students – our future leaders – are provided opportunities to showcase their research and be inspired to innovate. The Chemical Engineering Awards of Excellence dinner will be a highlight of Chemeca 2017 to honour and celebrate the exceptional people who contribute to chemical engineering and industrial chemistry.

8th International Conference on Green and Sustainable Chemistry

GSC8 will build upon the successful outcomes and achievements of the previous International Conferences on Green and Sustainable Chemistry. GSC8 will highlight significant advances related to the discovery, development and application of green and sustainable chemistry and engineering, including new compound classes and materials derived from biorefinery approaches, new catalytic reactions, new energy storage systems, and many other new concept and product opportunities – advances that are all leading to the betterment of the human condition.



18th Asian Edition Tetrahedron Symposium

The Tetrahedron Symposia are the major international annual meetings and information points for reporting advances in organic, bioorganic and medicinal chemistry. In 2017, two symposia will be held, in Budapest (27–30 June) and in Melbourne (23–27 July). The intention of this Tetrahedron Asia Symposium is to bring together some of the major leaders in the field, to provide an intimate and relaxed environment, and to stimulate fresh thinking and creative ideas in those scientific fields impacting so importantly on life and medical sciences. Unlike many meetings, there is only a single session running at any time. This allows for clarity of focus by the participants. International experts will lead a topical program supplemented by selected contributed oral presentations and a comprehensive poster session.



To register for the conference, visit racicongress.com.



Members of the team sampling 480-million-year-old black shales from the Meguma Terrain in Nova Scotia, Canada.

Fool's gold and the ascent of man

BY **ROSS LARGE**

Ancient samples of pyrite, or fool's gold, have revealed the role of plate tectonics in bursts of evolution and mass extinction events. Did humans ultimately originate from mega-mountains?

As a young scientist I often dreamt about going back in time to observe the surge and decline of life that makes up Darwin's evolutionary theory. Imagine the excitement of riding a time machine that takes you back to when the Earth was 3.6 billion years old, and then progressing forward every 100 million years, making 36 stops along the way to observe changes to the Earth and the march of evolution: when life first appeared; the 'boring billion' years when life stagnated; the Cambrian explosion that kick-started complex life; the five great mass extinction events; and the final appearance of humans.

Now I have been fortunate enough to achieve this dream. A team I have led at the University of Tasmania has developed such a 'time machine' by measuring more than 5000 crystals of pyrite using a laser beam attached to a super-sensitive chemical analyser. The results have led to a revolutionary change in our understanding of the symbiotic relationship between geological and evolutionary processes on Earth.

The pyrite crystals we analysed recorded changes in the chemistry of ancient oceans, enabling us to determine how the evolution of bacteria and higher life forms was affected, or even controlled, by concentrations of ocean trace elements.

The analytical data showed that the earliest oceans, more than 2 billion years ago, contained much higher levels of nickel, cobalt, iron, arsenic and gold than modern oceans. By studying pyrite textures in the sedimentary rocks, we were able to observe the beginnings of life in the oceans. The evolution of the first prokaryotic bacteria depended on high levels of nickel and cobalt at this time.

Over the next billion years, known among geologists as the 'boring billion', our time machine indicated that the chemistry of the oceans became more alkaline. Many trace elements critical for life dropped to very low levels. At this time, life slowed to a virtual standstill, and other metals such as zinc and copper replaced nickel and cobalt as the controls on evolutionary pathways.

Between time machine landings at 600 million and 500 million years ago, we observed a dramatic change in the oceans. Trace elements critical for life, particularly molybdenum, selenium, nickel and manganese, increased dramatically in the ocean, creating a massive increase in bacterial blooms leading to the Cambrian explosion of life. This event was accompanied by a dynamic flux in oxygen in the atmosphere to levels similar to those required to sustain complex life.

The next five landings (500 million years to the present) turned out to be the most exciting for our team, with such rapid evolutionary change that extra landings were required to enable us to join the dots.

Connecting the dots of life

Our dataset of more than 3500 pyrite crystal laser analyses for the past 500 million years showed that the nutrient elements critical for life – selenium, molybdenum and cadmium – had a cyclic pattern of variation. This suggested that high concentrations of nutrient elements in the oceans were ideal for life and evolutionary change, while

evolutionary stagnation was likely at low levels. Thus we could explain why bursts of evolution were interspersed with periods of little evolution. We are currently in a period of high nutrient levels, ideal for life in the oceans.

However, what totally surprised us was that three of the periods of extremely low nutrient elements corresponded precisely with three of the five major mass extinction events in the oceans.

Based on this result, we determined to set our time machine precisely on these three mass extinction events at 450 million years ago, 375 million years ago and 200 million years ago, by analysing hundreds of pyrite crystals of these three ages.

The chemical window of life

At this stage of the research, we needed to match the results of geology and ocean chemistry with palaeontology, evolutionary biology and toxicology to solve the next big question: 'What precisely caused the mass extinction events?'

I invited Professor John Long of Flinders University to become involved, and he formed a new group of international scientists that joined our team and targeted the element selenium as the devil in the detail. This group unearthed some important facts about selenium.

First, selenium is a unique element, with a critically small concentration window for life: too much is toxic, but too little cannot sustain life. Selenium is also strongly held in the structure of pyrite crystals, and can be accurately identified by our laser time machine.

Second, selenium is required by nearly all species to promote life. In fact, humans are dependent on minute traces of selenium. Disease in humans and animals is common in parts of the world where the soils are either overenriched or deficient in selenium.

Third, a survey of human blood concentrations of selenium in healthy adults from 69 countries found that nutritional selenium deficiency is

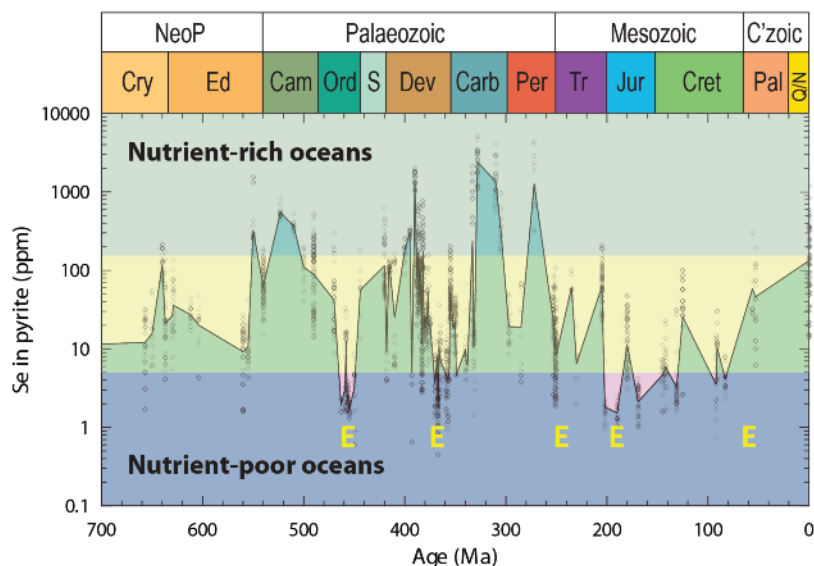
... the nutrient elements critical for life – Se, Mo and Cd – had a cyclic pattern of variation.

highly prevalent in 21 countries and moderately prevalent in 16 countries. This suggests that many people do not consume enough selenium to support selenium-dependent enzymes that are required for optimum brain functions. The scientific data indicates that selenium concentration is too low in food produced in most of Europe, parts of Africa, Asia and New Zealand. It has been estimated that the number of selenium-deficient people in the world is in the range of 500–1000 million.

When we combined these studies with our pyrite data, it became obvious that short periods of extreme selenium deficiency in the ancient oceans was the most likely cause of the three major global mass extinction events, hundreds of millions of years ago.

- 1 The Late Ordovician event 445 million years ago wiped out 85% of all species in the oceans, including nautiloids, brachiopods and corals.
- 2 The Late Devonian event 375 million years ago wiped out 80% of species, including the giant armoured placoderm fish.
- 3 The Triassic/Jurassic boundary, 200 million years ago, wiped out 75% of species, including large amphibians and giant reptiles.

Our data indicated that the other two major mass extinctions at the Permian/Triassic boundary and Cretaceous/Tertiary boundary were not due to selenium deficiency. Their cause is generally accepted to be due to megavolcanic eruptions and a giant meteorite impact, respectively.



Cycles of selenium (Se) concentration in marine pyrite over the past 700 million years. The low points marked by 'E' are the five major mass extinction times. Ocean periods with high selenium are nutrient-rich oceans, whereas periods with low selenium are nutrient-poor oceans.

Did humans evolve from the mountains?

A major feature of the Earth's surface that would be obvious to time travellers stopping every 100 million years is the slow rearrangement of the continents due to plate tectonics.

I was aware of a theory previously proposed by a team of scientists from the Australian National University that the Cambrian explosion of life 540 million years ago was ultimately driven by the collision of supercontinents during plate tectonics. As the theory goes, nutrients critical for life in the oceans principally come from the weathering and erosion of rocks on the continents. Weathering breaks down the minerals in the rocks and releases nutrient trace elements, which are the key to life and evolutionary change.

This theory provided a link to our results. As erosion rates of mountains increase for extended periods, more life-supporting elements, including selenium, are supplied to the oceans. In the long term of geological history, erosion rates rise dramatically, enriching the oceans in nutrients during mountain-building events, and

these major events are caused by the collision of tectonic plates.

However, as erosion reduces the scale of mountains, the supply of nutrients to the oceans declines and a period of nutrient-poor oceans leads to stagnant evolution and ultimately mass extinction. Our research defined five cycles of nutrient-rich oceans followed by nutrient-poor oceans (see diagram).

Geologists have known since the 1960s that collisions of tectonic plates (called orogenic events) lead to the formation of continent-scale mountain ranges. Our research team has provided, for the first time, strong evidence to link plate tectonics, nutrient content in oceans, evolutionary patterns of life and mass extinction events. Our pyrite data shows that within the past 600 million years, the periods of nutrient-rich oceans correspond with global mountain-building events that coincide with major evolutionary activity.

The peak of the first nutrient-rich ocean around 555–510 Ma corresponds with the East African–Antarctic orogenesis event, which produced a mountain range greater

than 8000 kilometres long and coincided with the onset and peak of the Cambrian explosion of life.

The peak in the second nutrient cycle around 410–380 Ma in part corresponds with the termination of the main phase of orogenesis in the Appalachian–Caledonian system and with the first appearance of giant fish and very large terrestrial animals.

The third nutrient cycle peak at 330–310 Ma corresponds with the early Pangaea assembly, with the Appalachian (Hercynian) orogenesis event, and with a period of maximum forest expansion.

The next nutrient peak at 280–260 Ma relates to the main phase of Pangaea assembly, including widespread mountain building in marginal regions (e.g. the Central Asian orogenic belt and Terra Australis Orogen) and diversification of terrestrial amphibians and conifers.

The fifth peak around 150 Ma in the Late Jurassic corresponds with the Alpine orogeny and the appearance of birds.

The final nutrient-rich ocean is at the present day, corresponding to the start of the Amasia (also termed Neo-Pangaea) assembly and the appearance of *Homo erectus*.

Taken in its entirety, our new theory provides a giant twist to Darwin's theory, and places biological evolution in a geological context: geological processes on Earth have been the driver of biological evolution. This is an exciting possibility that obviously requires further research before we can expect it to be fully accepted by other scientists. However, key questions are now apparent. Did humans evolve from the mountains? Will complex life only be found on other planets with evidence of plate tectonic and mountain-building processes?

Ross Large is Distinguished Professor of Economic Geology at the University of Tasmania. The research described here was awarded the 2016 UNSW Eureka Prize for Excellence in Interdisciplinary Research. This article is reproduced from *Australasian Science* (austscience.com).

Australia Day honours recipients 2017

More than 40 scientists, including several RACI Fellows, received Australia Day honours this year. Honours in chemistry and related fields include:

Companion (AC) in the General Division of the Order of Australia

Professor Andrew Bruce Holmes AM, FRACI CChem

Melbourne Laureate Professor Emeritus of Chemistry; President, Australian Academy of Science

For eminent service to science through developments in the field of organic and polymer chemistry as a researcher, editor and academic, and through the governance of nationally recognised, leading scientific organisations.

Officer (AO) in the General Division of the Order of Australia

Dr Graeme Blackman FRACI CChem

Chair, National Stem Cell Foundation

For services to the pharmaceutical industry, to scientific research and policy development, to theological education and to aged care.

Professor Raymond Leslie Frost

Emeritus Professor, and Adjunct Professor, Science and Engineering Faculty, Chemistry, Physics, Mechanical Engineering, Nanotechnology and Molecular Science, Queensland University of Technology

For distinguished service to science, and to higher education, as an academic, researcher and author, particularly in the field of vibrational spectroscopy, and as a mentor of young scientists.

Professor Gaoqing Max Lu

President and Vice-Chancellor, University of Surrey, UK

For distinguished service to education, to national and international research in the fields of materials chemistry and nanotechnology, to engineering, and to Australia–China relations.

Professor Gordon George Wallace FRACI CChem

Executive Research Director, Australian Research Council Centre of Excellence in Electromaterials Science; Founder and Director, Intelligent Polymer Research Institute, University of Wollongong

For distinguished service to science and research in polymer materials and their use in biomedical applications, and to national and international collaboration with industry.

Member (AM) in the General Division of the Order of Australia

Emeritus Professor John Hamilton Bowie FRACI CChem

Emeritus Professor of Chemistry, University of Adelaide

For significant service to science in the field of mass spectrometry, and to education as an academic, researcher and author.

Dr Donald Charles Hector

President, Chemistry Foundation, University of Sydney

For significant service to science in the field of chemical engineering, and to business.

Mr Ross Peter McCann

Deputy Chair, Sustainability Victoria

For significant service to the environment, to the promotion of sustainable resource use, to chemical engineering, and to the community.

The late Dr Peter Wren Parodi

Consultant, Dairy Australia (to 2015)

For significant service to science as a biochemist, and to the dairy industry through contributions to studies in human nutrition.

Medal (OAM) in the General Division of the Order of Australia

Dr Ronald Woods

Visiting Professor, Griffith University

For service to science, particularly in the field of electrochemistry.

For a full list of Australia Day honours, visit www.gg.gov.au/australia-day-2017-honours-list.



Tickets on sale NOW through RACI office

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The RACI Victorian Branch cordially invites you to the

Centenary Gala Dinner & Ball

\$150 for 3 course dinner, drinks and dancing
Celebrate in style . . . dinner and cocktail attire

Plaza Ballroom, Collins St., Melbourne
Saturday 22nd July 2017
7pm - midnight



James Howard Bradbury

Dedicated to eradicating konzo

Howard Bradbury AM FRACI CChem (7 September 1927 – 28 November 2016) was one of the first chemistry academics to be appointed to the Australian National University in 1961. He completed his undergraduate and Masters

degrees at the Melbourne Technical College and University of Melbourne and his PhD at the University of Birmingham in polymer chemistry. Subsequently, he undertook postdoctoral research at Harvard University, where he published his most cited paper on the solvent dependence of the conformation of polyglutamic acid. Upon his return to Australia in late 1954, he worked at the CSIRO Wool Research Laboratories in Geelong. At ANU, Howard carried on his research in polymer, wool and keratin research but he also expanded into investigating peptide, protein and carbohydrate structure, particularly using NMR spectroscopy.

His first sabbatical leave at Cornell University was highly influential as it led to a groundbreaking paper in 1966 that described the use of proton NMR to probe specific sites in a protein. For the first time, Howard showed that it was possible to investigate, in detail and specifically, the solution structure of a large biomolecule. It was pioneering and highly important work that kick-started the now-extensive field of protein NMR spectroscopy and led to his international reputation. Howard's laboratory was also one of the early adopters of the use of lanthanide shift and relaxation agents to probe biomolecular structure and interactions. Howard's work on biomolecular NMR was undertaken in parallel with studies on wool, keratin and synthetic polymers. He also used NMR spectroscopy to investigate the structure of carbohydrates and synthetic polymers.

In the late 1970s, Howard started his research into the chemistry of foods, initially rice and then crops of the South Pacific such as taro and sweet potato. His interest in this area stemmed from witnessing extreme poverty in India in 1974, and his desire to use his skills in protein chemistry to assist in improving staple foods of developing nations. The work was funded initially by the Australian Centre for International Agricultural Research (ACIAR).

In 1988, he took early retirement from the Department of Chemistry and moved to the Department of Botany, which subsequently became incorporated into the Research School of Biology at the ANU, where he worked as an emeritus fellow for the next 28 years. His primary research focus during this time was developing and applying methods to test and remove cyanide from cassava, a root crop that is a major food source in tropical regions. In sub-Saharan Africa, consumption of cassava can cause cyanide poisoning, leading sometimes to death and often to the development of the disease konzo, which causes

paralysis, particularly in the young. During his 'retirement', Howard developed kits to determine cyanide in cassava and thiocyanate in urine and a method to remove cyanogens from cassava flour. The latter is a simple wetting and drying method that drives off hydrogen cyanide from the flour. It has been successfully implemented in many villages across the Democratic Republic of Congo, saving thousands of people from the crippling effects of konzo. His research received support from ACIAR and AusAID. In September 2016, the ANU's Day of Giving campaign raised over \$85 000 towards Howard's konzo eradication program.

Howard's chemical research was recognised by the award of the RACI's Rennie and H.G. Smith Memorial Medals and Fellowship and DSc degrees from the University of Melbourne and ANU. He was also awarded the David Syme Research Prize from the University of Melbourne for his work on wool. In 2007, he received the inaugural '\$2 a Day Award' from the international Institute of Chemical Engineers for his discovery of the wetting method to treat cassava flour. In the same year, he was appointed a Member of the Order of Australia.

We were both supervised by Howard for our PhD degrees. Howard was an outstanding supervisor. He had a somewhat hands-off approach to supervision and allowed his students plenty of freedom, but at the same time, was brilliant at providing oversight and quality ideas into one's project. Universally, Howard's research students have had impressive careers. We have counted 10 professors from the Bradbury stable who span the disciplines of chemistry, biochemistry, biology and structural biology across the world. Others have done well in business and government and one is currently Australia's Ambassador to Austria.

Howard was a man of great intellect, integrity, enthusiasm, fortitude, charm, wit and good will. He was also a humanitarian. His admirable ideals and principles stemmed from his strong Christian faith and his desire to help others less fortunate than himself. Howard was a strong family man who was lovingly supported throughout his career by his wife of 64 years, Ruth. We shall miss his softly spoken voice, his broad smile, his great sense of humour, his sound advice and mentorship and his enthusiastic descriptions of everything, particularly of his family.

Howard is survived by his wife Ruth, their three daughters, Joanne, Annette and Meredith, nine grandchildren and 21 great-grandchildren.

John Carver FRACI CChem and Ray Norton



Leone Spiccia

Chemist who worked at the forefront

It is with great sadness that we share the news of the passing of our good friend and colleague Professor Leone Spiccia.

Leone was born in Sinagra in Sicily, Italy, in 1957. When he was young, his parents decided to leave Italy and make a

new life in Australia for their three children. Leone was always proud of his Sicilian heritage and often maintained that English was his second language, and therefore deserved a break. He also reminded one and all that he had friends back in Sicily, so they needed to fall in line, or deal with the consequences.

The Spiccias arrived in Australia in 1968 when Leone was 11 and his family settled in Balga, Western Australia. He attended primary school having no English but he worked doggedly in order to excel at school. Leone performed excellently at Balga High School, and his parents were extremely proud when he began his tertiary education at the University of Western Australia (UWA) in 1975.

Leone excelled at his studies at UWA and decided to major in his passion, Chemistry. During his Honours year, he met Vivien and they became lifelong partners. They married in 1983, eventually having two children, Nadia and Nicholas. Leone graduated with a BSc(Hons) 1979 and received his PhD in physical and inorganic chemistry from UWA in 1984 under the supervision of Professor Don Watts and Dr Jack Harrowfield. Following postdoctoral positions with Professors Tom Swaddle at the University of Calgary, Canada (1983–4), Werner Marty at the Institut de Chimie Université de Neuchâtel, Switzerland (1984–6) and Alan Sargeson, ANU, (1986–7), he was appointed as lecturer in chemistry at Monash University in Melbourne in 1987. He was promoted to reader in 1999 and full professor in 2006.

At Monash, Leone became a world-renowned chemist, who transformed himself from a fundamental coordination chemist to work at the forefront of sustainable energy, medical diagnostic and therapeutic technologies. For his contribution to the field of inorganic, medicinal and materials chemistry, he received a number of awards: the Forschungszentrum Dresden Rossendorf Fellow (Germany, 2007), the Senior Research Award from the Alexander von Humboldt Foundation (Germany, 2010), the RACI H.G. Smith Medal (2012), Honorary Appointed Professor in the Catalysis Research Centre at Hokkaido University (Japan, 2012), the RACI Inorganic Division Burrows Award (2013), an ARC Discovery Outstanding Researcher Award (2013) and a Helmholtz International Fellowship (Germany, 2014). He published over 315 refereed papers and lodged four patents.

Leone's research on solar energy conversion explored the application of metal complexes in dye-sensitised solar cells, water-splitting devices for the production of hydrogen as a

clean and renewable energy source, and the development of lead iodide perovskite-based thin film solar cells. His wide interests included the development of metal complexes and inorganic materials that mimic metallo-enzymes, aiding the understanding of geochemical and environmental processes or applicable in solar energy conversion, cancer diagnosis and therapy, recombinant protein purification and biosensing.

He held major administrative positions, including Deputy Head of the School of Chemistry (2002–6), and Deputy Dean and Associate Dean Research of the Faculty of Science (2006–8). He was a member of the ARC College of Experts (2008–10) and Chair of the Physics, Chemistry and Earth Sciences Panel 2010. He was a member of the international advisory boards of several leading journals including NanoEnergy and Inorganic Chemistry. He was a member of the RACI for many years and took on a number of roles in the institute, including Honorary Treasurer of the Inorganic Division (1992–6), Organising Committee of 9th National Convention (1992), Organising Committee of the Inorganic Division Conference with RACI 9NC (1991–2), Victorian Representative on Inorganic Division Committee (1989–92).

Leone was very proud that he supervised 55 students and more than 50 postdoctoral fellows. His interactions with his research group were one of his highlights and many group parties involving a swathe of international students were enjoyed. In 2005, in recognition of his supervisory excellence he received the Vice-Chancellors Award for Postgraduate Supervision.

Leone was a very competitive person and he displayed this in sports. He was a tearaway bowler and fearsome hard-hitting batsman and he played social cricket all over the world. He often played squash with his colleagues where his competitive nature became truly evident. He was a keen follower of Australian Rules football, with East Perth and Carlton (in the VFL) his favourite teams, and later was a staunch (one-eyed) supporter of his beloved West Coast Eagles. He loved his food and was an aficionado of red wine.

Leone left us way too early at the prime of his career and life, but to all those around him, we knew he lived life to the fullest. He was intelligent and scholarly and had a diligent work ethic. Through all his hard work, he maintained a wicked sense of humour. He was a great chemist, family man, sportsman and on top of all that, a genuinely good bloke. We were all very fortunate to have Leone in our lives.

Leone is survived by the love of his life Vivien, his two children, Nadia and Nic, and their partners Matt and Celeste. He will be sorely missed by all who knew him.

Peter Junk FRACI CChem and **Phil Andrews** MRACI CChem. We thank Vivien Spiccia for providing us with finer details of Leone's life.

Scientist employment and remuneration: 2016 survey results

The Professional Scientists Employment and Remuneration Survey is an annual snapshot of remuneration including base salary and other benefits across sectors, responsibility levels, years of experience, job functions, industries and branches of science.

The survey report provides detailed analysis of current base salaries and total remuneration packages, annual salary movements, employment intentions, variable pay, differences in reported male and female earnings, and working hours and how additional hours are compensated.

The survey shows that in the previous year, remuneration for scientists increased by 2.4%, outperforming both the Consumer Price Index and general wages growth. This increase underlines the value that scientists deliver every day at the enterprise and sector levels.

While average remuneration for scientists grew, the survey also found a level of dissatisfaction around pay levels. More than a third of respondents reported being dissatisfied with their current level of remuneration and over a third said they were considering leaving their current employer. For those who were considering leaving, pay was among the most frequently cited contributing factors. Over a third of respondents in both the public and private sectors had received no pay increase at all in the previous year. Many were concerned that their remuneration package was falling behind market rates for those undertaking similar work, and that their package did not reflect the level of responsibility they undertook in their day-to-day work.

There was broad concern about science skills, with around seven in ten respondents saying cost-cutting was affecting science capability in their organisation and over four in ten saying their equipment capabilities were growing faster than their staffing. Over half said deprofessionalisation in their organisation was a major concern.

My organisation's scientific capability is very strong and getting stronger but the key is having sufficient technical personnel and expertise to support the scientific research.

Survey respondent



Wages growth

The survey found average remuneration for scientists grew by 2.4% over the previous 12 months. Scientists in the Local Government and Education sectors fared best with increases of 3.1 and 3.0% respectively. Wages also rose significantly in the State Public Service and Government Business Enterprises, with average increases in both sectors of 2.6%. The Australian Public Service and Research Agencies averaged no increase at all. A total of 32.9% of respondents reported that they had not received any increase over the previous 12 months – 35.8% in the private sector and 34.5% in the public sector. This is in comparison with the cost of living increasing 1.0% over the previous 12 months to June 2016 and the Wage Price Index rising by 2.1% over the same period.

By branch of science, salaries of scientists in the Botany, Food Science and Technology and Mathematics fields grew at the greatest rate, receiving average increases of 4.2, 3.0 and 2.8% respectively. The weakest wages growth was in the Physics and Environmental Science fields, with increases of 1.3 and 1.2% respectively.

Average salaries

Across all sectors employing scientists, a full-time professional scientist takes home an average annual base salary of \$107 557 and total package of \$124 648, with the highest average packages in the Education and Government Business Enterprise sectors with total packages of \$140 438 and \$137 929 respectively.

Satisfaction with remuneration

While average remuneration for scientists grew overall, the survey also found a level of dissatisfaction around remuneration levels. Overall, 35.2% of scientists surveyed reported being

Our knowledge and skills are not appreciated or rewarded in terms of recognition or pay rates.

Survey respondent

dissatisfied or very dissatisfied with their current level of remuneration; 46.5% were satisfied or very satisfied. A total of 44.1% reported that their remuneration package was falling behind market rates for those undertaking similar work, and 32.4% said their package did not reflect the level of responsibility they undertook in their day-to-day work.

Remuneration and employment intentions

Some 34.8% of respondents were considering leaving their current job and pay was among the most frequently cited determining factors; 8.5% had changed jobs in the previous 12 months, and, of those, 27.3% had moved for a pay increase, 40.9% had moved due to an unhealthy workplace culture and 36.4% had moved for further professional development opportunities. Of those who were considering changing employers, a pay increase, promotion, greater access to continuing professional development and improved work-life balance were the most commonly cited factors that would alter their intention to leave.

Variable pay and performance incentives

A total of 13.5% of those surveyed across all sectors were paid bonuses or incentives in the last year. The highest average bonuses were in the Private sector and Education sectors.

The survey found that the completion of postgraduate qualifications – Graduate Diploma, Masters and PhD – delivered average earnings premiums (total package figures) of 18.3, 15.1 and 30.8% respectively.

Working hours

Respondents worked on average 44.2 hours per week including 5.7 hours of overtime. Only 11.9% received monetary payment in recognition of their overtime, a significant issue in view of the 18.1% of respondents reporting that they were expected to work longer hours in the past year compared to the previous one. The average number of hours worked per week was greatest for those working in Computing, Teaching or Training and Sales and Marketing.

Deprofessionalisation, professional standards and cost-cutting

Deprofessionalisation – defined as the diminution of science capability across responsibility levels, industries and job functions – was seen as a major concern by 53.1% of respondents. A total of 13.9 and 22.4% of respondents respectively said adherence to professional standards and the level of service quality had declined in their organisation over the previous 12 months; 80.9% agreed or strongly agreed that cost-cutting was affecting their organisation's science capability.

Work priorities, morale and fatigue

Respondents ranked job security, remuneration and a positive workplace culture as their top three personal work priorities, followed by work-life balance, career progression and flexible work arrangements. Some 56.4% of respondents said that staff morale had declined and 61.0% reported that worker fatigue had increased in their organisation over the previous 12 months.

We have a female majority workforce, but leadership roles are still male dominated. Several groups have male group leaders supervising all-female teams.

Survey respondent

Gender pay gap

Overall, the survey found the mean base salary reported was \$117 473 for males compared with \$96 748 for females, and the mean total package for males was \$135 929 compared with \$112 385 for females. Female respondents' reported earnings were less than their male counterparts across job functions with the exception of Quality Control and Production and Computing, and less irrespective the level of qualification. Lower remuneration for female respondents was apparent across all levels of responsibility with the exception of the graduate level.

This is a modified excerpt of key results from the *Professional scientists employment and remuneration summary report 2016*. The summary and full reports are available at www.professionalsaustralia.org.au/financial-edge/salary-survey-reports/scientists5.

Chemistry with everyday equipment

In the February issue (p. 38) I wrote up a chemistry experiment to try at home using simple stuff found in the kitchen.

Although it's undoubtedly fun and interesting for anyone to try, some may say it's a little removed from what a working chemist understands chemistry to be.

I disagree.

Something I try to promote is that chemistry is everywhere, involved in pretty much everything. There is a reason why chemistry is sometimes referred to as the 'central science'. Indeed, the American Chemical Society states that 'Chemistry is not limited to beakers and laboratories. It is all around us, and the better we know chemistry, the better we know our world.'bit.ly/2l2mcZj) In high school through to university, chemistry students often find following a chemistry procedure to be largely like reading a recipe in the kitchen. I find the reverse is also true – cooking starts to feel like working in a chemistry lab (especially the washing up part ...).

Without this kind of thinking, my current PhD project would not have been possible. I work in natural products chemistry, and I'm primarily interested in the extraction of organic molecules from plant material. Many pieces of equipment and techniques can be used for this. These are often expensive or

use toxic solvents – two things chemists try to avoid!

There are a number of reasons why you might want to extract from plant material. Our primary motivation in the Smith-Bissember research group at the University of Tasmania is to explore Tasmania's diverse range of native and endemic plants for molecules that might show interesting properties such as anticancer, antibacterial or antifungal activity.

As it happens, millions of people around the world (non-chemists and chemists alike) are doing plant extraction every day. Some do it for the taste of their creation, and others for that all-familiar kick to get them going in the morning. I am, of course, talking about brewing a coffee. This aromatic activity is simply taking a plant material (coffee beans), grinding it and extracting compounds, the most well known of these being caffeine.

There are numerous ways to brew a coffee, many of which are similar to those used by chemists for plant extraction. Nobody except for our department, however, seemed to have thought that a benchtop espresso machine might be a valid piece of lab equipment.

Using an espresso machine has several advantages over the equivalent scientific instrument. It has a low-cost, simple

Bubble wrap was invented 60 years ago by engineers Alfred Fielding and Marc Chavannes. After unsuccessful attempts to sell their product as textured wallpaper, they tried their luck marketing it as greenhouse insulation.

iStockphoto/peplow



... millions of people around the world (non-chemists and chemists alike) are doing plant extraction every day. Some do it for the taste of their creation, and others for that all-familiar kick to get them going in the morning.

operation, uses non-toxic solvent, and has a short extraction time. Initially we (and others) were sceptical about whether this work would go anywhere, but the results speak for themselves. We have shown this method to be a quick and efficient way to extract from various types of plants. Our original published paper of results for the extraction of Tasmanian native pepper is open access (rsc.li/2kXAiiq). In addition to the espresso machine, we use other household items such as kitchen knives, spice grinders and cheese graters to prepare our samples.

Since we started publishing this work, a research group in Spain has started using espresso machines for chemistry as well. They use a pod-type espresso machine for the analysis of soil and sediment samples (bit.ly/2l0FFiI).

Another great example of household items used for science is that favourite toy – bubble wrap. It's not just me saying that – 'World Bubble Wrap Appreciation Day' happens on the last Monday of January each year. And the interest is not confined to people – if you're so inclined, you can watch a dog popping some bubble wrap (cnn.it/2knamtD). But I digress.

Bubble wrap has many practical uses, including for insulation, and as packaging material for transporting food and other goods. More recently, thanks to work out of Harvard University, it has been shown to be a useful material for science as well.

This particular Harvard report was largely proof of concept, but the authors were able to show many different applications. They could inject various samples into the bubble wrap and then re-seal the wrap straight away, which made for easy sample preparation. Following this, they used the bubble wrap to measure glucose and iron concentrations from blood samples. This could mean that a material such as bubble wrap might be useful for disease testing in remote areas. The authors were also able to measure amounts of other chemicals by electrochemistry, and grow cultures of bacteria (bit.ly/2kXtd1u).



A brew with a difference at the Smith-Bissember research group.

One common advantage of these examples is that they enable work to be done with less investment in equipment or supplies, meaning money can be directed elsewhere to get things done more efficiently. Hopefully this kind of thinking inspires more of the same.

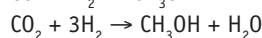
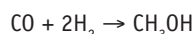


Jeremy Just MRACI is a Hobart-based PhD candidate in organic chemistry and a passionate science communicator, specialising in chemistry shows and demonstrations.

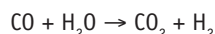
Volatility in the methanol market

World methanol demand is now approaching 80 million tonnes per year. Its main use is as an intermediate in the production of formaldehyde (for urea-formaldehyde resins used extensively in the wood industry), acetic acid (for polyacetate polymers) and methyl t-butyl ether (MTBE, a petrol additive). It is also used as a freezing point depressant in oil pipelines, as a solvent and, in China, directly as a petrol additive and extender. Developments in China over the last decade have seen the rise in methanol use for dimethyl ether (DME, a blending component and extender for LPG) and the production of olefins (MTO/MTP), which enables the production of petrochemicals from coal as opposed to imported oil or naphtha. The approximate breakdown of methanol use is given in the diagram on the right.

Methanol is made from synthesis gas, a mixture of carbon monoxide, carbon dioxide and hydrogen, which is made from any low-cost carbon source such as coal or natural gas. The pertinent reactions are:



The main commercial catalyst (copper on zinc oxide supported on alumina) is active for the water-gas-shift reaction:



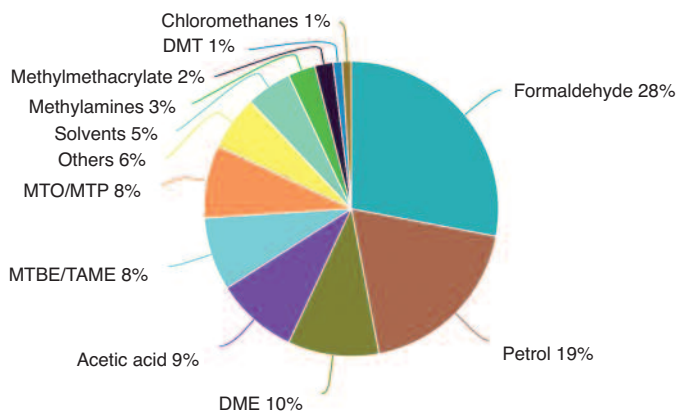
This allows a wide range of composition of the synthesis gas useful for methanol synthesis. In fact, the most commonly used catalyst ($\text{Cu/ZnO/Al}_2\text{O}_3$) appears to work by the second reaction above via carbon dioxide so some carbon dioxide is beneficial to the reaction rate (too much oxidises the catalyst and inhibits the reaction).

Methanol production and supply outside of China is dominated by relatively few players whose facilities ship methanol, typically in parcels of 10 000–40 000 tonnes to the major users in the US, Europe, North Asia and the east coast of China.

Methanol production is an alternative method of monetising large gas reserves rather than LNG or long-distance pipelines, for example in Canada, Russia, the Middle East and Iran. Gas demand for a world-scale facility is much lower than the optimum scale for LNG, which attracts countries with large but not super-large gas reserves. Prominent producing countries in this sector are Chile, New Zealand and Trinidad and Tobago. These countries were prominent suppliers in the past decades but depletion of the initial reserves has curtailed production in recent times.

The shale gas revolution in the US has prompted several new facilities to be constructed, especially in the chemical centres of Texas and Louisiana. The fall in gas prices in North America is spurring renewed interest in Canada. In our region, there are large operations in Malaysia, Indonesia and Brunei.

The world's largest producer is China where coal is the main feedstock. Facilities range from small older plants to modern



World usage of methanol: 2016 demand was 77 MMt.

large-scale facilities. China is unusual in that large amounts of methanol are used in petrol blending. Outside China, although there have been a large number of demonstration programs, methanol blending in fuel is prohibited in most jurisdictions and is opposed by the vehicle manufacturing industry.

In Australia, large corporations have concentrated on LNG developments to monetise their gas resources and have ignored the methanol option. Proposals to develop methanol projects have generally come from smaller players. Of note is that back in the 1980s, BHP's petroleum division demonstrated technology that could be placed on a ship for off-shore methanol production. The aim was to use gas associated with off-shore oil developments using FPSO (floating production, storage and off-take) technology and where the associated gas would have no alternative use and have to be flared. They built a demonstration plant at Laverton in Melbourne (now owned by Coogee Energy), which remains Australia's only methanol facility servicing local industry. However, recent volatility in the price of east coast natural gas has made the facility uneconomic against imports and at the time of writing is moth-balled.

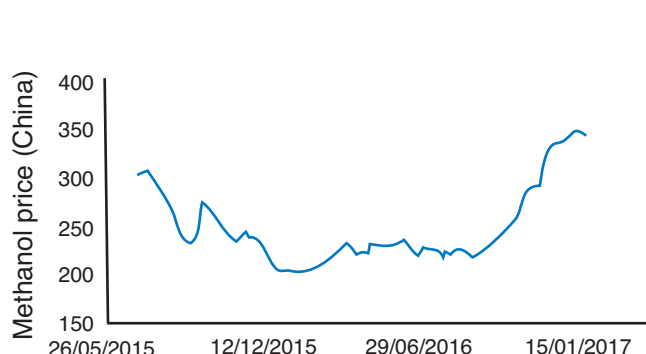
There is a large spot market for methanol that guides the prices for methanol sold on contract. As with all commodity chemicals, the price fluctuates over time. For methanol, there are often long periods of relatively low but stable prices that are disrupted by a rapid rise (less than six months) to often double or more the previous base. This is often followed by a similar rapid fall to somewhere near the base. In many cases, this price volatility seems to be a function of the supply-demand balance of the methanol market rather than changes in the general business cycle. Recent price history is shown in the graph (top left, p. 37).

At the time of writing, the methanol market appears in a period of rising price, with the price doubling over the past six months. The present cycle could have been started when some

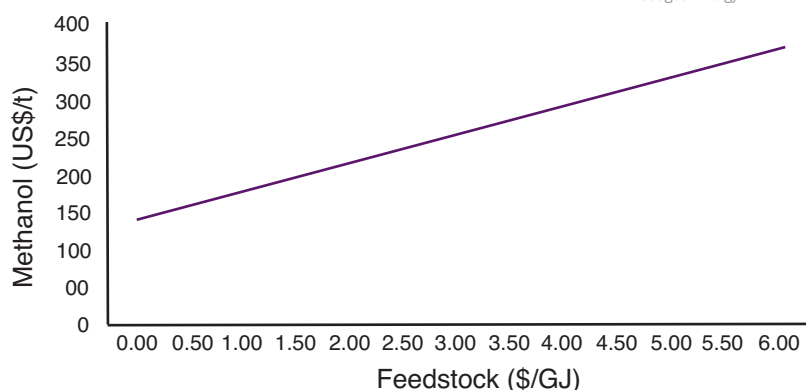


Coogee Energy's methanol plant at Laverton, Victoria.

Coogee Energy



Recent price cycle for methanol (CFR China east coast), illustrating rapid fall, plateau period and rapid rise.



Estimated production cost of methanol from gas for US Gulf facilities.

large export plants in the Middle East entered a scheduled shut-down for maintenance and the production shortfall was exacerbated by lower supply from the large Trinidad operations due to restrictions in the gas supply. Furthermore, the rally in thermal coal prices over the past year has resulted in cost increases in Chinese production. It will be interesting to see how long the present high prices persist and if this assists the re-opening of the Laverton methanol plant.

The world growth in methanol demand is sufficient to support the introduction of one new large methanol plant per year into the world market. However, chemical facilities never come on-stream in an orderly manner and the supply-demand balance is influenced by 'lumpiness' in the number of facilities coming on-stream over time. This further exacerbates the volatility in the market price.

From the perspective of production economics, a new facility should aim to produce methanol at a price below the minimum in the cycle. This ensures profitability over the cycle and generates the opportunity for windfall profits when prices rise.

The general production economics are illustrated in the graph top right.

As is illustrated in the graph, with methanol prices in the region of US\$250/t and allowing US\$50/t shipping cost, the FOB (free-on-board) production cost has to be in the vicinity of US\$200/t. This means that at a gas-based plant, gas costs have to be US\$2/GJ or less for an export-driven operation. In the case of the US where transport costs are minimised by being near to the user, gas prices of US\$3/GJ can be viable (this is typical for prices for US gas in recent months).

These levels of gas prices are well above Australian east coast gas prices but could be achieved from the very large gas developments off western and northern Australia. It is moot to consider if any of the current players would consider methanol as an alternative way to monetise gas other than LNG.



Duncan Seddon FRACI CChem is a consultant to coal, oil, gas and chemicals industries specialising in adding value to natural resources. The author thanks DK Associates (Singapore) for information on methanol prices.

The sticking point

Chemists make and break. This is their yin and yang. They do it with chemical bonds; they do it with physical bonds.

Chemists study adhesion and cohesion and this leads to making a motza from the bewildering array of adhesives sold in the hardware store or, more seriously, gluing aeroplane components together instead of having to rivet them.

The rules are straightforward. You need clean surfaces of compatible nature in close contact and an agent that bonds to both and is so strong that the adhesive needs to break internally before breaking away from the substrate.

The opposite is true when searching for anti-adhesives, anti-bonding products, to wit stain removers. These elicit less publicity but more consumer interest. So what is required?

You need to reverse the requirements. And this needs nuanced chemistry.

Let's get physical.

Many stains are not chemically attached to the substrate; they are just wedged in the little nooks and crannies. So tickle them out.

Steam makes for softer and more flexible fibres. This allows stain particles to dislodge more easily.

Being very hot (often $>100^{\circ}\text{C}$), steam can melt a food stain or blister and peel off a cross-linked polymer (for example, paint). High pressure further dislodges small, trapped particles.

Less hi-tech is to offer a little competition for the stain to leave the substrate. So for a carpet or tablecloth, sprinkle the stain with a very fine powder, such as talcum powder, washing or baking soda, all of which have many more crevices than the stained piece. Then wet with dilute dishwashing detergent (which helps it soak in) and let it dry. Shaving foam contains crannies and detergent, whereas salt (for wine) may be traditional but dissolves completely. As with all these methods, you have to leave time for the stain to be drawn up by the competition. The number of repeats needed depends on the ratio of competing sites.

Now let's get chemical.

A greasy stain, i.e. mainly triglyceride fat, can be 'cut' in two with alkali, literally, while making a little soap and glycerine en passant, to help wash it off. Household alkalis in order of increasing ferociousness are baking soda followed by washing soda and finally oven cleaners and dishwashing 'detergents'.

Blood gets its colour from haemoglobin. To decolorise, you need to extract haem's iron. Supermarket citric acid will complex and extract the iron. Repeat as needed. If the bloodstain has set (denatured through heat or time), this will take longer.

A related example is found when removing the tarnish from copper-based coins (or other objects) with the chelation agents found in that most beloved of local products, the all-natural Vegemite™. As for citric acid above, these larger organic wrap-around molecules take the metal in the tarnishing compounds out of circulation, allowing them to be rubbed off, and the coin looks like new. For removing the rust from iron or steel, go for molasses as this contains an array for molecules with similar enveloping attributes (bit.ly/2kdZr5e).

Leaving the kitchen pantry, you can always go back to the traditional solvents for organic stains – ethanol, isopropanol (rubbing alcohol) and acetone in increasing polarity and effectiveness as a solvent but also increasingly aggressive towards the substrate. When all else fails, hit the stain with chlorine bleach or peroxide (as released from perborate,



iStockphoto/EvgeniiAnd

persulfate, percarbonate or straight hydrogen peroxide). Whatever you use, always remember to check it out first on an inconspicuous portion of the substrate.

More common in supermarket products both for its effectiveness and its natural 'appeal' is the citrus peel extracted, D-limonene. It provides a refreshing fragrance.

Surprisingly, formulated with detergents to provide a suitable emulsion, D-limonene can do some really heavy lifting, such as of oil and grease from concrete (bit.ly/2k0VSPR). Orange peel is in great demand so keep drinking the juice (bit.ly/2jSy9Tz).

An all-purpose old favourite of similar properties is eucalyptol, found in eucalyptus oil, with a related compound being found in tea tree oil.

Much is discussed on this topic in cyberspace, providing a mix of good and bad information, although some of the relationships between contributors can be stained, I mean strained (bit.ly/2kUQLAy). So fellow chemists come down from your anti-bonding orbitals in electron cloud nine and bond more energetically with grounded state issues.

Ben Selinger FRACI CChem is Emeritus Professor of Chemistry at ANU and, along with ANU colleague Associate Professor Russell Barrow, will be releasing the sixth edition of *Chemistry in the marketplace* (CSIRO Publishing) in June 2017. For more information, visit www.publish.csiro.au/book/7366.

Sulfur compounds in wine – an evolving story

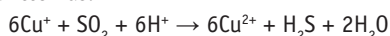
The chemistry of sulfur compounds in wine presents some fascinating chemistry. In my February to May 2015 columns, I introduced aspects of the chemistry of volatile sulfur compounds (VSCs), including hydrogen sulfide. This chemistry is constantly evolving, in a 'never-ending story' way, it seems, and the chemistry group at the Australian Wine Research Institute (AWRI) is at the forefront of research into the chemistry of these compounds that underpins their production and fate in wine.

In 2015, the AWRI chemistry group published a review on the sources of VSCs in wine (Smith et al., *Aust. J. Grape Wine Res.*, vol. 21, pp. 705–12). The review addressed three VSCs that are significant in affecting a wine's aroma: H₂S (rotten egg), methane thiol (MeS, burnt rubber, sewage, cabbage) and dimethyl sulfide (DMS, boiled cabbage, asparagus, canned corn, blackcurrant, truffle). While some of these descriptors, such as 'truffle', may not seem unpleasant, their detection is often coupled with other, non-attractive aspects of a wine's aroma. The odour detection thresholds for these compounds are low (1.1–1.6 µg/L for H₂S, 1.8–3.1 µg/L for MeS and 25 µg/L for DMS), meaning that not much is needed to be of concern.

While it is well established that yeasts can catabolise sulfur-containing amino acids and thus release H₂S during fermentation, there are many other factors, some established, some speculative, regarding the formation of VSCs. The AWRI review addressed the role of redox chemistry involving copper and iron in the formation and loss of the VSCs. For example, the oxidation of thiols to disulfides is catalysed by Cu²⁺ and the hydroperoxyl radical, produced from the interaction of oxygen and Fe³⁺, can play havoc with other sulfur-containing compounds, as well as with phenolic compounds in general. Oxygen is also critical and I will follow up this issue in the next column.

The role of Cu²⁺ and pH on the production of VSCs in Chardonnay and Shiraz has been examined by the AWRI group (Bekker et al., *Food Chem.*, 2016, vol. 207, pp. 158–6). A lower pH resulted in reduced concentrations of H₂S, MeS and DMS. When Cu²⁺ was present, a significantly higher concentration of H₂S was found, whereas the correlation with MeS and DMS production was not so clear cut. In model systems with added cysteine or glutathione, known H₂S precursors, the combination of low pH and Cu²⁺ reduced H₂S production. In fact, no H₂S was detected in the model containing glutathione, low pH and Cu²⁺. Nanoparticle tracking analysis implied that the Cu-tartrate particle size was dependent on pH, raising the need for more exciting copper chemistry studies in relation to the production of the VSCs.

In my May 2015 column (p. 39), I referred to some 1940s work in France, followed up in the 1950s in the US, regarding the reaction between Cu⁺ and SO₂ to generate H₂S. This is commonly written as:



I have always been somewhat sceptical about this reaction, given that it is a six-electron redox step. However, I did point out in my May 2015 column that Marilize Viviers from the AWRI had presented some preliminary results, suggesting that the combination of copper and SO₂ led to an enhanced concentration of H₂S. Marilize and others from the AWRI chemistry group have recently published details of this study (*Molecules*, 2016, doi: 10.3390/molecules21091214). The results with Verdelho in particular showed that the combination of Cu²⁺ and SO₂ significantly increased H₂S formation. With Shiraz, there was little difference in H₂S production between the 'Cu²⁺ alone' and 'Cu²⁺ + SO₂' treatments, possibly due to SO₂ binding to the pigments in red wine. Modelling the process using 4-methylbenzoquinone identified that competition between SO₂ and H₂S binding with the quinone is a major factor in influencing the final H₂S concentration. It is possible that the effects of Cu²⁺ and SO₂ may be via independent pathways, but more needs to be known.

The results do identify a problem for winemakers. Both SO₂ and Cu²⁺ are used at various stages during the winemaking process and thus the possibility of establishing conditions that lead to H₂S formation during the lifetime of a bottled wine may be encountered. Refining the scientific outputs for the best industry outcomes is still a work in progress.

While VSCs are of some concern in wine, spare a thought for seabirds and their attraction to DMS. Here I am indebted to Deidre Tronson for referring me to an article in *Science Daily* (bit.ly/2ffpWRg). DMS is a trigger for some seabirds to seek food. For example, when krill chew up algae, DMS is released and the birds dive for one of their favourite meals. Some plastics break down in seawater to release DMS, a 'dinner bell' (to use the study authors' term) for the seabirds, with the consequence that the meal is plastic bags. A sad example of our mindless pollution of the environment.



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.

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<p>Quality System Quality Endorsed Company ISO 9001:2008 UK 10372 SA-Certified</p>	<p>If chemists in Australia are experiencing difficulty in obtaining supply, please send me an email: peter.sommers@rowe.com.au and I promise to help you.</p> <p>This is not a 'subtle' attempt to obtain more business, but a sincere pledge to help fellow scientists source the items they need to do their work, and thereby help Australia grow. This is the raison d'être for Rowe Scientific Pty. Ltd.</p> <p>Peter Sommers (FRACI)</p>	

EPA Victoria reforms

Change is afoot in Victoria! After a 10-month public enquiry, the State Government has announced a raft of changes to the Environment Protection Authority (EPA Victoria), and some new roles and responsibilities for other government agencies, and for local councils. The Government has adopted (in whole or in part) 47 of the 48 recommendations from the Enquiry, but I want to focus on only two.

EPA Victoria is Australia's oldest environmental regulator and other Australian states have had the opportunity to build on the successes, and learn from the setbacks, of their Victorian counterpart. However, following a number of incidents in the past decade that have not reflected well on the EPA, the Government announced a review of EPA's role, structure and functions, to ensure it can respond to the challenges of the future.

The Enquiry placed strong emphasis on enhancing EPA's scientific expertise ...

EPA Victoria has a long history of being a science-based regulator. It has undertaken landmark monitoring programs, developed analytical techniques, pioneered contaminated sites auditing, and sought to use sound science in its decision making. The Enquiry placed strong emphasis on enhancing EPA's scientific expertise and recommended that:

- members of the newly constituted Board be chosen with a strong emphasis on science and engineering backgrounds
- the CEO have a science or engineering background
- there be a Chief Environmental Scientist (CES), reporting to the CEO
- a Science, Engineering and Health subcommittee of the Board be created, comprising Board members and external experts.

Under previous Chairmen and CEOs, there has been a Scientific Advisory Board, which has included some well-known RACI members, but it was established internally and with a purely advisory role. As Chairman and CEO, the late Brian Robinson AM also took on many of the tasks envisaged for the new CES. His former colleagues would argue that his skills in areas such as communication, innovation and influence, envisaged for the CES, were what contributed to EPA's strong credibility in his time. Certainly, as a chemist, Robinson insisted on making statutory decisions based on sound science. Many staff members quickly came to realise this when presenting less than robust recommendations to the Chairman for approval. While the new role of CES is unlikely to have specific statutory powers, many interested observers would

hope that whoever takes on this role will foster the strong scientific credentials in the organisation that were a hallmark of the Robinson era.

One of the recurring areas of public disquiet with EPA Victoria in recent years has been the lack of a list or register of all the known contaminated sites in the state. *The Age* newspaper has been particularly persistent on this topic, regularly running articles about how there is no such list, and the dangers some sites pose. To make a point, in late 2015 *The Age* reported that it had identified 11 former asbestos manufacturing sites that weren't known to EPA. A new database of 'sites that pose a high risk to the community because of past use' is proposed, to be developed by the Department of Environment, Land, Water and Planning, using a range of government sources including information held by EPA.

One of the reasons there has been no such database in the past is that there has been no legislated requirement for many potentially contaminating activities to be licensed or registered. EPA's licensing regime has focused on large scale, 'smokestack' industries, and small-to-medium-sized enterprises have not been caught in the regulatory net. This includes service stations, automotive repairs and servicing businesses, and dry cleaners, all of which are registered or notified to local government in other states. (Another of the Enquiry's recommendations will increase the range of regulated activities.) Much work will need to be done to develop a complete database of all such sites, in addition to smaller factories and workshops, which have, hitherto, slipped under the EPA radar. There is also potential for some confusion to arise if the site identification process is not handled well; information about previous site use can be hard to find, especially after local government records were archived following council amalgamations in the 1990s. There will likely also be questions about who will be responsible for the accuracy of information, and liability for any loss or damage suffered by other parties due to errors in, or omissions from, the database.

The other major news accompanying the Enquiry's report and recommendations was the Government's commitment of serious money, at least over the next four years, to ensure that EPA has the resources to make the changes recommended and to continue to use its new powers into the future. Some may view these changes as a chance of a new beginning for EPA Victoria, after 45 years of operation. I doubt that we will have to wait that long to know whether the changes have been successful.



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‘Ms’-ing in action

This rumination started when I noticed this headline in the Melbourne Age – ‘Calling women in racing “Ms” is poor form’. The article, written by a male journalist, drew attention to the way jockey’s names are listed in the paper’s form guide for that week. Men simply got an initial, while women got Ms and an initial. The example shown had L. Currie, W. Egan, Ms L. Meech and someone called ‘scratched’. It harked back to the 2015 Melbourne Cup, for which the winning jockey was Michelle Payne, listed as Ms M. Payne. In the 2016 Cup, there was Ms K. Mallion, but there was one sign of change – one of the male jockeys had a given name.

This is way that things used to be done in science publishing, too. In the course of some other research I had encountered ‘Some Stereochemical Studies of Lignans’, published in the *Journal of the Chemical Society* in 1958 under the names of A.J. Birch, Barton Milligan, (Mrs) E. Smith and R.N. Small but when I broadened the scope of my research into the names of authors, I found it to be more complicated than I had expected. Using a prenomial for women’s names was common in 1958 but including a male author’s given name, as in Barton Milligan’s case, was unusual. This may have been a special case, because one of Birch’s PhD students was Brian Milligan so ‘B. Milligan’ might have led to confusion.

I took the *Australian Journal of Chemistry* as my study site, and began with 1953 (volume 6), the year in which *AJC* was separated from the *Australian Journal of Scientific Research*. I found among the authors A.J. Birch and Patricia Hextall and so I deduced that the style guide demanded initials for men but given names for women, thus identifying their sex. I followed this demarcation into the 1970s, spotting G.G. Ferguson and Jeanette H. Hickford in March 1970 (volume 23(3)). That style continued until late 1974, when I found an article by P.B. Woodgate and Catherine R. Fitchett in the November issue, volume 27(11). Starting in the last issue of 1974, however, all authors got their given names. In the years that followed, I noticed that the proportion of female authors increased but they were still in a minority. At least there was nomenclative equivalence.

Just to see how the Australian journal ranked in international company, I made a brief examination of authors’ names in the *Journal of the Chemical Society*. In the first issue of 1966, I found an article by S.J. Angyal, (Mrs) V. Bender and J.H. Curtin from the University of New South Wales. Soon afterwards, I found that women authors had given names and over the next five years given names for men began to appear. I presumed that authors were given the choice of how they would be specified.

My research seemed to have delivered a more-or-less consistent set of results, but this hubris was dashed when I came across a 1930 paper in the *Journal of the Chemical Society* with authors Dorothy Lilian Fox and Eustace Ebenezer Turner. Another gap was my failure to find a case where the given name is not gender-specific. I expect that there are such cases – Pat not being expanded to Patricia or Patrick, for example – but I couldn’t find one. The inclusion of a full second name, of course, would remove the ambiguity.

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In broader society, the etiquette of personal names has changed rapidly during the last few decades and it’s only occasionally today that I come across examples of the old order. For a decade or more after World War II, mail would be addressed to the likes of Jonathon Smith esq (esquire). His wife would be Mrs Jonathon Smith, only becoming Mrs Elizabeth Smith when Jonathon predeceased her, although many Mrs Smiths rejected the personal touch and retained their husbands’ given names by which they had been known for many years. These days, many wives never do take their husband’s family name and unmarried partnerships are common, too, so the old etiquette seems doubly quaint.

Using first names in publication is not problematic, actually helpful, although lexicographers face a difficult task in deciding whether J. Smith is the same person as J.A. Smith, Jonathon Smith, and Jonathon A. Smith, not to mention Jason, Joan, Jacqueline and so on. And then there is the problem of addresses such as department, school, institute and centre. When I make a reservation, and I’m asked my name, I say ‘Rae’ and I know that when I arrive at the restaurant I could be greeted with ‘Hullo Ray’. Family names like Martin, James and so on could cause the same problem, but as long as we get fed, who cares?



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.

Australian Society of Cosmetic Chemists (ASCC 2017)

3–5 May 2017, Sunshine Coast, Queensland

<http://ascc.com.au>

11th New Diamond and Nano Carbons Conference

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www.ndnc2017.org

3rd International Conference on Organic and Inorganic Chemistry

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<http://organicchemistry.conferenceseries.com>

Vic Branch Centenary Gala Dinner and Ball

22 July 2017, Plaza Ballroom, Melbourne, Vic

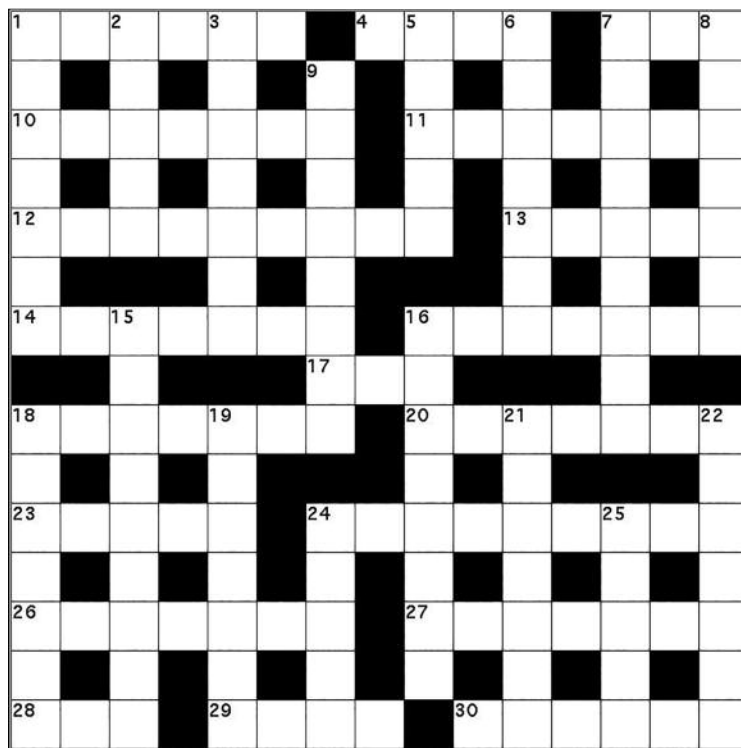
<https://icmsaust.eventsair.com/raci2017/centenary-gala-dinner/Site/Register>

International Conference and Exhibition on Pharmaceutical Nanotechnology

27–29 October 2017, Rome, Italy

<http://nanotechnology.pharmaceuticalconferences.com>

RACI events are shown in blue.



Across

- 1 & 4 Across** You could add just a little more to small flu shot. (6,4)
- 4** See 1 Across
- 7** Each and every totality. (3)
- 10** It's mesoionic, heterocyclic and aromatic and it comes from Sydney town without first you wasting time. (7)
- 11** Could zinc oxide be derived from the simplest aromatic carboxylic acid?! (7)
- 12** Roof lifted: four kilograms made into lactose. (4,5)
- 13** 13151A first. (5)
- 14** Next rid mixture of substance produced by the hydrolysis of starch. (7)
- 16** Salicylic acid and hydroquinone, perhaps, used for hen slop. (7)
- 17** Cast iron exhibits total internal reflection. (3)
- 18** Makes one less of the compounds of general formula $R_2C=Se$. (7)
- 20** Fought at odds. (7)
- 23** Large numbers of animals? (5)
- 24** Getting mean; claim getting older. (9)
- 26** End lies about the oil source. (7)
- 27** Net tactile change. (7)
- 28** Latin thing for the reticuloendothelial system. (3)
- 29** Do go around. (4)
- 30** Checks School thesis centres and repeats. (6)

Down

- 1** Took as known put on. (7)
- 2** Design poser. (5)
- 3** Advocate fund. (7)
- 5** Pigment of uranium! Doctor erbium. (5)
- 6** Bond relationship. (7)
- 7** Amour! Shop for something! But definitely not diamonds. (9)
- 8** Cyclic amides. Spooner, nail the animals. (7)
- 9** About a man's application to analysis and synthesis. (8)
- 15** Sexy Nelly formed these compounds from quinones by replacing the oxygen atoms with CH_2 groups. (9)
- 16** Strangely rely on support in the correct manner. (8)
- 18** It looks like lost mail, sir. (7)
- 19** Sodium odour is newly generated. (7)
- 21** Yielding PVC, perhaps. (7)
- 22** Qualities of bachelors? (7)
- 24** Both? Neither? Just one? Tolkien's Land of the Gift. (3/2)
- 25** $=N-R$ held back on imitation. (5)

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

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17 ACC

17th Asian Chemical
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FACS



6th Asian Conference on
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24-28 July 2017 | Melbourne, Australia

ACCC6

6th Asian Conference on
Coordination Chemistry



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