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August 2014

in Australia

International Year of Crystallography

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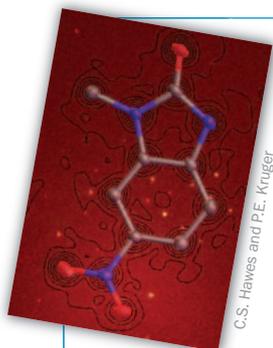
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chemistry
in Australia



C.S. Hawes and P.E. Kruger

cover story

In recognition of the importance of crystallography, the UN has declared 2014 the International Year of Crystallography. Read more in this month's guest editorial and in our page 18 feature.

Diffraction pattern, electron density map and molecular structure of a minor product from the degradation of 1-(ethyl carboxymethylene)-2-(1-pyrazolyl)benzimidazole in dilute aqueous nitric acid, sent to the Cambridge Crystallographic Data Centre (deposition no. 955573) as a private communication. The data was used as a tutorial at the 2013 Australasian Crystallography School as an example of the elucidation of an unknown small molecule structure based on high-quality diffraction data.

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18 The inner space race

The emergence of X-ray crystallography is the story of an earnest dash to the then-elusive double helix.

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Renewable energy sources pose the problem of intermittency. Is storage the answer?

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The Battle of Hamel on 4 July 1918 was the first operational task planned and executed by John Monash as a Corps Commander. It broke conventional military wisdom and demonstrated that with new tactics the static nature of trench warfare could be overcome.

30 Does urban sewage have a drug problem?

To most of us, out of sight is out of mind for anything that goes down the toilet, but some environmental scientists are giving it serious thought.

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From the President

The federal government announced its budget priorities for the coming years in May. Considerable commentary has appeared in the media on the impact of the budget proposals on the conduct of science in Australia. The RACI President-Elect, Professor Paul Bernhardt, and I wrote an open letter to the Prime Minister and Treasurer in June in defence of the role that chemistry plays in our socioeconomic fabric. This letter was emailed to members on 16 June, and is reproduced below.

An open letter to the Prime Minister of the Commonwealth of Australia, the Honourable Tony Abbott MP, and the Treasurer of the Commonwealth of Australia, the Honourable Joe Hockey MP, from the leadership of the Royal Australian Chemical Institute.

9 June 2014

Dear Prime Minister and Treasurer,

The Royal Australian Chemical Institute (RACI) is concerned about the potential negative impact on the conduct of the chemical sciences in Australia as a result of the recent federal budget announcements.

Chemistry is an enabling science; chemists and those educated in the chemical sciences make substantive contributions to Australia's

socioeconomic performance. There are more than 60,000 people employed in the Australian chemical industry, which comprises our second largest manufacturing sector. The chemical industry contributes over \$11.6 billion to our GDP per annum (PACIA 'Adding Value – Strategic Roadmap', 2011). Australia's future growth in building and construction, mining and agriculture are fed by materials supplied by the chemical industry; chemicals and plastics alone supply 109 of Australia's 111 industries.

Chemists work collaboratively with scientists from a range of disciplines spanning the physical, biological and mathematical sciences – as well as engineers and technologists – to deliver innovative and practical solutions to a diverse range of problems. Chemists provide tangible innovation, productivity, efficiency and education outcomes which underpin Australia's economic development.

The future of chemistry in Australia starts with its young. The RACI is deeply concerned that the government's proposed changes to the fee structure charged to university students may have an adverse impact on the attractiveness of undergraduate science degrees. Australia needs highly trained chemistry (and science) graduates. A structural disincentive, in the form of significant university fee increases

for science degrees, is not in the national interest.

Similarly, the government's unprecedented proposal to introduce fees for domestic research higher degree (RHD) students will have a significant impact on our country's future capacity for innovation. RHD students already make a significant financial sacrifice by committing to a further 3-to-4 years' university education beyond their undergraduate study. Remuneration at the level of an Australian Postgraduate Award (\$25,392 p.a. or \$488.31 per week in 2014) is well below the National Minimum Wage (\$640.90 per week; Fair Work Australia 2014) so RHD graduates are typically in their mid-20s before they have the opportunity to earn an income appropriate to their level of training and expertise. The proposed additional impost on top of an existing HELP debt from their undergraduate education can only further discourage prospective RHD students from following a career path towards innovation. Our nation desperately needs scientists trained to the highest international standards to lead the science-driven advances of tomorrow.

The 2012 Excellence for Research in Australia (ERA) evaluation has shown that chemistry is punching well above its weight. When examined at the sub-discipline level (e.g. inorganic chemistry, physical chemistry, etc.), 78 out of a total of

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

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Australia's ability to foster the next generation of innovators and to enable them to fulfil their research and problem-solving potential in the global marketplace is put at risk by the federal government's proposals to reduce funding to key science and research agencies ...

82 chemistry units of assessment were rated at, above, or well above world standard (95%). This exceptional level of performance across Australia's universities has been due to the efforts of generations of researchers (in particular, RHD students) and the support of successive governments.

This long-standing investment and support of Australian science by both sides of Australian politics is being jeopardised. Australia's ability to foster the next generation of innovators and to enable them to fulfil their research and problem-solving potential in the global marketplace is put at risk by the federal government's proposals to reduce funding to key science and research agencies by approximately \$425 million (DSTO, \$120m; CSIRO, \$114.8m; Cooperative Research Centres, \$80m; Australian Research Council, \$74.9m; ANSTO, \$27.6m; Australian Institute of Marine Sciences, \$7.8m).

The Government's planned \$20 billion medical research future fund is a bold proposal. However, the RACI is concerned that quarantining such a large proportion of Commonwealth research funding at the exclusion of the other sciences will be counter-productive in the long term. Without breakthroughs in the enabling chemical, biological and physical sciences, progress in disease prevention, diagnosis and treatment is put at serious risk of foundering.

A sustainable, bipartisan vision for science is urgently needed from Australia's political leaders. Fundamental research in the chemical, physical and biological sciences underpins our nation's future prosperity and capacity to deal with pressing challenges in energy, food, health and advanced manufacturing. The RACI is concerned that the current focus on biomedical research with an aim to pick research 'winners' does not address the bigger (long term) picture. Major scientific advances also stem from serendipitous, curiosity-driven inquiry. There is no better example than CSIRO's development of WiFi technology; a product of researchers overcoming the challenge of sharing large volumes of astronomy data. This is a telling case study of Australian innovation that has had deep impact on a global scale, but one which would never have been supported by a biomedical research fund.

The RACI calls on the federal government to reconsider decisions that will have an adverse impact on Australian science and the nation's future prosperity. We would welcome the opportunity to engage with the Government in a shared vision for the Australian chemistry community.

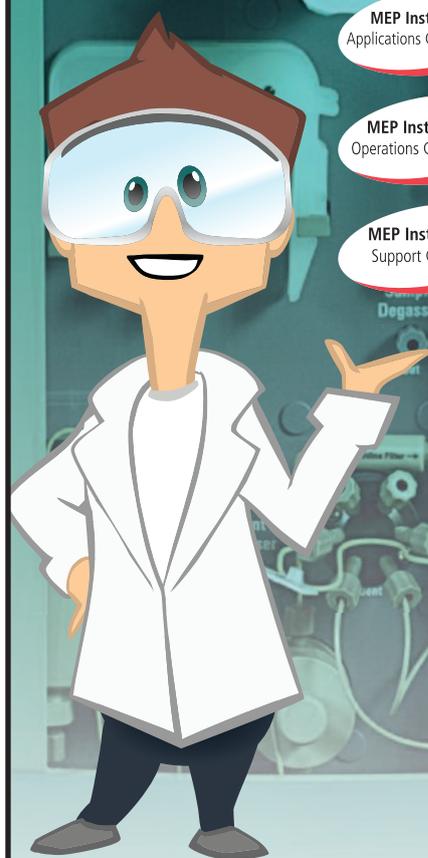


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International Year of Crystallography

Crystallography is the most powerful technique for obtaining detailed information of the three-dimensional structure of molecules (in the solid state). No fewer than 29 Nobel Prizes have been associated with this technique, and it has been instrumental in our understanding of chemistry, biology and materials science. To quote one of those Nobel Prize winners, Max Perutz (Chemistry, 1962):

Why water boils at 100° and methane at -161°, why blood is red and grass is green, why diamond is hard and wax is soft, why glaciers flow and iron gets hard when you hammer it, how muscles contract, how sunlight makes plants grow and how living organisms have been able to evolve into ever more complex forms ... the answers to all these problems have come from structural analysis.

In recognition of the importance of crystallography, 2014 has been designated by the United Nations as the International Year of Crystallography (IYCr). This year represents the centenary of the awarding of the Nobel Prize in Physics to Max von Laue 'for his discovery of diffraction of X-rays by crystals'. It is also 50 years since Dorothy Hodgkin was awarded the Nobel Prize in Chemistry for her determination of the structures of a number of important biochemical compounds, including the first steroid structure (cholesteryl iodide), insulin (finally solved in 1969, five years after her Nobel), penicillin and vitamin B₁₂.

However, while IYCr had a lavish launch at UNESCO House in Paris earlier this year, Australia started their celebrations considerably earlier, with a special Bragg Centennial Symposium, held in Adelaide in December 2012 in conjunction with meetings of the Asian Crystallographic Association (AsCA) and the Society of Crystallography in Australia and New Zealand (SCANZ). This Symposium marked the centennial of W.L. (Lawrence) Bragg's discovery of Bragg's law, to my mind still one of the most elegant equations in science ($n\lambda = 2d\sin\theta$), and the foundation upon which crystallography is built. For this discovery, as well as for the solving of the first crystal structures, Lawrence shared the 1915 Nobel in Physics with his father (W.H. (William) Bragg), and is still the youngest ever winner of a Nobel (only 25!).

The hosting of this event in Adelaide was no accident; while the key discoveries were made after the Bragg family returned to the UK, Lawrence was born in Adelaide and obtained his undergraduate degree at the University of Adelaide, where his father was professor of physics at the time. The Australian connection, however, runs even deeper; Lawrence's mother (William's wife) was the daughter of Charles and Alice Todd. Charles Todd oversaw the building of the Overland Telegraph, completed in 1872, which was Australia's first direct connection to the rest of the world. Thus, Alice Springs and the Todd River are named after Lawrence Bragg's grandparents.

Crystallography has, of course, come a long way since those early days. Structures that would take months, even years, to solve a few decades ago (or were simply too difficult to solve at

all) can now be done routinely in a matter of hours. In the local context, the early self-styled 'bush crystallographers' of the 1970s have evolved into SCANZ, and we now host not only the latest X-ray diffractometers in many chemistry and biochemistry departments, but also have large national facilities, namely the Australian Synchrotron and the OPAL research reactor, which have multiple beamlines dedicated to diffraction techniques.

Australia therefore has much to celebrate during IYCr, and there are numerous activities planned or underway around the country, many with the support of the RACI, SCANZ or the Australian Academy of Science (AAS). Notably, all three are supporting the RACI's crystal growing competition, run in schools all around the country. Other things to look out for include:

- the fascinating *Crystallography365* blog (a crystal structure a day – crystallography365.wordpress.com)
- displays of crystallographic artwork, including pictures and three-dimensional models, at galleries (including the Verge Gallery, University of Sydney, 16–23 August) and other public spaces around the country
- a 'Crystallography in Everyday Life' photo competition and travelling exhibition
- special issues of *CrystEngComm* (Asia-Pacific region issue) and *Aust. J. Chem.* celebrating IYCr
- a national lecture tour in August by Professor Stephen Curry (Imperial College); for a sneak peak, have a look at Stephen's excellent public lecture on crystallography on either YouTube or the Royal Institution's website
- the Science at the Shine Dome *Minerals to Medicines* event in May 2015 at the AAS. While after the IYCr, this will mark the centenary of the Braggs' 1915 Nobel Prize.

So keep an eye out for these activities, have a look at the fantastic resources on the official website (www.iycr2014.org), or celebrate like one research group is by having crystallography-themed cakes at their group meetings this year. And remember that the real power of crystals is not their fictitious healing properties, but their ability to reveal the three-dimensional structures of molecules, and to explain the properties of matter.

Stuart Batten FRACI CChem is President of the Society of Crystallographers in Australia and New Zealand.

MOOCs and more

Thank you for another great edition (June). Kieran Lim's article about MOOCs is spot on. To take the matter further, this method could very well be an integral part of most Australian university award courses in the future. Indeed, I believe that Deakin already does this. Despite laboratories being the 'signature pedagogy' in chemistry education, there is a possibility that this component could be done on a week 'block basis' as it is now done for off-campus learning enrolled students. The major problem is the geographic spread and large numbers of participants that MOOCs attract. I'm sure a solution will be found, if one doesn't already exist.

For any members who have not had a look at the offerings, then perhaps visit www.coursera.org. You will find a large list (about 80) of participating institutions including the University of Melbourne and Stanford University. You will also find an astounding range of subjects on offer. Type 'chemistry' into the search engine and hold your breath. At the moment, I have almost finished an eight-week course on epigenetic control of gene expression, run free on Coursera, badged by the University of Melbourne and presented by Dr Marnie Blewitt, who is head of molecular genetics at WEHI. At last count, the course has 22 000 participants globally, with participant levels from undergraduate to postdoc. I think MOOCs might also be used as a means of professional development.

Thanks also to Oliver Jones for the cover story 'Using your Loaf'. I was very interested in the matter of coeliac's disease as we have a daughter-in-law who suffers from the problem. I have been baking bread now for about 12 years and have never thought much about its history or chemistry. It really isn't that difficult an art, and one is amply rewarded with the rich aromas of freshly baked bread, not to mention better flavour and texture made to your own taste. You also know exactly what is in it. For those who want to have a fling, try the book that I have been using for all these years – *The bread bible* by Rose Levy Beranbaum, published by W.W. Norton & Company (ISBN 9780393057942). Her materials and methods work. The only warning that I give is that I have broken two domestic mixers over the past 12 years and have moved to a small commercial mixer. It, however, will not whisk a couple of egg yolks as it is a bit big for the normal domestic chores.

Denis McCann MRACI

Hake's over ambition?

Was Cecil Hake being overly optimistic about cordite output for Victoria's cordite factory (150 tpa) or did annual production actually reach this target at some point (June 2014, p. 16)? I note that monthly output for the initial six months was 5.5 tonnes (66 tpa), well below Hake's goal. As the article proffered no further production values, I was left to wonder whether Hake's 'ambitious' annual cordite total was ever achieved or not.

I really enjoyed Dave Sammut's road test of the continuum source atomic absorption spectrometer (June p. 24). I think an

occasional review of an instrument, tool or some other chemistry-related equipment or technique would be a worthwhile addition to the magazine. Book reviews have been a staple magazine feature since inception, so maybe it's time to consider including some other kinds of reviews by members too.

Damien Blackwell MRACI CChem

It appears that the theoretical maximum amount of cordite produced by the Maribyrnong factory was 150 tpa *if three shifts were implemented*, though I can't find any reports that this was ever attempted. *The Sydney Morning Herald* (Monday, 24 April 1911, available via Trove.nla.gov.au) reports on 'interesting facts' in Hake's final report that had been delivered on his resignation the previous week. 'The output of the factory is based at 50 tons annually, but should it be necessary to double the output at any time, it can be done with the same plant by working two shifts instead of one. The plant erected is capable of manufacturing gun cotton and nitro-glycerine, the two main ingredients of cordite, also nitric acid, and it can recover and concentrate waste acids. Large cordite for the guns can be easily manufactured at the factory with a few additions to the plant, but this would involve the equipment of proof grounds also. The factory will be capable of manufacturing either cordite Mark 1 for rifles, or cordite mark MD for guns, up to 150 tons per annum, by working three shifts. Raw materials, such as nitrate of soda, cotton waste, acetone, and mineral jelly, will have to be imported.'

Apparently poor Defence planning in the following decades meant that cordite production was insufficient at the outbreak of the World War II. A document lodged at the Australian War Memorial (<http://static.awm.gov.au/images/collection/pdf/RCDIG1070363-1-.PDF>) states that the cordite production line at the factory had ramped up to 1500 tpa by 1935. However, it states in Chapter 16 'Ammunition and Explosives' that 'Calculations based on the assumption that the defence forces should be prepared for a "minor scale of attack" – the officially-accepted view – revealed that the capacity of the government factories for producing cordite and TNT (which was at the rate of 1500 and 600 tons per annum respectively) fell short of requirements.'

Four days before the outbreak of World War II Australia's Minister For Supply and Development (Mr Casey) approved a proposal for decentralising the manufacture of these explosives. The Imperial Chemical Industries Australia and New Zealand (ICANZ) would build an annexe to its Deer Park factories (later known as No. 5 Government Explosives Factory, Albion), which would be designed in the first instance for an annual output of 2000 tons of TNT, 1000 tons of cordite, and 250 tons of carbamate (used in the production of cordite).

David Kilmartin



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A comment on RACI's open letter

It is pleasing to see the RACI lifting its head above the parapet to challenge some of the nonsense of the federal budget, and in general terms I agree with what has been said in the open letter to the Prime Minister and the Treasurer (see p. 4).

However, it is deeply disappointing that the letter makes no attempt at all to correct the budget's (and more generally the government's) irresponsible attempts to trivialise anthropogenic global warming. Just as chemistry is an enabling science for medical research, so too does it inform most aspects of climate change research – a subject in which spectroscopy, thermodynamics, aqueous carbonate chemistry and many other branches of chemistry play major roles.

Why is the RACI so reticent to mention this elephant? Like it or not, it is in the room, stomping about and threatening to charge. It must be confronted, and preferably with science rather than wishful thinking. Chemists can help.

Jim Bonham FRACI CChem

Tribute to Katritzky

Thank you for sending me a copy of *Chemistry in Australia*, June 2014, with the obituary of my husband, Alan R. Katritzky.

Several of his students and collaborators went on to positions in Australian universities and it was a great privilege to visit them there on several occasions, and to forge new links and refresh longstanding ones with chemistry in Australia. Among them 'Kappa' Cornforth, who like Alan took his PhD with Sir Robert Robinson. So the article on him (p. 5) brought back happy memories with him and his admirable wife Rita.

I am very touched by the tribute paid to my husband's endeavours and have already thanked Dr Peter Lehman. He has remained a life-long friend, like so many others, who have worked with my husband.

With thanks and many good wishes ...

Linde Katritzky

Got something to say?

As your RACI member magazine, *Chemistry in Australia* is the perfect place to voice your ideas and opinions, and to provide feedback on chemistry issues and recently published articles.

Send your contributions (approx. 400 words) to the Editor (wools@westnet.com.au).

Journey to the centre of the Earth

The Earth's interior could contain more than three times the amount of water in all our oceans combined, existing within the structures of silicate materials that are stable at the prevailing conditions deep inside the Earth. New research from ETH Zürich has helped to elucidate exactly how deep water gets transported into the Earth's interior.

Water is fundamental for processes that occur at the Earth's surface, but also plays a critical role in many geological processes occurring deep inside of it that shape its evolution. Small amounts of water incorporated into the structure of minerals have a major effect on their stability, behaviour and phase equilibria. Global processes such as mantle convection, plate tectonics and naturally occurring catastrophic events such as earthquakes and volcanic eruptions are strongly influenced by the activity of this water.

Water is reintroduced into the Earth's interior by hydrated tectonic (oceanic) plates that return into the mantle in subduction zones, and released when hydrous minerals/phases are decomposed due to the high pressure and temperature of the Earth's interior. Much of this water returns to the surface by volcanism, but a large fraction is retained in newly formed high-pressure hydrous phases that are stable at much higher depths, opening the possibility for water to recirculate deeper into the mantle beyond 400 km depth. However, the exact amount of water stored in the solid Earth, and how (and how much) of this water is recycled back to the surface, remains obscure.

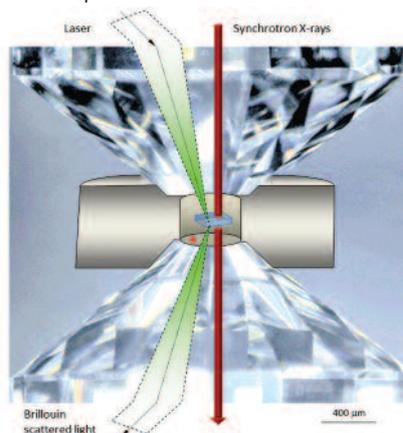
Carmen Sanchez-Valle, assistant professor of experimental geochemistry and mineral physics at the Swiss Federal Institute of Technology, Zurich, has worked with her team to develop several novel analytical techniques to investigate this environment. 'Through learning about the Earth's interior, we become more aware of what actually occurs on the surface,' she explained.

A group of dense hydrous silicate phases discovered in laboratory experiments in the mid-1960s, the so-called alphabet phases (phase A, E, D and superhydrous B), are plausible candidates for the transport of water at depth due to the large stability field. The physical and chemical properties of these materials, obtained through mineral physics studies, are fundamental to revealing the deep water cycle.

A device called a diamond-anvil cell is the primary tool used by researchers to replicate extreme conditions that exist at the Earth's interior, and explore how hydrous phases behave. By powerfully compressing micrometric-size samples between the flat surfaces of quarter-carat diamonds, the apparatus authentically simulates pressure conditions down to the Earth's core. To recreate the infernal temperatures present in these realms, heating elements or infrared lasers are introduced to the tests.

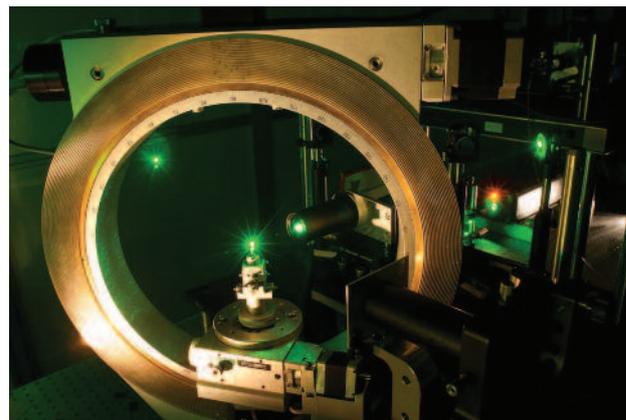
'Crucially, the diamonds are transparent, which means that brilliant X-rays produced by synchrotron sources and laser

analysis can be used to probe the physical and chemical state of samples while they are submitted to extreme pressure and temperature conditions,' added Sanchez-Valle. 'These experimental simulations provide us with a virtual window into the deep Earth.'



A diamond-anvil cell

qualities. The team also use the brilliant X-rays produced at synchrotron sources to monitor the development of textures in hydrous materials deformed at conditions that mimic those of subducting slabs penetrating in the lower mantle.



Set-up for Brillouin scattering spectroscopy

'Our combined studies on hydrous phases has allowed us for the first time to interpret seismic anomalies observed in deep subducted slabs,' said Sanchez-Valle. 'The work has shown that hydrous slabs penetrating below the transition zone in areas such as Tonga could contain at least 1.2% in weight of water bound to dense hydrous phase D. The dehydration of phase D at greater depths is a potential mechanism to activate very rare (and less damaging) deep focused earthquakes, and the water released into the lower mantle has important consequences for the geodynamical and geochemical evolution of the deep Earth.'

INSIGHT PUBLISHERS

Fortunately, seismic waves can be simulated within the team's facilities. Using a unique laser spectroscopy called Brillouin scattering spectroscopy, the speed of seismic waves and elasticity of materials can be monitored under pressure, divulging their water-bearing

Metal crystals from a single atom

Researchers have announced the first ever method for controlling the growth of metal crystals from single atoms.

Published in *Nature Communications* and developed at the University of Warwick, the method – nanocrystallometry – allows for the creation of precise components for use in nanotechnology.

Professor Peter Sadler from the University's Department of Chemistry commented that: 'The breakthrough with

nanocrystallometry is that it actually allows us to observe and directly control the nano-world in motion'.

Using a doped-graphene matrix to slow down and then trap atoms of the precious metal osmium, the researchers were able to control and quantify the growth of metal crystals. When the trapped atoms come into contact with further osmium atoms, they bind together, eventually growing into 3D metal crystals'.

'Tailoring nanoscopic objects is of enormous importance for the production of the materials of the future', said Dr Barry from the University's Department of Chemistry. 'Until now the formation of metal nanocrystals, which are essential to those future materials, could not be controlled with precision at the level of individual atoms, under mild and accessible conditions.'

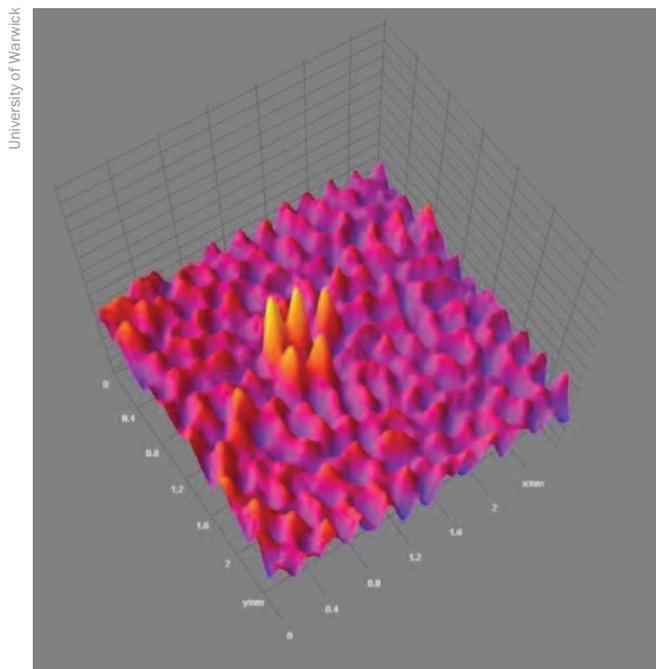
Sadler said: 'Nanocrystallometry's significance is that it has made it possible to grow with precision metal crystals which can be as small as only 0.000 000 15 cm, or 15 Å, wide. If a nanodevice requires a million osmium atoms, then from one gram of osmium we can make about 400 000 devices for every person on this earth. Compared to existing methods of crystal growth, nanocrystallometry offers a significant improvement in the economic and efficient manufacture of precision nanoscopic objects.'

The researchers argue that the new method possesses a range of potential uses. 'We envision the use of nanocrystallometry to build precise, atomic-level electronic circuits and new nano-information storage devices. The method also has significant potential for use in the biosensing of drugs, DNA and gases as well for creating unique nano-patterns on surfaces for security labelling and sealing confidential documents. Nanocrystallometry is also an innovative method for producing new metal nano-alloys, and many combinations can be envisaged. They may have very unusual and as yet unexplored properties', commented Barry.

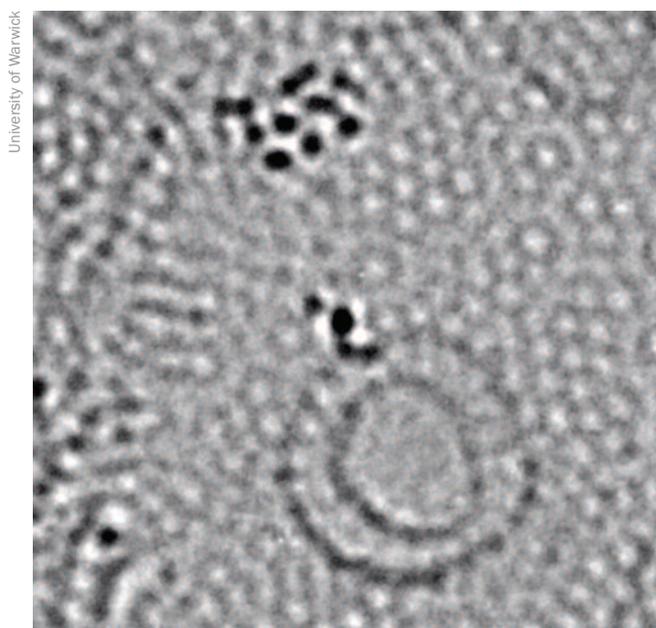
'The advances have been made possible thanks to our use of a state-of-the-art aberration-corrected high-resolution transmission electron microscope, the only microscope of this kind in the UK, that has the potential to image individual atoms in this way. We know that things are made of atoms, but it is really rare to see them dancing in front of your eyes', said Dr Richard Beanland from the University's Department of Physics.

Commenting on the commercial potential for nanocrystallometry, Andrew Lee, Business Development Manager at Warwick Ventures said: 'We think that the team's technique could be a real break-through in terms of offering the capability for micromanipulation and derivatisation of a graphene surface; seeing multiple commercial opportunities arising in the future. We have put a patent application in place and we are actively seeking industrial partners with whom to collaborate in the future.'

UNIVERSITY OF WARWICK



3D projection of the crystal growth



Osmium atoms forming the crystal on the graphene matrix

Push for lower blood lead levels in children



Broken Hill is one of two lead mining and smelting cities in Australia where lead levels are rising.

Although Australia continues to be a world leader in lead metal mining, smelting and processing, international scientists have raised urgent concerns in a new *Environment International* paper about a lack of understanding on the hazards of these operations.

'The lead pandemic is not a problem of the past,' said lead author Professor Mark Taylor.

'There is now an overwhelming body of evidence showing that Australia's lead level for children is too high. We're asking why would it take Australia's leading public health body, the National Health and Medical Research Council (NHRMC) so long – from 2012 to 2014 – to undertake what appears to be a review of reviews. Are they anticipating that they might conclude something different from other global experts?'

In their report, Taylor, Professor Chris Winder and Professor Bruce Lanphear show how childhood blood lead levels have fallen sharply across the world's developed countries in recent decades, as a result of work by the WHO and Food and Agricultural Organization (FAO) of the United Nations.

However, Australian policy responses have stalled, despite 'the incontrovertible evidence that adverse neurocognitive and behavioural effects occur at levels well below the current national goal of 10 µg/dL', the paper reports.

'This delayed response is happening when blood lead levels are actually rising by some measures in two of Australia's three primary lead mining and smelting cities: Port Pirie, South Australia, and Broken Hill, New South Wales,' said Taylor.

The authors argue that urgent changes are required to both state and national policy approaches, to bring them in line with contemporary international standards.

They recommend a lower blood lead intervention level of no more than 5 µg/dL, with a national goal for all children under five years of age to have a blood lead level of below 1 µg/dL by 2020.

The scientists warn that procrastination on this issue will be 'the thief of an equitable and healthy start to life for Australia's lead-exposed children.'

MACQUARIE UNIVERSITY

74th IChemE president takes office

Geoff Maitland, professor of energy engineering at Imperial College London, has become the 74th president of the Institution of Chemical Engineers (IChemE).

A graduate in chemistry from Oxford University, Maitland is a Fellow of IChemE, Royal Society of Chemistry, Energy Institute and the Royal Academy of Engineering.

During a distinguished industrial and academic career, Maitland enjoyed spells with Bristol University, Imperial College London, ICI and Schlumberger before returning to Imperial College London in 2005.

He is a vocal advocate of low-carbon, renewable energy and technologies such as carbon capture and storage (CCS) to mitigate what he describes as 'sleep-walking into a catastrophic climate change future'.

Maitland replaces Judith Hackitt CBE, chair of the GB Health and Safety Executive. Current honorary treasurer, Andrew Jamieson OBE, has been appointed IChemE deputy president.

Maitland said: 'During this year I will place particular emphasis on celebrating the contributions chemical engineering is making to the quality of life across the world.'

'Today, I am launching my campaign, ChemEng365, which will feature 365 chemical engineering successes and achievements throughout my year-long presidency. I will be encouraging my fellow members to visit my blogging website and contribute to a celebration of our profession.'

Joining IChemE's Council in 2014, the governing body for the Institution's 40 000 members worldwide, are Ken Rivers, former chief executive of Refining NZ; Iain Martin, divisional technology director for the Process Technologies Division at Johnson Matthey PLC; and Dr Jarka Glassey, reader in chemical engineering education at Newcastle University, UK.

INSTITUTION OF CHEMICAL ENGINEERS

Geoscientist recognised for pioneering work on volcanic glasses

Professor Donald Bruce Dingwell is the winner of the 13th Otto Schott Research Award, valued at €25 000. The Canadian experimental volcanologist has headed the Department of Mineralogy and Petrology at the Ludwig Maximilian University (LMU) in Munich since 2000 and is Director of the Department of Earth and Environmental Sciences. Dingwell received the award for his many years of research in the field of physical and chemical properties of volcanic glasses. 'His work on glass formation under extreme conditions like those that occur during volcanic activity provide us with valuable insights for use in industrial glass melting,' noted Dr Hans-Joachim Konz, Chairman of the Board of Trustees of the Ernst Abbe Fund and Member of the Board of Management of SCHOTT AG, during the award ceremony that was held

at an international conference on glass technology in Aachen.

Dingwell's research centres on the role of melts and glasses in geologic processes. He succeeded in documenting the central role that the glass transition plays in explosive volcanism. This makes him a pioneer in the quantification of thermodynamic and transport properties of molten silicates of both simple and complex compositions.

The Otto Schott Research Award is presented every two years by the Ernst Abbe Fund to recognise outstanding achievements in the area of fundamental research and technology development in the fields of glass and glass-ceramic sciences for the areas of application optics and electronics, renewable energies, health and lifestyle.

SCHOTT AG



Professor Donald Bruce Dingwell (second from left) receiving the Otto Schott Research Award 2014 from Dr Hans-Joachim Konz (second from right), member of the Board of Management of SCHOTT AG and Chairman of the Board of Trustees of the Ernst Abbe Fund. Also present, member of the Board of Trustees and laudator Professor Carlo Pantano (Penn State University) (right), and member of the Board of Trustees Professor Reinhard Conradt (RWTH Aachen) (left).

Stronger, lighter, tougher – creating better carbon fibre for the future

Deakin University researcher Linden Servinis is using clever chemistry to change carbon fibre surfaces, in a bid to make materials stronger and lighter with better crash-resistance. Servinis is using chemistry techniques to add ‘chemical arms’ to sections of the fibre surface previously thought to be unreactive.

Carbon fibre composites are solid materials made up of weaved carbon fibres covered in a layer of plastic resin. Servinis said when these materials were subjected to high impact, the fibres often pulled away from the resin, causing failure.

‘This research seeks to prevent composite failure by adding new chemical arms with reactive chemical hands at the ends. These hands can then grab onto the resin in a chemical reaction, and prevent failure, making a stronger material,’ Servinis said.

‘Carbon fibre composites are looking to be the next aluminium, with incredibly strong and light-weight properties they have incredible potential to maximise fuel efficiency.’ Servinis said recent interest in large-scale production of carbon fibre for automotive and aerospace had highlighted the importance of investigating the interaction between fibre and resin to maximise composite performance.

‘This and other research at Deakin is providing a better understanding of the subtle molecular interactions which can have a large impact on composite performance,’ Servinis said.

‘Current carbon fibre production includes an electrolytic oxidation process, which introduces oxygen functional groups to the surface, and roughens the fibre, which improves bonding between fibre and resin.

‘While the oxidation helps bonding, it does not introduce the “reactive chemical hands”, which can hold onto the resin layer the same way our chemical arms can.’

Servinis, whose project is part of a PhD she is undertaking with Deakin’s Carbon Nexus research facility, said not only had three separate chemistry techniques been shown to effectively graft these arms onto the surface, but they could also be designed to react specifically with each resin system chosen.

A combination of X-ray photoelectron spectroscopy, single-fibre testing, and single-fibre fragmentation techniques are used to validate each new technique, to ensure chemistry doesn’t degrade the fibres, while improving performance. Servinis said the research was part of a collaboration with the Australian Future Fibres Research and Innovation Centre and the CSIRO. She said her presentation as a finalist at the FameLab competition, which is designed to find, develop and mentor young science and engineering communicators, provided a valuable national platform to articulate the benefit of carbon fibre research.

SCIENCE IN PUBLIC

Abbebat juice station – precise Brix measurement of beverages containing pulp



Fruit juices are natural products with many ingredients. To ensure the expected product quality, these beverages have to meet the defined product specifications.

One of the most important quality analysis parameters in juice production is °Brix (°Bx), which represents the sugar concentration as well as the composition of the juice. Abbebat refractometers are fast and reliable instruments commonly used for °Brix measurements. However, many juices, especially orange juices, contain pulp, which remains in the beverage.

During measurement with a conventional refractometer, this pulp starts to deposit on the measuring prism, leading to unstable readings. The vertical set-up of the Abbebat juice station avoids the sedimentation of particles on the prism and ensures reliable and stable measuring results.

Abbebat juice station refractometers are easy to operate. The attached filling funnel allows fast and simple serial analyses: cleaning of the measuring prism is not required because the next sample flushes out the previous one. The automatic temperature control of the sample assures accurate measuring conditions.

For more information, please contact MEP Instruments on (02) 8899 5200 or info@mep.net.au or visit www.mep.net.au.



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Quality System
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Turning mining wastewater into rainwater

A new cost-effective technology to treat mining wastewater and reduce sludge by up to 90% has been used for the first time at a commercial mine.

The technology, called Virtual Curtain, was used to remove metal contaminants from wastewater at a Queensland mine and the equivalent of around 20 Olympic swimming pools of rainwater-quality water was safely discharged.

Sludge is a semisolid by-product of wastewater treatment and reducing the amount produced has huge environmental and economic benefits.

'Our treatment produced only a fraction of the sludge that a conventional lime-based method would have and allowed the mine water to be treated in a more environmentally sound way,' CSIRO scientist Dr Grant Douglas said.

'Reducing the amount of sludge is beneficial because the costly and timely steps involved to move and dispose it can be reduced.'

Given the Australian mining industry is estimated to generate hundreds of millions of tonnes of wastewater each year, the technology opens a significant opportunity for companies to improve water management practices and be more sustainable.

'The technology can produce a material high in metal value, which can be reprocessed to increase a miner's overall recovery rate and partially offset treatment costs,' Douglas said.

Virtual Curtain utilises hydrotalcites, which are minerals sometimes found in stomach antacids, to simultaneously trap a variety of contaminants – including arsenic, cadmium and iron – in one step.

Douglas and his team developed the technology after discovering that hydrotalcites could be formed by adjusting the concentrations of common



(Top) The new treatment in progress to remove a range of metal contaminants.
(Bottom) The mine pit following the release of the treated water

wastewater contaminants aluminium and magnesium to an ideal ratio and then by increasing the pH.

'By using contaminants already present in the wastewater we have avoided the need for expensive infrastructure and complicated chemistry to treat the waste,' he said.

'If required, the treated water can be purified much more efficiently via reverse osmosis and either released to the environment or recycled back into the plant, so it has huge benefits for mining

operators in arid regions such as Australia and Chile.

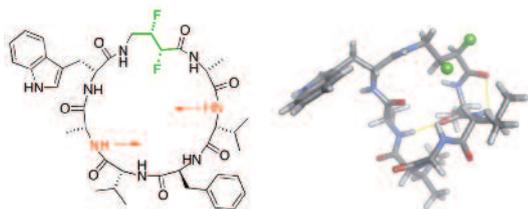
'It is a more efficient and economic way to treat wastewater and is enabling the global mining industry to reduce its environmental footprint and extract wealth from waste.'

The licensed technology, which can be applied to a range of industrial applications, is available through Australian company Virtual Curtain Limited.

CSIRO

F-tuning the shapes of cyclic peptides

Cyclic peptides have great potential as therapeutic agents because they can mimic larger proteins and thereby modulate protein–protein interactions. However, synthesising cyclic peptides is often an inefficient process and, furthermore, it is difficult to fine-tune the precise shape of the macrocycle in order



to optimise the biological potency. Researchers at the University of New South Wales have now demonstrated, for the first time, that stereoselective fluorination chemistry can overcome these limitations (Hu X.-G., Thomas D.S., Griffith R., Hunter L. *Angew. Chem. Int. Ed.* 2014, **53**, 6176–79). A team led by Dr Luke Hunter has efficiently synthesised several vicinal difluorinated analogues of the natural cyclic heptapeptide unguisin A. Remarkably, it was found that alterations to the configuration of the fluorine-bearing carbons had a profound effect on the peptide secondary structure, even at distant parts of the macrocycle. This discovery opens up future possibilities for optimising the properties of many other cyclic peptide drug leads.

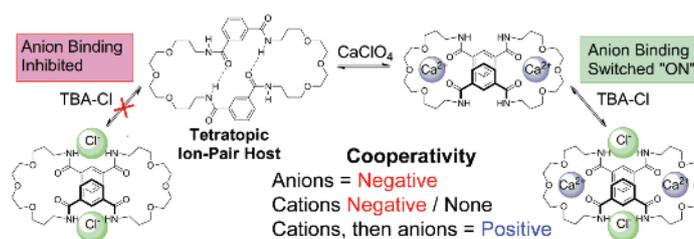
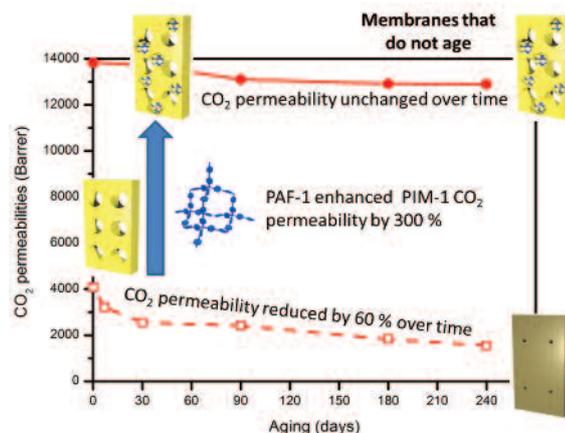
Cooperativity in an ion-pair host: Ca²⁺ switches ‘on’ Cl⁻ binding

Cooperative interactions play a very important role in both natural and synthetic supramolecular systems, as exemplified in the allosteric regulation of metabolic enzymes and oxygen binding to haemoglobin. Fundamental questions regarding cooperativity continue to challenge and fascinate researchers, and simple supramolecular systems provide an excellent platform for addressing these questions. The Thordarson group at the University of New South Wales has reported a tetratopic ion-pair host (receptor) that can bind up to two anions and two cations simultaneously, showing a rich collection of cooperative binding properties (Howe E.N.W., Bhadbhade M., Thordarson P. *J. Am. Chem. Sci.* 2014, **136**, 7505–16). Anions and cations on their own (i.e. with a non-binding counterion such as

Ageless separations

Industrial separations are responsible for up to 40% of the world’s energy demands. Membranes, with their continuous mode of operation, are one of the most energy-efficient options for reducing this demand. Due to their internal

porosity, stemming from low-density chain packing, super-glassy polymers deliver prolific transport pathways, and are most attractive for use in membranes. Unfortunately, they age badly over time, the chains packing to a denser and hence less permeable state, making them unattractive for long-term application. Researchers at CSIRO in Melbourne, in collaboration with Monash, ANU and the University of Colorado, have discovered that a specific ultraporous framework known as PAF-1 can prop open the polymer chains and stop ageing, while also tripling the gas permeability in the system (Lau C.H., Nguyen P.T., Hill M.R., Thornton A.W., Konstas K., Doherty C.M., Mulder R.J., Bourgeois L., Liu A.C.Y., Sprouster D.J., Sullivan J.P., Bastow T.J., Hill A.J., Gin D.L., Noble R.D. *Angew. Chem. Int. Ed.* 2014, **53**, 5322–6). The bulky side chains of polyacetylenes, or bulky chemical moieties on polymers with intrinsic microporosity, are physically tethered within the pores of PAF-1; consequently, polymer chain relaxation is prevented. The study has implications for carbon capture, dye removal, natural gas purification, hydrocarbon separations and biofuel purification.



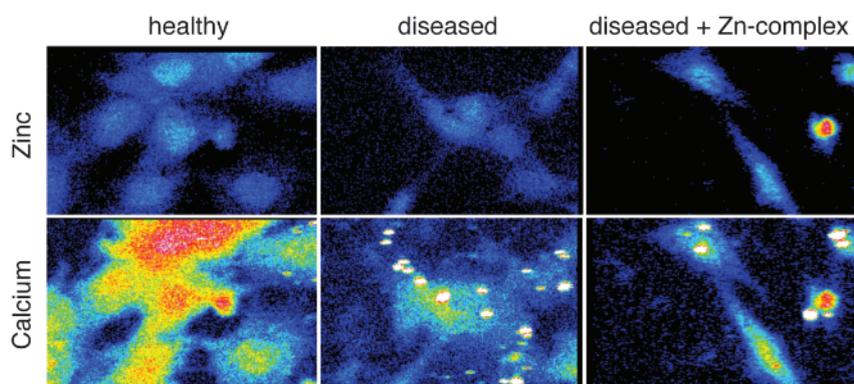
tetrabutylammonium or perchlorate) show negative cooperativity towards this host, and in a protic solvent mixture, anion binding is completely inhibited. However, in that same protic solvent, the addition of Ca²⁺ switches ‘on’ Cl⁻ binding, with Cl⁻ now showing positive cooperativity towards the host! The insight that this work gives into cooperativity could allow better design of cooperative synthetic supramolecular systems for information transfer and catalysis.

Probing subcellular biometal disturbances in neurodegeneration

Biometals are important in the pathogenesis of neurodegenerative brain disorders. However, limited resolution of current analytical approaches to measuring metal biodistribution has led to a roadblock in our understanding of the disease process. Bulk tissue metal analysis often masks important subtle changes at the subcellular level. To

address this problem, the groups of Associate Professor Anthony White and Dr Paul Donnelly, University of Melbourne, together with Australian Synchrotron scientists, and collaborators in the US and Finland, have applied X-ray fluorescence microscopy (XFM) to neurons grown from an animal model of the childhood brain disease neuronal ceroid

lipofuscinosis (Grubman A., James S.A., James J., Duncan C., Volitakis I., Hickey J.L., Crouch P.J., Donnelly P.S., Kanninen K.M., Liddell J.R., Cotman S.L., de Jonge M.D., White A.R. *Chem. Sci.* 2014, **5**, 2503–16). Bulk biometal analysis by inductively coupled plasma mass spectrometry revealed no changes to overall metal levels in the neurons. However, XFM revealed major disturbances to subcellular biometal homeostasis, with a critical loss of correlation between nuclear and cytosolic zinc and calcium levels in diseased cells. These defects could be largely rectified by application of a cell-permeable zinc-complex (bis(thiosemicarbazone)) to the cells. The researchers are now probing at higher resolution to determine where the subcellular biometal changes are most prominent and how homeostasis is restored by metal complexes.

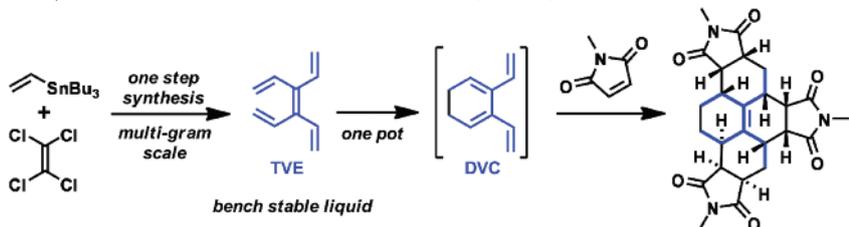


Tetravinylethylene resurrected

The unique hydrocarbon tetravinylethylene (TVE), featuring both cross- and through-conjugation, first succumbed to total synthesis some 50 years ago. Surprisingly, this milestone in hydrocarbon chemistry provided little information about its chemical and physical properties, presumably due to difficulties associated with accessing significant quantities of material from its low-yielding synthesis (<0.1% yield, four steps). ANU PhD student Erik Jan

Lindeboom, from the Sherburn group, has resurrected this understudied hydrocarbon in spectacular fashion, by developing a scalable one-step synthesis of TVE using cross-coupling chemistry from commercially available starting materials (Lindeboom E.J., Willis A.C., Paddon-Row M.N., Sherburn M.S. *Angew. Chem. Int. Ed.* 2014, **55**, 5440–3). The new synthesis, featuring a four-fold Stille cross-coupling reaction between vinyltributyltin and tetrachloroethylene,

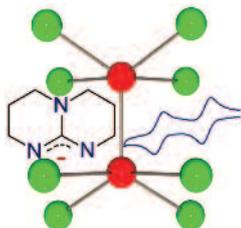
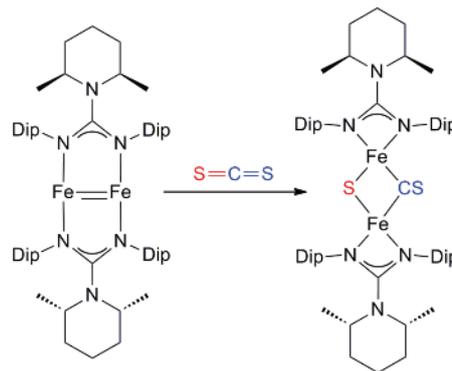
provides TVE in a single-pot operation and, importantly, in gram quantities. This type of multi-cross-coupling reaction is the first of its kind. Perhaps surprisingly, the parent hydrocarbon TVE was found to be bench stable at room temperature, and easily transformable into 2,3-divinyl-1,3-cyclohexadiene (DVC) through a 6π electrocyclic reaction under either thermal or photochemical conditions. DVC could then be taken on, without further purification, through a triple-Diels–Alder reaction sequence that produces a single compound of remarkable structural complexity (six new C–C bonds, three new rings and 10 stereogenic centres). Research is now underway to utilise this π -bond rich hydrocarbon in the synthesis of complex bioactive natural products.



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

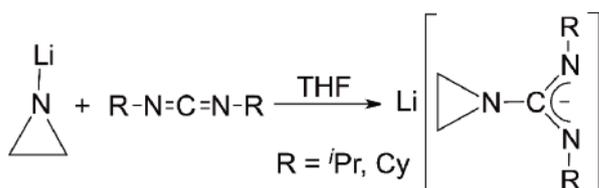
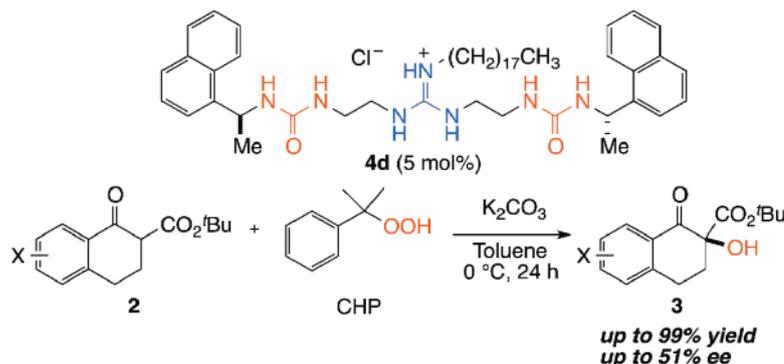
Aust J Chem

The July issue is dedicated to the chemistry of guanidine, guanidinium and guanidinate derivatives. Leo Fohlmeister and Cameron Jones (Monash University) synthesised and investigated the reactivity of low-valent $\text{Fe}^{\text{I}}\text{-Fe}^{\text{I}}$ complexes stabilised by a bulky guanidinate ligand, such as the $\text{Fe}=\text{Fe}$ compound shown, which has a very short $\text{Fe}\text{-Fe}$ distance. Its reaction with CS_2 led to reductive $\text{C}=\text{S}$ bond cleavage and the isolation of the $\{[(\text{Pipiso})\text{Fe}]_2(\mu\text{-S})(\mu\text{-CS})\}$ compound.



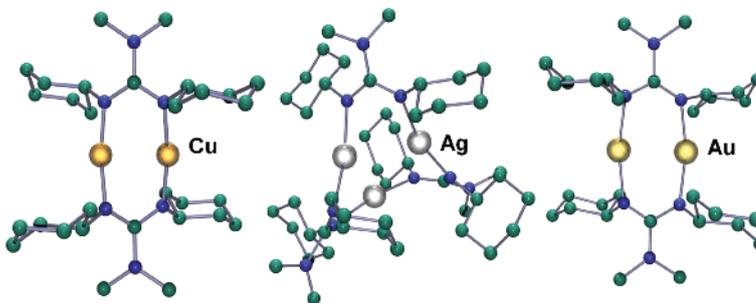
Carlos A. Murillo (Texas A&M) describes 'A Magic Equation: Delta Bonds Plus Bicyclic Guanidates Equals Strong Reducing Agents'. Reactions of bicyclic guanidates with dimolybdenum and ditungsten precursors possessing quadruply bonded dimetal units with $s^2p^4d^2$ electron configuration generated very strong reducing agents. Analogous rhenium compounds led to the formation of dimetal species in unusually high oxidation states. The properties of these compounds are attributed to the interaction of the p electrons of the $\text{C}(\text{N})_3^-$ guanidinate core with the electrons in the delta bond of the dimetal units.

Kazuo Nagasawa and co-workers (Tokyo University of Agriculture and Technology) report on a new class of bifunctional guanidine-bisurea organocatalysts such as **4d**, with chiral centres located outside the urea groups. With these catalysts, α -hydroxylation of β -keto esters is achieved in yields up to 99% and ee up to 51%.

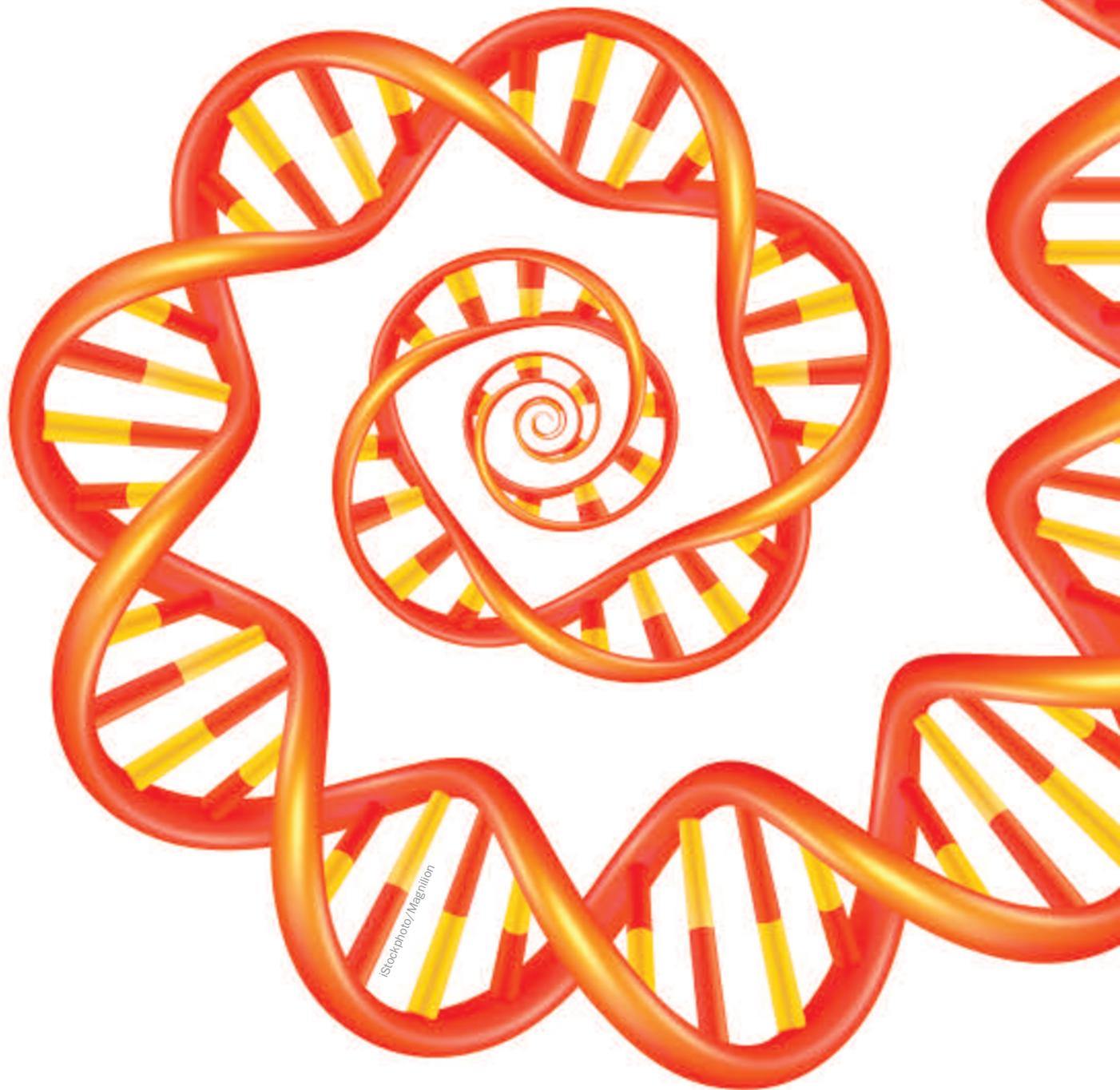


Frank T. Edlmann et al. (University of Magdeburg, Germany) report on the first aziridinyl-guanidates as new precursors for potentially volatile metal complexes. The lithium-aziridinylamidates, $\text{Li}[(\text{C}_2\text{H}_4\text{N})\text{C}(\text{NR})_2]$ shown were prepared by addition of *N*-aziridinyl lithium, $\text{C}_2\text{H}_4\text{NLi}$, to dialkyl carbodiimides. The cyclohexyl derivative was obtained in the form of crystalline solvent adducts $\{\text{Li}[(\text{C}_2\text{H}_4\text{N})\text{C}(\text{NR})_2]\text{S}\}_2$ ($\text{S} = \text{THF}$ or Et_2O). X-ray crystallography characterised them as ladder-type dimeric molecular structures. The chemistry of guanidinate anions is of significant current interest in terms of the synthesis of homogeneous catalysts and volatile metal precursors.

Scott Bunge et al. (Kent State University) report synthesis and characterisation of group 11 guanidinate complexes derived from dicyclohexylcarbodiimide. The addition of lithium dialkylamides to dicyclohexylcarbodiimide yielded lithium 2,2-dialkyl-1,3-dicyclohexylguanidates. Further reaction with a group 11 halide (CuCl , AgBr and AuCl) generated oligonuclear complexes with the general formula $\{\text{M}[\text{CyNC}(\text{NR})_2\text{NCy}]\}_n$, where M, R, and n are respectively Cu, CH_3 , 2; Cu, CH_2CH_3 , 2; Ag, CH_3 , 3; Ag, CH_2CH_3 , 3; Au, CH_3 , 2; and Au, CH_2CH_3 , 2 (examples shown). Group 11 guanidinate compounds are of interest because of their potential to have closed shell $d^{10}\text{-}d^{10}$ metal interactions, as reagents for atomic layer deposition, and for their luminescent properties.



Curt Wentrup FAA, FRACI CChem (wentrup@uq.edu.au) <http://researchers.uq.edu.au/researcher/3606>



BY **DAVE SAMMUT**

This year is the International Year of Crystallography, an area of science important to me due to my own family ties (see box p. 20). Given the connection, I have been keen to write something to acknowledge the celebration.

I initially thought along the lines of Australia's Bragging rights to the science, most particularly because William Lawrence Bragg was born and raised in Adelaide. It is, after all, a grand Australian tradition to lay claim to its share of the accolades of its sons and daughters, no matter how far flung

their exploits. Indeed, the tradition can stretch to our country's nephews and nieces, and any immediate neighbours who have ever resided here, no matter how fleetingly (I'm looking at you, Russell Crowe).

However, as I continued to read, I found myself utterly compelled by the great race that took place following the initial establishment of the science. The competition between research houses, between the great luminaries of the day, and between the internal factions and personalities makes for a simply thrilling story.



THE INNER SPACE RACE

The emergence of X-ray crystallography is the story of an earnest dash to the then-elusive double helix.

William Lawrence Bragg (1890–1971) was born into the Australian colonies at a time of great change. Just months before, Henry Parkes had delivered his Tenterfield address, and the colonies were wrangling with the formation of a new nation. Within just four years, the South Australian parliament would be only the second in the world to grant women the vote. Shortly after his tenth birthday, the first electric lights would appear on the streets of Adelaide.

Before Lawrence was even a teenager, new discoveries had revolutionised physics. In 1895, Wilhelm Roentgen discovered the existence of X-rays, although at that point they were still considered a particle. Henri Becquerel and Marie Curie had both made key discoveries in the radioactive properties of uranium and other elements. Indeed,

the first recorded surgical use of X-rays in Australia was by William Henry Bragg (Lawrence's father and future co-recipient of the Nobel Prize), investigating five-year-old Lawrence's broken arm after he fell from his tricycle.

A brilliant young man, Lawrence graduated at age 18 from the University of Adelaide; then, moving back to England with his family, he went on to graduate with honours from Cambridge at age 22. He was just starting as a research student at Cambridge when it was announced that Max von Laue had observed the diffraction of X-rays by crystals, for which he won the Nobel Prize just two years later in 1914. The rapidity of the awarding of this honour shows just how evident was the importance of this discovery. And after just three years of work, the two Braggs published the

seminal work *X rays and crystal structure* in 1915, for which they were awarded the Nobel Prize the same year.

... the first recorded surgical use of X-rays in Australia was by William Henry Bragg ... investigating five-year-old Lawrence's broken arm after he fell from his tricycle.

Bragg's group published first in 1950, but their model was shown to be flawed, and he was once again trumped by Pauling's team with the correct solution in 1951 – the helical structure of fibrous protein.

From there, Lawrence Bragg's rise was meteoric. He became the professor of physics at Manchester University in 1919, and the head of the Cavendish Lab in 1938 – succeeding Ernest Rutherford in the role.

Across the Atlantic, a rival was emerging – Linus Pauling (1901–94). Inspired by the Braggs' book, Pauling had conducted his own first determination of molybdenite crystal structure in 1922. On a Guggenheim Fellowship, Pauling studied revolutionary quantum mechanical theory under Niels Bohr and Erwin Schrodinger. Returning to the

USA, he spent five prolific years to 1932, during which he published approximately 50 papers, was awarded the Langmuir Prize by the American Chemical Society for the most significant work in pure science by a person 30 years of age or younger, and produced the seminal work 'The Nature of the Chemical Bond', published in the *Journal of the American Chemical Society*.

During this time, both Pauling and Bragg developed sets of rules for interpreting X-ray diffraction patterns from more complicated crystals. But to Bragg's chagrin, Pauling published first, and a rivalry was established that would last for another 20 years.

In the years that followed, X-ray crystallography was applied to increasingly complex molecules. New discoveries were being compared against theoretical considerations – in some cases as sophisticated as cutting pieces of paper into the shapes of molecular subunits (such as the amino acids that make proteins) and then pushing them around to consider and eliminate alternatives. In combination, these pieces of information were being used to elucidate the structures of the molecular building blocks to life itself.

The British took the lead in the 1920s, with William Astbury working in Bragg's group at the Royal Institute to provide the first X-ray diffraction pictures of fibrous protein. By the 1930s, Astbury had correctly showed that globular protein modules such as haemoglobin are made up of long-chain proteins (polypeptides) that are folded to make balls.

However, the Americans were not to be outdone. Caltech researchers Roscoe Dickinson (doctoral adviser to Pauling) and Albert Raymond definitively showed in 1923 that

A crystallography career

My late father-in-law, Don Craig (1936–2009), will have been known to many RACI members through his 54-year career in crystallography at the University of New South Wales, stretching right back to the days when it was still the Technical Institute. The UNSW School of Chemistry wrote that Don 'will always be linked with crystallography at UNSW. His tireless work, enthusiasm and encyclopaedic crystallographic knowledge benefited many UNSW postgraduate students over his 51 years of service to the University, resulting in over 400 peer-reviewed articles.'

Don is remembered at the university through the Don Craig Memorial Prize to honour the very significant contributions that he made to the School and the field of crystallography. The prize was won in 2014 by PhD student Matthew Gyton, with the prize presented by Don's long-standing friend, Emeritus Professor Brynn Hibbert.

As a loving family member, I would add that Don had the rare gift of being able to recognise what he loved doing in life, and the determination to stick with it. He didn't want promotion or wealth. For the love of science, he just did his research, raised a family and a social 'cleansing ale', and was content with his life. He will always be missed.

molecules have a three-dimensional arrangement and that within a crystal these molecules are discrete and separated by distances greater than the molecular covalent bonds.

In the mid-1930s, Pauling struck out from his early interest in inorganic molecular structures to biological, citing Astbury's work in his considerations.

Both sides were severely interrupted by the war, but by the late 1940s, both were actively working towards the problem of coiling a polypeptide in three dimensions.

Bragg's group published first in 1950, but their model was shown to be flawed, and he was once again trumped by Pauling's team with the correct solution in 1951 – the helical structure of fibrous protein. The Caltech team published no fewer than seven papers in the May 1951 *Proceedings of the National Academy of Sciences*, laying out the detailed chemical structure of hair, feathers, silk and other proteins.

The obvious next step was DNA itself, first identified in the 1940s. The race was in full swing, but politics and personality came to play a critical role. Both of the facilities in Britain capable of conducting the research were funded by the Medical Research Council. With limited funding available, a gentleman's agreement was made that the team at King's College under Maurice Wilkins would get the first go at the DNA problem. But within the King's team personalities, and apparently also misogyny, meant that the gifted young researcher Rosalind Franklin was being frozen out by Wilkins.

It therefore fell to an interloper team – US chemist James Watson and British physicist Francis Crick, with the latter working unofficially from a deep interest in the issue. Indeed, Crick was reportedly twice told by Bragg to leave DNA to the King's team and concentrate on his own PhD. According to my reading, Bragg only came to support the work when in late 1952

Pauling claimed in a letter to his son (at Cambridge) that his team was coming close to solving the problem.

X-ray diffraction photographs were critical to this work, but the only images available were those from Astbury from 1938. The images were not improved until Franklin took up the subject, and Watson's work was hampered by the lack.

Watson attended a talk given by Franklin at King's, which by his own later account (*The double helix*) he did not fully understand, but based upon which he and Crick came up with a first model of DNA that was presented to Franklin and Wilkins. This was so roundly criticised as to leave the pair thoroughly chagrined.

Serendipitously, in 1952 the pair chanced to have two critical conversations. Discussing the issue with mathematician John Griffith, Crick first raised the idea that nucleotide bases might somehow fit together to hold the DNA molecule. And in a chance discussion with biochemist Erwin Chargaff (inventor of Chargaff's rules, of which Watson was ignorant), it was noted that samples of DNA always contain equimolar base ratios of adenine and guanine, thymine and cytosine. Together, this pointed Watson and Crick to a DNA structure involving pairs of long-chain molecules, linked by A–G and C–T.

Armed with an advance copy of Pauling's paper incorrectly proposing a three-stranded DNA model, Watson visited Wilkins at King's, who responded by showing him (without Franklin's knowledge or permission) one of Franklin's best X-ray photographs. The photo was the critical piece of missing evidence, and in combination with the information from Griffith and Chargaff, Watson and Crick were able to finish their work.

This major breach arguably cost Franklin her due recognition and her share of the ensuing Nobel Prize. Just one day before the event, she had finished the first draft of her own paper, which appeared alongside that

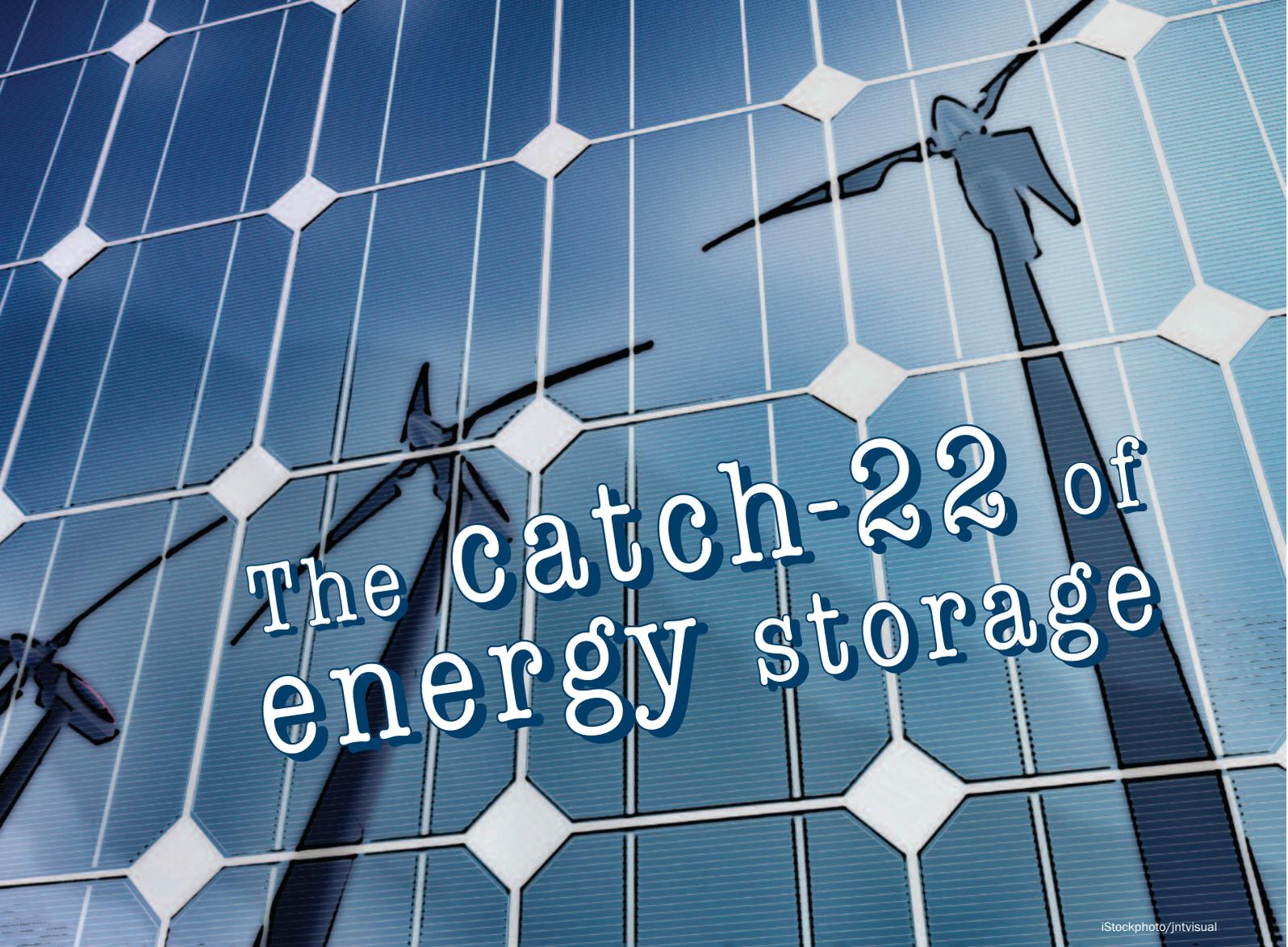


William Henry Bragg's X-ray spectrometer as used by him and his son William Lawrence Bragg to investigate the structure of crystals

of Watson and Crick, and a third paper by Wilkins and his colleagues in the 25 April 1953 issue of *Nature*. Franklin died of cancer in 1958, never receiving her due acknowledgement in the 1962 awarding of the Nobel Prize in Physiology or Medicine (awarded to up to three recipients per year; Nobel Prizes were rarely given posthumously), which went to Crick, Watson and Wilkins. Had Franklin lived, would she have received a Nobel Prize? Watson was only to come clean on the matter in his autobiographical account in 1968.

This was neither the first controversy in the relentless advance of science, nor was it the last, but who could fail to be inspired by the race to discover our inner space?

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The catch-22 of energy storage

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Pick up a research paper on battery technology, fuel cells, energy storage technologies or any of the advanced materials science used in these fields, and you will likely find somewhere in the introductory paragraphs a throwaway line about applications to the storage of renewable energy. Energy storage makes sense for enabling a transition away from fossil fuels to more intermittent sources such as wind and solar, and the storage problem presents a meaningful challenge for chemists and materials scientists.

Or does it? Several recent analyses of the inputs to our energy systems indicate that, against expectations, energy storage cannot solve the problem of intermittency of wind or

solar power. Not for reasons of technical performance, cost or storage capacity, but for something more intractable: there is not enough surplus energy left over after construction of the generators and the storage system to power our present civilisation.

The problem is analysed in an important paper by Weißbach et al. (*Energy* 2013, vol. 52, p. 210) in terms of energy returned on energy invested, or EROI – the ratio of the energy produced over the life of a

BY **JOHN MORGAN**

Renewable energy sources pose the problem of intermittency.

Is storage the answer?

power plant to the energy that was required to build it. It takes energy to make a power plant – to manufacture its components, mine the fuel, and so on. The power plant needs to make at least this much energy to break even. A break-even power plant has an EROI of 1. But such a plant would be pointless, as there is no energy surplus to do the useful things we use energy for.

A minimum EROI, greater than 1, is required for an energy source to be

Origins of EROI

The concept of EROI was introduced by US fisheries ecologist Charles Hall, who noted that the energy a predator gained from eating prey had to exceed the energy expended in catching it. In 1981, Hall applied this net energy analysis to our own power generation activities, charting the decline of the EROI of US oil as ever more drilling was required to yield a given quantity, and suggesting the possibility that oil may one day take more energy to extract than it yields. Hall and others have since estimated the EROI for various power sources, a difficult analysis that requires identification of all energy inputs to power production.

EROI is a fundamental thermodynamic metric on power generation. Net energy analysis affords high-level insights that may not be evident from looking at factors such as energy costs, technological development, efficiency and fuel reserves, and sets real bounds on future energy pathways. It is unfortunately largely absent from energy and climate policy development.

able to run society. An energy system must produce a surplus large enough to sustain things such as food production, hospitals, transport, construction, universities to train the engineers to build the plant, and all the elements of the civilisation in which it is embedded.

For countries like the US and Germany, Weißbach et al. estimate this minimum viable EROI to be about 7. An energy source with lower EROI cannot sustain a society at those levels of complexity, structured along similar lines. If we are to transform our energy system, in particular to one without climate impacts, we need to pay close attention to the EROI of the end result.

The EROI values for various electrical power plants are summarised in the figure on page 24. The fossil fuel power sources we're most accustomed to have a high EROI of about 30, well above the minimum requirement. Wind power at 16, and concentrating solar power (CSP, or solar thermal power) at 19, are lower, but the energy surplus is still sufficient, in principle, to sustain a developed industrial society. Biomass, and solar photovoltaic (at least in Germany), however, cannot. With an EROI of only 3.9 and 3.5 respectively, these power sources cannot support with their energy alone both their own

fabrication and the societal services we use energy for in a developed nation.

These EROI values are for energy directly delivered (the 'unbuffered' values in the figure). But things change if we need to store energy. If we were to store energy in, say, batteries, we must invest energy in mining the materials and manufacturing those batteries. So a larger energy investment is required, and the EROI consequently drops.

Weißbach et al. calculated the EROIs, assuming pumped hydroelectric energy storage. This is the least energy-intensive storage technology. The energy input is mostly earthmoving and construction. It's a conservative basis for the calculation; chemical storage systems requiring large quantities of refined specialty materials would be much more energy intensive. Carbajales-Dale et al. (*Energy Environ. Sci.* doi: 10.1039/c3ee42125b) cite data asserting batteries are about ten times more energy intensive than pumped hydro storage.

Adding storage greatly reduces the EROI (the 'buffered' values in the figure). Wind 'firmed' with storage, with an EROI of 3.9, joins solar PV and biomass as an unviable energy source. CSP becomes marginal (EROI ~9) with

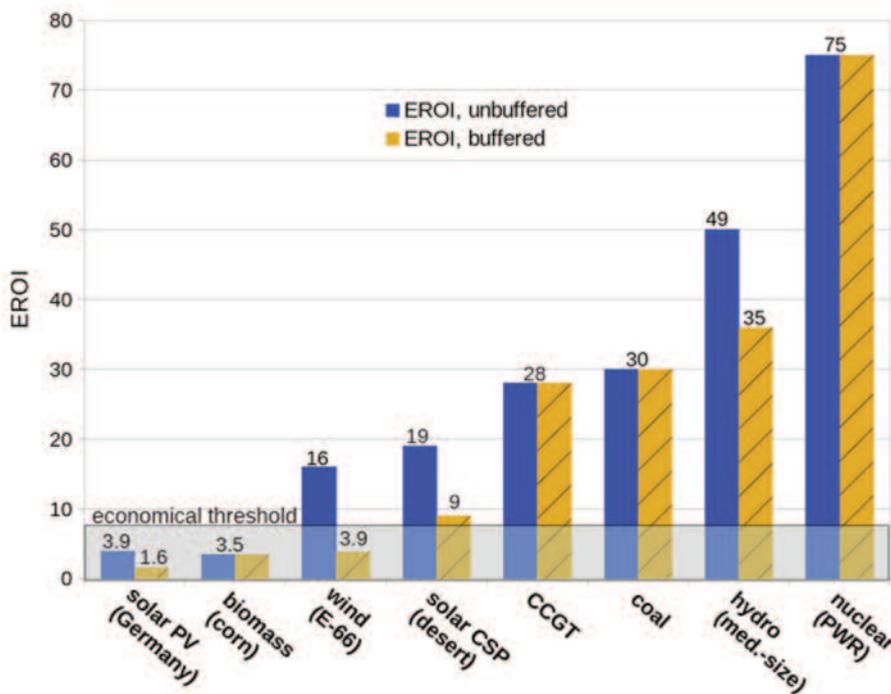
pumped storage, so is probably not viable with molten salt thermal storage. The EROI of solar PV with pumped hydro storage drops to 1.6, barely above break even, and with battery storage is likely in energy deficit.

This is a rather unsettling conclusion if we are looking to renewable energy for a transition to a low-carbon energy system: we cannot use energy storage to overcome the variability of solar and wind power.

In particular, we can't use batteries or chemical energy storage systems, as they would lead to much worse figures than those presented by Weißbach et al. Hydroelectricity is the only renewable power source that is unambiguously viable. However, hydroelectric capacity is not readily scaled up as it is restricted by suitable geography, a constraint that also applies to pumped hydro storage.

This particular study does not stand alone. Closer to home, Springer have just published a monograph (G. Palmer, *Energy in Australia: peak oil, solar power, and Asia's economic growth*, 2014) that contains an extended discussion of energy systems with a particular focus on EROI analysis, and draws similar conclusions to those of Weißbach. The study by Carbajales-Dale et al. is more optimistic, ruling out storage for most forms of solar, but suggesting it would be viable for wind. However, this viability is judged only on achieving an energy surplus (EROI > 1), not sustaining society (EROI ~ 7), and excludes the round-trip energy losses in storage, finite cycle life, and the energetic cost of replacement of storage. Were these included, wind would certainly fall below the sustainability threshold.

It is important to understand the nature of this EROI limit. This is not a question of inadequate storage capacity – we can't just buy or make more storage to make it work. It is not a question of energy losses during charge and discharge, or the number



Energy returned on energy invested with and without energy storage (buffering). CCGT is closed-cycle gas turbine. PWR is a pressurised water (conventional nuclear) reactor. Energy sources must exceed the 'economic threshold', of about 7, to yield the surplus energy required to support an OECD level society. Reprinted from *Energy*, vol. 52, D. Weißbach, G. Ruprecht, A. Huke, K. Czerski, S. Gottlieb, A. Hussein, Energy intensities, EROIs (energy returned on invested), and energy payback times of electricity generating power plants, pp. 210–221, Copyright 2013, with permission from Elsevier.

The best way to think about wind and solar is that they can reduce the emissions of fossil fuels, but they cannot eliminate them.

of cycles a battery can deliver. We can't look to new materials or technological advances, because the limits at the leading edge are those of earthmoving and civil engineering. The problem can't be addressed through market support mechanisms, carbon pricing or cost reductions. This is a fundamental energetic limit that will likely only shift if we find less materially intensive methods for dam construction.

This is not to say wind and solar have no role to play. They can expand within a fossil fuel system, reducing overall emissions. But without storage, the amount we can integrate in the grid is greatly limited by the stochastically variable output. We could, perhaps, build out a generation of solar and wind and storage at high penetration. But we would be doing so on an endowment of fossil fuel net energy, which is not sustainable.

Without storage, we could smooth out variability by building redundant generator capacity over large distances. But the additional infrastructure also forces the EROI down to unviable levels. The best way to think about wind and solar is that they can reduce the emissions of fossil fuels, but they cannot eliminate them. They offer mitigation, but not replacement.

Nor is this to say there is no value in energy storage. Battery systems in electric vehicles clearly offer potential to reduce dependency on, and emissions from, oil (provided the energy is sourced from clean power). Rooftop solar power combined with four hours of battery storage can usefully timeshift peak electricity demand, reducing the need for peaking power plants and grid expansion. And battery technology advances make possible many of our

recently indispensable consumer electronics. But what storage can't do is enable significant replacement of fossil fuels by renewable energy.

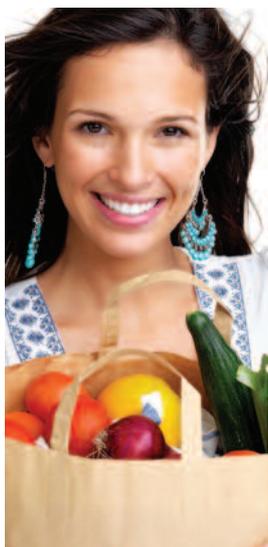
If we want to cut emissions and replace fossil fuels, it can be done, and the solution is to be found in the upper right of the figure. France and Ontario, two modern, advanced societies, have all but eliminated fossil fuels from their electricity grids, which they have built from the high EROI sources of hydroelectricity and nuclear power. Ontario in particular recently burnt its last tonne of coal, and each jurisdiction uses just a few per cent of gas-fired power. This is a proven path to a decarbonised electricity grid.

But the idea that advances in energy storage will enable renewable energy is a chimera – the catch-22 is that in overcoming intermittency by adding storage, the net energy is reduced below the level required to sustain our present civilisation.

John Morgan is Chief Scientist at Pooled Energy, developing smart grid and grid-scale energy storage technologies. He is Adjunct Professor in the School of Electrical and Computer Engineering at RMIT, holds a PhD in physical chemistry, is an experienced industrial R&D leader and is an inventor on over 80 patents.

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Lieutenant-General Sir John Monash

An engineer on the battlefield

BY **FRANK EASTWOOD**

The Battle of Hamel on 4 July 1918 was the first operational task planned and executed by John Monash as a Corps Commander. It broke conventional military wisdom and demonstrated that with new tactics the static nature of trench warfare could be overcome.

Sir John Monash, c. 1919 (photograph with hand colouring)
State Library of Victoria

John Monash (1865–1931) joined the militia in 1887 at the age of 22 and was commissioned into the Garrison Artillery, responsible for the Victorian coastal guns. In 1914, at the age of 49 and with the rank of Major, he was chosen to command the 4th Infantry Brigade.

Monash had degrees in arts, engineering and law and had decided to make his career in engineering and in the military. He had learnt chemistry, physics and mathematics and had trained for years in the artillery. His knowledge of the explosives being developed by Alfred Nobel for use in munitions, quarrying and mining and the shift from muzzle-loading smooth-bore cannons to breech-loading rifled artillery with new propellants, and the changes from muskets to rifles and machine guns, made him more knowledgeable than his peers about weaponry and he kept abreast of all such developments throughout his career. His practice in law gave him a remarkable ability to expound a subject and to write unambiguous orders, and he was renowned for his attention to detail.

Senior officers in the militia or the permanent army had no way of experiencing wartime command. Inexperienced men were led by inexperienced officers. At Gallipoli, commanding the 4th Brigade (4100 men), Monash was learning his trade and was promoted to Brigadier and then Major General. The men were equipped to fight open warfare but had to fight in trenches, which were totally outside anybody's experience – all had to learn quickly. Throughout his life, Monash welcomed any chance to broaden his knowledge, understanding and experience, and he showed he could withstand the immense strains of command in warfare.

In 1916, Monash moved with the 4th Brigade from Egypt to Flanders, but after a short time on the front went to England to train the newly formed 3rd Australian Regiment (27 000 men),

which he led in Flanders under the command of superiors in 1917. Monash could demonstrate leadership, expertise and ability but, while under orders from senior commanders, not his own creative originality.

On 21 March 1918, with his troops resting near Boulogne in France, Monash was ordered to create a defensive line east of Amiens, to help stop the German spring offensive. Then, most of the Australians making up the Australian Corps were brought together under the command of General Sir William Birdwood. Monash took command of the Australian Corps (166 000 men) on 31 May as part of the 4th British Army under the command of Lord Rawlinson and began his period of leadership with the battle of Hamel, 20 kilometres due east of Amiens, to remove a German intrusive strong point and straighten his front line.

Monash's career as a project engineer building railways and bridges convinced him of the need to complete work on time and within budget, and of the need to care for his workforce and maintain their numbers. He had seen the terrible waste of men on the battlefields. Monash expressed his view that:

The true role of the infantry was not to expend itself upon heroic effort, not to wither away under merciless machine gun fire, not to impale itself on hostile bayonets but, on the contrary, to advance under the maximum possible array of mechanical resources, in the form of guns, machine guns, tanks, mortars and aeroplanes; to advance with as little impediment as possible; to be relieved as far as possible of the obligation to fight their way forward.

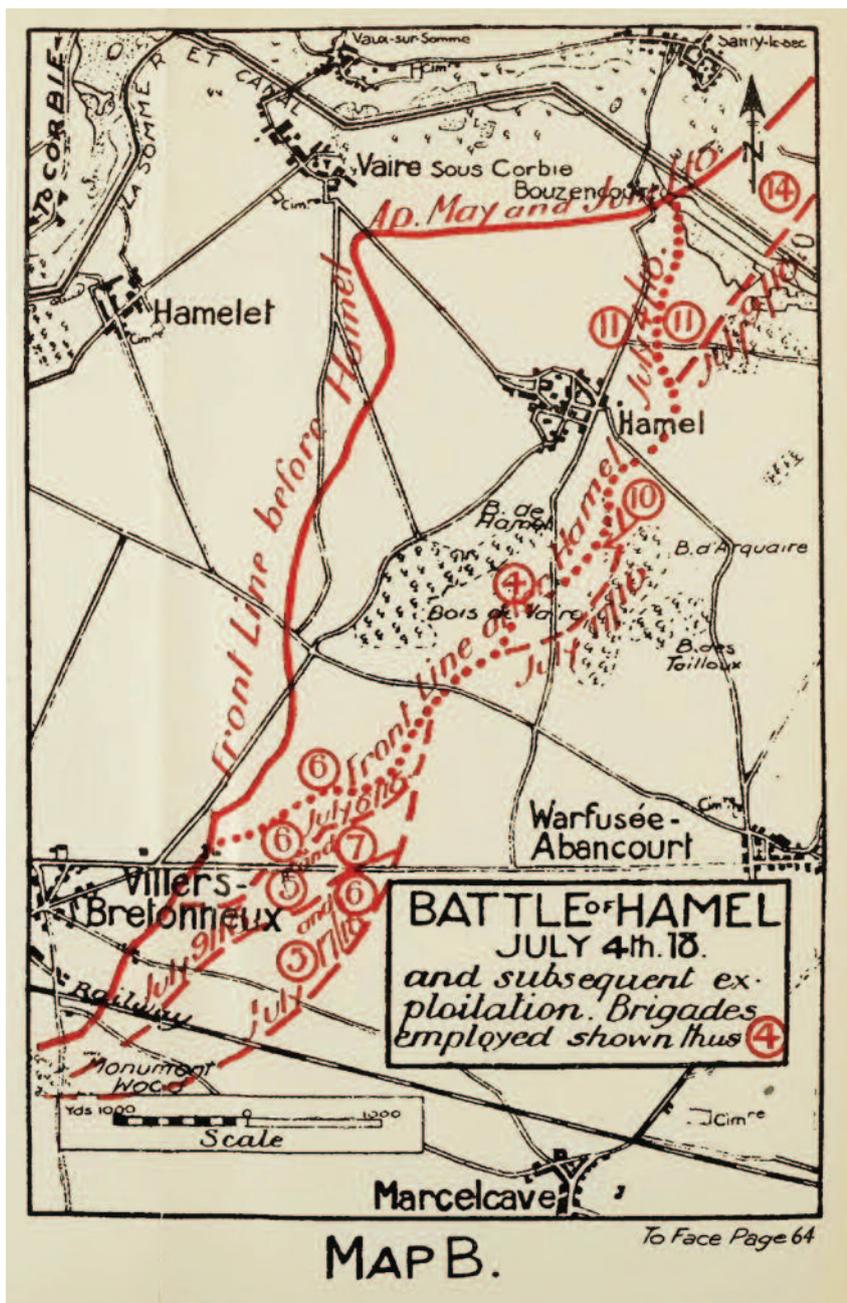
A.G. Serle, *John Monash. A biography*, Melbourne University Press, 1982, p. 386.

The job of the infantry was to mop up all resistance and consolidate the gains. There had been no Allied offensive since the Passchendaele fighting in autumn 1917 and Monash was ambitious for the Australians to

show the way in pushing back the Germans. His thinking at Hamel was based on the arrival of new Mark V tanks, which were greatly superior to earlier models with which the Australians had had bad experiences. The tanks and their crews and the men were introduced well to the rear where the men could climb over and in the tanks, watch them being driven and try their hand at driving. What Monash insisted on was that each tank had one job to perform and took orders from the infantry officer commanding the troops it was accompanying. The tanks would flatten the barbed wire and eliminate the machine guns by pirouetting on the emplacements.

Monash said the starting line for a major attack should be straight so that the artillery could move the barrage in steps in front of the advancing tanks and troops. Errors in ranging and sighting the guns, which changed with wear, were measured on a special range in the rear so that ranging shots were not needed. At intermediate objective lines, troops halted to ensure command systems were in order and to permit fresh men to lead the advance. The final line must not be

Monash's career as a project engineer building railways and bridges convinced him of the need to complete work on time and within budget, and of the need to care for his workforce and maintain their numbers.



Battle of Hamel, 4 July 1918

From Monash J., *The Australian victories in France in 1918*, Hutchinson and Co., London, 1920; ebook produced by Ned Overton and available at <http://gutenberg.net.au>

overrun by the men so that the defences could be consolidated while the barrage protected them from counter-attack.

Two men, whose job it was to provide small arms ammunition, were required to carry one box of 1000 rounds, which a machine gun might use in five minutes, and they were

vulnerable on the battlefield. Monash used supply tanks and aeroplanes to deliver such ammunition, the planes dropping two boxes with parachutes from bomb racks. This allowed the machine guns to be used offensively. Aircraft were also used to harry the enemy by bombing gun emplacements and disrupting supply

systems in the rear, for observation to assist the artillery and by strafing (attacking ground targets from low-flying aircraft) German troops.

Monash had instituted the practice of, in general harassing fire, artillery firing both smoke and gas shells. This meant that the Germans always put their gas masks on when they saw the smoke and smelt the gas. On the morning of an attack, only smoke shells would be fired, which gave the Australians an immediate advantage because they did not have to wear masks. Smoke bombs, which were introduced for mortars, made it possible to blind a single machine gun.

The most dangerous period in a battle was at the start, when the men were concentrated; secrecy was paramount both for surprise and to avoid a German artillery barrage. All preparatory movements were at night and reconnaissance planes inspected the Australian positions each day to ensure there were no visible changes. On the morning of the attack at Hamel, the day started normally with harassing fire beginning at 03:02 to mask the noise of the advancing tanks with which the infantry appeared out of the mist and surprised the Germans. Later, Monash used patrolling heavy bombers to mask the noise of the tanks.

Monash's method of warfare depended on a continuous stream of information from the battlefield to the central command. Reconnaissance aircraft were used to note the position of the foremost troops and the information was recorded and dropped, using a weighted coloured streamer, near headquarters where it was collected and delivered within a total time of 10 minutes.

In a renowned simile Monash explained:

A perfected modern battle plan is like nothing so much as a score for an orchestral composition, where the various arms and units are the instruments, and the tasks they perform are their

respective musical phrases. Every individual unit must make its entry precisely at the proper moment, and play its phrase in general harmony. The whole programme is controlled by an exact time-table, to which every infantryman, every heavy or light gun, every mortar and machine gun, every tank and aeroplane must respond with punctuality; otherwise there will be discords which will impair the success of the operation, and increase the cost of it.

J. Monash, *The Australian victories in France in 1918*, Lothian, Melbourne and Sydney, 2nd revised edition, 1923, p. 61.

Hamel began at 03:10 on 4 July 1918 and was over in 93 minutes, with all its objectives taken. Monash had predicted a battle time of 90 minutes. Many Germans were wearing gas masks when captured. The orders issued by Monash were published and circulated to the British army, and they became standard practice.

Monash readied his troops for a series of battles beginning on 8 August with the Battle of Amiens, which was much bigger than Hamel. It was completed during a day, rolled over the German defensive lines and their artillery line, and allowed armoured cars to enter enemy territory and press the German troops further east. Nothing like this had been possible previously, and the principles used were those established at Hamel. Further battles were fought at rapid intervals, with continuous skirmishes and the taking of machine guns and open warfare to prevent the Germans consolidating a defensive line or making a counter-offensive. The battles culminated in the taking of the Hindenberg Line with a Corps of 208 000 men. The last action was when the Australians took the fortified village of Montbrehain just beyond that line on 5 October.

The Australian troops regarded themselves as better fighters than the crack German battalions. Monash describes them in the following words:

... the outstanding feature of their campaign was their steadily rising moral, always high, it was in spite of fatigue and stress, never higher than in the final days. A stage had been reached when they regarded their adversary no longer with cautious respect but with undisguised contempt.

J. Monash, *The Australian victories in France in 1918*, Lothian, Melbourne and Sydney, 2nd revised edition, 1923, p. 311.

Monash had been in command of these troops for just four months and five days, with two months of unrelenting offensive.

Frank Eastwood FRACI CChem retired as Reader in Chemistry at Monash University in 1995, since when he has continued his education.

Further reading

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Does urban sewage have a drug problem?

BY **OLIVER JONES**

To most of us, out of sight is out of mind for anything that goes down the toilet, but some environmental scientists are giving it serious thought.

It's the morning after the night before and Jack's head hurts. Groggily, he stumbles to the medicine cabinet in the bathroom and reaches for the packet of paracetamol he keeps for just such emergencies. After taking two tablets, he crawls back to bed. Later he'll excrete a large proportion of that dose and send it towards the nearest sewage treatment works.

Have you ever thought about what happens to the medications you take, after you swallow them? The population of most developed countries swallows an extraordinary amount and variety of drug substances every day. These include commonly known compounds such as antibiotics, anti-epileptics and anti-asthma medications, and more exotic

groups such as synthetic hormones, antidepressants and psychiatric drugs. Anywhere between 50 and 90% of what you take is not broken down in the body and can be excreted when you go to the toilet.

What happens next is the subject of a lot of research. Many compounds are not degraded during conventional sewage treatment and so can end up being discharged into rivers and streams. Interestingly, this is not a newly discovered problem. In the 1970s, scientists working at a sewage treatment plant in Kansas, US, found pharmaceuticals in its effluent, and the first review of the fate of pharmaceutical chemicals in British rivers was conducted in 1985. Unfortunately, these studies did not generate much interest at the time and



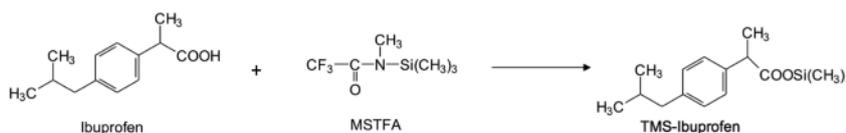
better known pollutants such as CFCs and pesticides took up centre position on the environmental stage.

Urban sewage's drug problem was not heard of again until 1992 when Swiss researchers doing routine water screening tests chanced upon a compound they couldn't identify. It resembled mecoprop (methylchlorophenoxypropionic acid), a herbicide they had been looking for, but it wasn't a perfect match. Their curiosity piqued, the scientists probed further. To everyone's surprise the mystery pollutant eventually turned out to be clofibric acid (2-(4-chlorophenoxy)-2-methylpropanoic acid), a metabolite of several widely used cholesterol-lowering drugs. This compound does not occur naturally and is not manufactured in

Switzerland, so it must have entered the water via sewage contaminated by people taking (and excreting) the medication. This chance discovery was the catalyst for the large and ever-growing amount of research on this subject; searching scientists found more drugs, and in more places. Lakes, rivers, canals, even some marine areas, were found to be contaminated.

In 2002, while in the first year of my PhD at Imperial College London, I published modelling data predicting concentrations of prescription pharmaceuticals in English rivers (*Water Res.* vol. 36, pp. 5013–22). This paper is still my most cited (416 times at the time of writing). Later on, I was able to use gas and liquid chromatography coupled with mass

Many compounds are not degraded during conventional sewage treatment and so can end up being discharged into rivers and streams.



Derivatisation of ibuprofen with MSTFA

spectrometry to show that these compounds were present in English wastewater. In 2003, the Environment Agency of England and Wales in conjunction with The Centre for Environment, Fisheries and Aquaculture Science (CEFAS) published the first study showing that these compounds were also present in British rivers. Although not as much research has been conducted in Australia as in Europe and the US, researchers such as Dr Rai Kookana at the CSIRO (bit.ly/1oODYuX), Dr Frederic Leusch at the Smart Water Research Centre at Griffith University (bit.ly/1hKMfAY) and my own group at RMIT (bit.ly/1xAnah2) have shown that these compounds do occur in Australian wastewaters and the receiving aquatic environment.

Pharmaceuticals present several problems when subject to analysis to GC-MS: they are polar, tend not to be very volatile and are not often thermally stable. A pre-analysis derivatisation reaction is needed to improve the analysis. Derivatisation methods can be classified into four main groups according to the reagents used and the reaction achieved: silylation, acylation, esterification and alkylation. During silylation, the most widely used technique, an acidic hydrogen is replaced with an alkylsilyl group, for example SiMe_3 , to form trimethylsilyl (TMS) derivatives, usually with the addition of *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA).

TMS derivatives are sensitive to moisture (even that in the air) so the reaction must be carefully conducted in a sealed glass vial and the resulting sample should be analysed quickly (<24 hours). The number of alternative

methods of analysis is increasing, particularly the use of LC-MS for both small compounds and for antibiotics, which are generally too large for GC-MS-based analysis.

The study of drugs in wastewater took a new turn when it was extended to include illegal narcotics. In 2005, Italian scientists detected the residues of several illicit drugs in the water of the river Po, which flows through Milan (1.usa.gov/1ihXtIs). This study generated a new field of sewage epidemiology, which measures drugs and drug metabolites in wastewater as a fast and accurate way to assess a community's illegal drug use. Official estimates for illegal drug use are based on population surveys, medical records and crime statistics. These methods are known to be unreliable and to under-estimate the extent of illegal drug use, mainly because they rely on users self-reporting their drug use, which people understandably tend to be elusive about (and thus under-report). It is, however, much harder to disguise what you flush down the toilet.

In 2005, Italian scientists detected the residues of several illicit drugs in the water of the river Po, which flows through Milan.

A 2008 study of 96 municipalities in Oregon (accounting for 65% of the state's population) found that cocaine use was higher in urban areas but methamphetamine was found everywhere (bit.ly/1tZRkqC). A smaller Norwegian study tested Oslo sewage for a year in 2011 and looked for cocaine, amphetamine, methamphetamine, ecstasy and the metabolites (bit.ly/1kfyepR). They found concentrations of cocaine went up on the weekends, and ecstasy use spiked in May (the month that includes *russefeiring*, the Norwegian equivalent of schoolies). Similar studies have been carried out in Tasmania and Queensland with funding from, among others, the Australian Federal Police. This field is getting so popular that some researchers have started to develop new ethical guidelines for it (1.usa.gov/1pe6KJ7).

Does this low-scale doping of our environment matter, either to humans or wildlife? Some of the most obvious concerns are the spread of antibiotic resistance in bacteria populations, and the feminisation of male fish after exposure to endocrine disrupters. A variety of other effects of low levels of drugs in the environment have been observed. For instance, the anti-inflammatory drug ibuprofen (isobutylphenylpropanoic acid) prevents the growth of some bacteria and the antibiotic streptomycin interferes with the growth of some plants.

And Jack's paracetamol? Well this compound has been shown to be quite effective in controlling pest populations of brown tree snakes (albeit at quite high doses). Believe it or not, the US regularly drops thousands of dead mice, packed with 80 mg of paracetamol, over the Pacific island of Guam in an effort to curb growing populations of invasive brown tree snakes there (n.pr/1hCnM10).

While the risks associated with exposure to drugs are probably most significant with regard to the natural environment, the public's concern is

understandably more focused on human exposure. These risks are especially important in areas that practise indirect water reuse, where sewage effluent is released to streams and rivers, which are in turn used as a source of raw drinking water for communities living downstream. Drinking water is a direct route to the human body and with it any drug compounds that may be present. Other pathways such as ingestion (consuming crops irrigated with contaminated effluent or grown on contaminated soil) and bodily interaction (bathing or showering in waters containing effluent) can potentially place the body in contact with drug compounds. While modern treatment technologies can remove the majority of these compounds from water, they are by no means routinely deployed, even in developed countries; people in developing countries are fortunate if their water has any kind of treatment.

Some drugs are resistant to even advanced forms of water treatment. A 2003 study found detectable concentrations of both the anti-

epileptic drug carbamazepine (5*H*-dibenzo[*b,f*]azepine-5-carboxamide) and the blood lipid regulator gemfibrozil (5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoic acid) in four out of the ten Canadian cities tested. All used modern treatment technologies to treat their drinking water. Although this report was not published in the peer-reviewed literature, but commissioned by two Canadian news broadcasters (CTV News and *The Globe and Mail* newspaper), the results make interesting reading. While only three of the 440 analyte-sample combinations gave detectable levels for carbamazepine, and only one gave detectable levels for gemfibrozil, the results showed there was a clear possibility for drug compounds to pass through even modern, advanced water-treatment facilities. Subsequent studies in the US, Europe and China have all found similar, minuscule levels (nanograms per litre) of drugs in some drinking water samples. However, such cases are rare and concentrations are so low that you would have to drink several swimming pools' worth of water to get an effective dose of any of

the compounds in question. Risk to healthy adults is therefore negligible, although there may be risks associated with some groups such as pregnant women and young children.

Today, the occurrence and fate of pharmaceutically active compounds in the aquatic environment is recognised as an important issue in environmental chemistry and a matter of public concern. This can all sound quite scary, but keep in mind that the concentrations we are talking about are very small. In part, the latest findings simply reflect advances in analytical technology, which increase the ability of researchers to spot pollutants in water, so there is no need to stop taking your medication just yet. The medical benefits most likely far outweigh any possible environmental problems. But next time you reach for a pill, for whatever reason, think about where it might end up.

Dr Oliver Jones MRACI CChem is a lecturer in analytical chemistry at RMIT University (School of Applied Sciences). His PhD involved looking for pharmaceuticals in wastewater – although at the time he preferred tell his friends that he was involved with drug testing.



Caricature by David Green
(www.davidgreen.com.au)

chemistry

in Australia

Congratulations to
Ian Rae on 30 years of columns
in *Chemistry in Australia*.

To read some letters of appreciation from Ian's readers, published in May to mark this special occasion, visit raci.org.au/chemaust and click on Past Issues in the Resource Centre.

Future chemistry: a decadal plan

A decadal plan for chemistry is an essential step if we are to maintain a healthy and vibrant manufacturing sector in Australia; it is essential for creating a skilled workforce; it is essential for setting research priorities and directions; and it is vital for developing the high school and tertiary sector curricula needed to prepare the next generation of Australian chemistry graduates.

Surprisingly, despite impressive figures (see box below), no true decadal plan for chemistry has ever been prepared. In 1993, the RACI commissioned a comprehensive review (by eminent chemists Spurling, Black, Savage and Robinson) (*Chemistry: a vision for Australia*, Australian Government Publishing Service, Canberra, 1993). This review made a number of important recommendations and predictions about the directions of chemistry but unfortunately most of the key recommendations were not implemented.

In 2005, a further review of chemistry was carried out by the RACI, but this focused tightly on the education and training aspects and did not provide a roadmap for the future (G. Simpson (ed.), *Future of chemistry study – the supply and demand of chemists*, RACI, 2005). A smaller report commissioned and managed by CSIRO explored the state of the chemistry industry in 2006 (G. Upstill et al. 'Innovation strategies for the Australian chemical industry', *J. Bus. Chem.* 2006, vol. 3, p. 9).

The Australian Academy of Science is the overarching steward for science in Australia (see www.science.org.au). Under its auspices, there are 22 national committees, with oversight for coordination and support of the various scientific disciplines. For example, through the AAS, there are travel scholarships and international fellowships to partner countries such as Japan and France. The AAS also ensures

Australian participation in international organisations such as IUPAC and supports attendance by young scientists at the Lindau Nobel Laureates Meeting. Currently, a number of national committees are undertaking decadal plans to help focus education, research and employment strategies within these individual fields. The National Committee for Chemistry (NCC) aims to carry out a systematic survey of the Chemistry discipline in 2014 and 2015.* This will culminate in the first Decadal Plan for Chemistry (2015–2025) and will involve collaboration across the university, CSIRO, industry, and high school sectors; this plan will identify the gaps, opportunities and needs for the discipline over the coming decade.

The 2015–2025 Decadal Plan for Chemistry will provide the key information and knowledge needed to help direct future investment in chemistry, enabling us to tackle the following fundamental questions:

- 1 Where are the new jobs in chemistry (e.g. nanotechnology, biotechnology) and what skills are really needed for chemistry graduates?
- 2 How can we better communicate the tremendous advances and contributions of chemistry to the community?
- 3 How can we improve interactions between the chemical industry, universities and government and maintain workforce numbers?
- 4 How does the core discipline of chemistry enable multidisciplinary research?
- 5 How can we increase the numbers of students studying chemistry at secondary schools?

In late 2013, in consultation with the Heads of Chemistry across Australia, the RACI and the AAS, a Working Group was

Chemistry is the largest scientific discipline, and is often termed the 'central science'.

- At least 29 of Australia's universities have dedicated chemistry departments.
- Contrary to popular belief, there is close to gender balance, with just 55.7% of all graduates in chemistry being male.
- Mean salaries are \$50 000 p.a., with a mean graduation age of 22.
- Around 50% of chemists work in industry, 25% in universities or teaching and most of the remaining 24% are employed in government laboratories.
- The peak body for chemistry is the RACI, which currently has some 5000 members and a rising membership.
- Chemistry is strongly coupled to industry. For example, chemicals and plastics supply 109 of Australia's 111 industries.
- More than 60 000 people are employed in the chemical industry and it is our second largest manufacturing sector. The sector contributes \$11.6 billion annually to Australian GDP.

Sources: <http://science.uniserve.edu.au/disc/chem/depts.html>, updated April 2012; Graduate Careers Australia (www.graduatecareers.com.au); www.raci.org.au, updated 2014; PACIA, *Adding value – strategic roadmap*, 2011 (www.pacia.org.au)

*The current members of the National Committee for Chemistry are Professors Paul Mulvaney (University of Melbourne), Evan Bieske (University of Melbourne), Mark Buntine (President RACI, Curtin University), Michelle Cooté (ANU), David Black (University of New South Wales) and Dr David Winkler (CSIRO).

An invitation to contribute

A major aspect of the data gathering needed for a Decadal Plan occurs through public consultation.

Throughout the second half of 2014, the Decadal Plan Working Group will be holding a series of open fora or 'Town Hall' meetings, where we will ask the community for feedback. These meetings will occur at universities but also at focal points such as CSIRO. These meetings provide everyone with a chance to talk about the key opportunities and challenges for chemistry and to ensure we can maintain the health of the central discipline of science!

We urge readers of *Chemistry in Australia* to participate in these upcoming open meetings and we hope you will encourage your colleagues from all corners of the chemistry community to contribute to this process. The future of chemistry is in your hands. Further details of the dates and locations of Town Hall Meetings will be available at www.chemistrydecadalplan.org.au.

Those of you who cannot make it to these events are welcome to make a direct submission via the website.

established to undertake the Decadal Plan. (For more information see <http://chemistrydecadalplan.org.au>.) It is expected that some key recommendations will be announced at the RACI National Congress in Adelaide in December 2014. However, the exposure draft and final submission will not occur until mid to late 2015. Following its ministerial launch, the Decadal Plan will be implemented through a collective approach across education, industry, research and government with clear-cut goals and milestones over the lifetime of the plan. The RACI will provide a focal point for much of this activity and will be a key player in the implementation of the Decadal Plan.

Paul Mulvaney FRACI CChem

Postgraduate student awarded for advances in fighting African sleeping disease



Lori Ferrins with Ross Pilling, Chairman and Managing Director, BASF Australia

Lori Ferrins is the winner of this year's BASF Science and Technology Award at the Victorian Young Achiever Awards, presented at Etihad Stadium in May. Ferrins is a PhD candidate at the Faculty of Pharmacy and Pharmaceutical Sciences at Monash University and a student member of the RACI.

Standing out in a competitive group of contenders, Ferrins was recognised for her efforts in developing a compound for treating human African trypanosomiasis (also known as sleeping sickness) – a parasitic disease that is devastating to many isolated communities across Africa.

With a prize of \$2000, entrants in the BASF Science and Technology Award are judged on the project's degree of difficulty, ingenuity and entrepreneurial skills, contribution to the community and contribution to the broader field of research and innovation.

Ross Pilling, Chairman and Managing Director of BASF Australia and New Zealand, said, 'Through the BASF Science and Technology Award, we aim to recognise, encourage and reward young scientists who follow a vision to drive innovative solutions that hold the key to our future. Ms Ferrins embodies these qualities and her work reflects this.'

As part of her research, Ferrins synthesised 170 compounds in four structurally different classes, in some cases having to develop novel routes. Some of the synthesised and screened compounds could potentially be used to treat the sickness. Dr Raphael Rahmani and Professor Jonathan Baell have been Ferrins' mentors throughout the project. The involvement of Vicky Avery and her team at the Eskitis Institute for Drug Discovery at Griffith University, responsible for compound testing, has been crucial to success and progression.

Human African trypanosomiasis is a vector-borne parasitic disease occurring in 36 sub-Saharan African countries. It is caused by infection with protozoan parasites belonging to the genus *Trypanosoma*. They are transmitted to humans through bites by tsetse flies (*Glossina* genus) that have acquired their infection from human beings or from animals harbouring the human pathogenic parasites. Diagnosis and treatment of the disease is complex and requires specifically skilled staff.

WITH BASF



New Fellows

Associate Professor Ashraf Ghanem

teaches organic chemistry and medicinal chemistry at the University of Canberra. He obtained his MSc (Chemistry) from the

University of Stuttgart, Germany, with Professor Franz Effenberger. In 1999, he joined the group of Professors Rolf D. Schmid and Uwe Bornscheuer at the Institute for Technical Biochemistry, University of Stuttgart, Germany. In 2000, he was awarded a German Research Council scholarship to conduct his PhD with Professor Volker Schurig at the University of Tuebingen, Germany. He received his PhD in 2002 and joined the group of Professor Paul Muller at the University of Geneva, Switzerland, as a postdoctoral fellow.

Ghanem was appointed Scientist and Head of the Biomedicinal Chemistry Unit, KFSHRC, Saudi Arabia, in 2004, and a Pfizer research fellow/lecturer at ACROSS with Professor Paul Haddad, University of Tasmania, in 2008. In 2010, he was awarded an Endeavour Research Fellowship and the Japan Society for Promotion of Science Award at the Kyoto Institute of Technology, Japan. He returned to Australia in 2011 and was appointed to the University of Canberra. In 2012, he received a Discovery Translation award from ANU Connect and the ACT government for developing high-potential commercial projects in Australia. In 2013, he received an Endeavour Research Fellowship.

Ghanem is the president of the RACI ACT branch and the Head of the Chirality Group in Canberra. Ghanem's research interests lie in the area of asymmetric and enantioselective catalysis and analysis. His work on lipase and dirhodium catalysis and chiral analysis has been well cited worldwide. He has more than 70 international publications and an *h*-index of 23.

Currently on the editorial board of *Chirality*, Ghanem is the editor of the special issue *Chirality in Australia*, which was published in June. Ghanem also has a passion for the promotion of science in ACT. The crystal growing competition, involving more than 4000 children, and his promotion of science in schools are both testimonies for his community engagements.



Dr Xiaoqing Zhang

is a principal research scientist and a research group leader for the polymer engineering group at CSIRO Materials Science and Engineering, Clayton, Victoria. He obtained his PhD in

polymer science (1991) from Hokkaido University, Japan. After several years' employment with R&D Centre of Nippon Zeon Ltd, Japan, Department of Physics at University of Dublin, Ireland, School of Chemistry and then Department of Chemical Engineering at University of Melbourne, he joined CSIRO in 1998.

Zhang's expertise is in the field of polymer science and materials, including bio-based polymers, biodegradable polymers, nano- and bio-composites, resin chemistry and high-resolution solid-state NMR spectroscopy. He has been leading a series of CSIRO strategic projects, Australian Cooperative Research Centre projects, CSIRO Flagship projects and industrial commercial projects in the areas of natural polymer modification and processing, biodegradable materials, advanced resin development, polymer composites, carbon composites, polymer emulsions, coatings, adhesions, packaging materials and paper recycling, to deliver scientific impacts and commercial outcomes. He has published over 70 journal papers, book chapters and over 50 conference publications. He has also been supervising PhD students

at the University of Melbourne. He was awarded the Newton Turner Award – a career award for exceptional senior CSIRO scientists – in May 2013.

Dr Colin Scholes is a lecturer in the Department of Chemical and Biomolecular Engineering, at the University of Melbourne. His research is into the development of polymeric membrane technology for the separation of gases. This technology utilises thin polymer films, which look much like cling-wrap, and allow one or more selective chemicals to pass through unhindered, while everything else experiences the polymer film as a barrier. This technology has applications in carbon capture, water recovery and purification, helium extraction and natural gas sweetening. Hence, his research touches on many critical chemical engineering fields.

Scholes has previously spent time at the University of Regina, Canada, in 2013, supported through a Victorian Fellowship from the Victorian State Government, as well as having been a research fellow at the University of Texas at Austin in 2009, supported through an Australian-American Fulbright Fellowship.

He is also known for his science engagement work, mainly through Scientifiques Sans Frontieres Australia. He has been involved in programs as diverse as science tutoring to underprivileged students, waterway rehabilitation and researcher outreach programs with institutions in the Pacific region. For Scholes' work in science engagement, he was awarded an Australian Leadership Award in 2013 and an AIPS Tall Poppy Award in 2012. He also sits on the management committee of *Chemistry in Australia*, and is a mean guitarist when he finds the time.



CO2CRC



Kevin John Heinrich

Analytical chemist

Kevin Heinrich was born 1 November 1938, and grew up in Goodwood and later Hindmarsh in South Australia. He completed secondary education (Leaving Honours) at Adelaide Technical High School in 1955 and in January 1956 commenced work as a laboratory

assistant at the Research and Development Branch of the South Australian Department of Mines at Thebarton, west of Adelaide. He then enrolled to study part-time for a science degree at the University of Adelaide.

Initially, he was engaged in sample preparation and digestion of ore samples, and pilot plant residues related to the uranium industry plus water analysis under the supervision of Clive Watts. He experienced a variety of chemical analyses, including volumetric, gravimetric, spectrophotometric and fluorometric techniques.

Later the Thebarton analytical group was transferred to Glenside as part of the larger analytical section and Kevin became involved in a wider range of analytical techniques, including atomic absorption spectroscopy, which was then very much in its infancy. Samples submitted for analyses ranged from phosphate rock samples to concentrates from pilot extraction plants and samples from mineral exploration ventures. His supervisor at Glenside was Doug Bowditch.

Kevin graduated in late 1961, BSc majoring in physical and inorganic chemistry and organic chemistry. Meanwhile, the R&D branch had become AMDEL and he was appointed as analyst with that organisation.

In September 1963, he was appointed as analyst in the South Australian Government Department of Chemistry at Kintore Avenue, having sought this move to be more involved in organic chemistry analysis. Initially, he worked in the agriculture section under Dean Harvey, engaged in the analysis of soils, water and agricultural chemicals by gravimetric, volumetric and spectrophotometric techniques and atomic absorption spectroscopy.

In 1965, he transferred to the Toxicology Section under Chas Crisp, where he was involved in a wide variety of analyses, the main clients being hospitals, the Coroner's Department and the Police Department. Analyses included blood alcohol and drugs from hospital patients suspected of overdosing, post-mortem specimens to assist in determining cause of death, blood alcohols related to 'driving under the influence' cases (this was before the breathalyser era), illicit drugs and miscellaneous forensic samples. Another area related to race horse swabs to assist in the detection of alleged horse doping.

The techniques employed were undergoing a transition; initially, alcohol in blood was determined by the Kozelka and Hine method, which involves distilling the alcohol from the

blood and determining by titration. This was replaced by gas chromatography around the late 1960s. This was an evolving trend with instrumentation replacing traditional analysis in many areas.

In the early 1970s, Kevin was promoted to assistant senior analyst, and from 1975 to 1978 he gained experience in each of the sections of the Department of Chemistry, including pesticides, food and drugs, cereals and explosives. Meanwhile, he had achieved a Graduate Diploma in Business Administration and was keen to gain a supervisory position.

In 1978, the Department relocated to new laboratories in Divett Place, Adelaide, and he was acting in charge of the Toxicology Section. Around 1979, the Department was absorbed into the newly created Department of Services and Supply, and in the new structure of the Chemistry Division, he was appointed to one of three Chief Scientific Officer (CSO) positions, under Chas Crisp as Director of Chemistry. As a CSO, he was now involved in supervision and management and removed from hands-on chemistry. Over the next three years, he supervised each of the sections in the revised structure of the Division, which was quite a challenge.

In 1983, he was appointed Operations Manager of the Division (essentially a deputy to the Director of Chemistry).

He became an Associate of RACI in 1971 and became involved in the activities of the Analytical Group in South Australia. Kevin was an active committee member in the mid-1970s and Chairman of the committee by late 1970s. He was elected as Chairman of the national Analytical Chemistry Division in 1981 and also Chair of the committee that hosted the Analytical Chemistry Division conference in Adelaide in 1983. Kevin was elected Fellow of RACI in 1986. His activities in the South Australian Branch Committee included, for many years, the role of editor of the very useful monthly information newsletter *SA Chemist*, and many of us recall being regularly hounded by Kevin for input.

In November 1985, he transferred from the Chemistry Division to the South Australian Department of Agriculture where he was appointed Chief of Animal and Plant Control and Executive Officer of the Animal and Plant Control Commission. Again, this was a supervisory and management position with no hands-on science.

Kevin retired in September 1993 and travelled extensively. He maintained membership of RACI and was an active participant in local Retired Chemist Group activities.

He married Dorothy (Dot) in 1960; they had two daughters, Julie and Karen (deceased), and were proud grandparents to Emily, Kevin, Bethany and Andrew. Kevin lived to strong Christian ideals and this was reflected in his excellent service to his profession and community.

Kevin was diagnosed with pancreatic cancer in April 2013 and fought hard against this cruel disease, never complaining, passing away in April 2014.

Prepared from notes supplied by Kevin Heinrich to **John Mason** FRACI CChem.

Pseudoscience in the science curriculum

Pseudoscience consists of concepts that are intended to look and sound as if they are supported by research, but in reality have no scientific basis. Some of the signs of pseudoscience include:

- the use of psychobabble – words that sound scientific, but are used incorrectly, or in a misleading manner
- substantial reliance on anecdotal evidence
- extraordinary claims in the absence of extraordinary evidence
- unfalsifiable claims
- an absence of connectivity to other research
- an absence of adequate peer review
- a lack of self-correction, frequently persisting despite refutation.

Unlike science, which eventually adapts its body of knowledge to assimilate negative evidence, pseudoscience remains largely insulated from contradictory data.

The Science Inquiry Skills Strand of the Australian Curriculum includes evaluating claims, investigating ideas, solving problems, drawing valid conclusions and developing evidence-based arguments. In particular, evaluating claims requires students to consider the quality of available evidence and the merit or significance of a claim. At tertiary level, the Academic Standards for Science and for Chemistry require students to articulate the methods of science and explain why current scientific knowledge is both contestable and testable by further inquiry. Most teachers and textbooks avoid discussion of pseudoscience because it is not science. However, it is the contrast between signal and non-signal (noise or background) that results in information. So discussion of the differences between science and pseudoscience can illuminate the true contestable and testable nature of science.

Consider homeopathy, which is a form of alternative medicine and regarded as a pseudoscience by the scientific community. It is based on the principle that 'like cures like' and the belief that molecules in highly diluted solutions retain a 'memory' of the original substance. Proponents claim that homeopathic remedies can treat coughs, colds, food poisoning, hangover, travel sickness, skin conditions, hormone imbalances, depression, asthma, arthritis, birth disorders, autism, HIV/AIDS etc.

The discipline uses terms such as 'similitude', 'potentiation' and 'dynamisation', and relies on anecdotal evidence, rather than large-scale data-driven studies. Homeopathy is difficult to disprove because remedies depend on personality, lifestyle, hereditary factors, as well as the history of the disease. The one disease or set of symptoms may require different homeopathic remedies for different individuals; conversely, if a remedy does not work, it is because the particular remedy has not been perfectly matched to the patient's unique combination of factors. In 2013, the National Health and Medical Research Council (NHMRC) Working Party (www.nhmrc.gov.au/your-health/complementary-medicines/homeopathy-review) concluded that the available evidence is not compelling and fails to demonstrate that homeopathy is an effective treatment for any of the reported clinical conditions in humans. Other examples of pseudoscience include alchemy, parapsychology, astrology, numerology, reflexology and creationism.

Why should students learn to evaluate the merit or significance of a claim? One of the key ideas in modern science education is that scientifically literate citizens can interpret and use information critically. Students who do not continue with further science studies or a science career should still be able to critically evaluate advertising and other claims. For example, what do the slogans 'Inspired by scientific research', '98% fat free' or 'No added salt' really mean? Furthermore, since previous resources and funding are extremely limited, our students (the citizens of the future) need to be able to judge what is possible and what is not, so that funds are not wasted on procedures and treatments that good science has already shown do not and cannot work (see for example, April 2012 issue, p. 36). However, teachers need to be careful when they discuss pseudoscience in their classes, as students might remember the example, but forget that the examples are misinformation.

In analytical chemistry, students learn the significance of blank or control measurements, because it is important to be able to distinguish true information from the absence of signal. Many teachers seem to ignore pseudoscience, but the importance of learning about pseudoscience is that students can better discriminate true science from the non-science. We should use the discussion of pseudoscience to teach scientific thinking.



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The two faces of *Botrytis cinerea*

Botrytis cinerea is a fungus that can attack grapes, and its expression exhibits two general types, commonly referred to as *grey rot* (grey mould) and *noble rot*. The two forms are shown in the images: the upper is a grey rot infection of Chardonnay grapes in an Australian cool climate region; the lower shows noble rot on Sémillon grapes in Bordeaux.

Grey rot is a major spoilage issue that can lead to a considerable loss of product. The infection leads to berry splitting, which then allows other fungi and bacteria to have access to grape sugar, producing undesirable characters. Several years ago, when I was working in the Yarra Valley, one vineyard suffered a major infection and a decision was made to hand harvest about 25% of the 'cleanest' bunches only. The harvested grapes were stored in a cold room overnight and next morning the aroma of acetic acid in the cold room was over-powering.

Warm temperatures (15–20°C), high humidity and dampness, either from rainfall or irrigation, can lead to the onset of grey rot infection. The spores germinate on a wet surface, so unless there is good sunshine to dry the surface, the infection will quickly spread. In red grapes, the grey rot can also lead to a loss of colour. Regular spraying may assist in minimising the degree of infection, but if the infection occurs close to harvest, this is not an option due to the potential for spray residues finding their way into the wine.

Noble rot (*pourriture noble* in French) can produce absolutely sublime wines. There are many styles of *Botrytis* wines and here I will focus on the noble wines based on Sémillon. There are some climate similarities between the Sauternes/Barsac regions in Bordeaux and the Riverina region in New South Wales. The similarities centre on evening/early morning mist or fog followed by warm, sunny afternoons, conditions that are ideal for the onset of noble rot. Sémillon is the predominant grape variety and Sauvignon Blanc and Muscadelle are also used, but more so in France. Noble rot results in a loss of water from the berries, concentrating the sugars to values at harvest from 300–350 g/L and even up to 450 g/L in the Riverina. The final wines may have a residual sugar concentration of 50–150 g/L with 13–14% alcohol in Sauternes/Barsac, while in the Riverina, the residual sugar tends to be higher (170–220 g/L) and the alcohol concentration lower (10–11.5%).

Grape processing and winemaking for noble rot wines both present major challenges, more than I can discuss here. Detailed information can be found in the excellent article by Dr Ildikó Magyar in *Advances in Food and Nutrition Research*, 2011, vol. 63, pp. 147–206. Acetic acid levels can be high due to yeast stress, and oxidative enzymes from the desiccated grapes require high concentrations of SO₂ to ensure protection. The great wines age gracefully, changing from light to dark gold. Aroma descriptors include apricots, honey, peaches, marzipan,



Professor Chris Steel, Charles Sturt University



Copyright: VINCENT BENGOLD

What to try

In March, I had the opportunity to sample over lunch the Château Coutet (Premier Cru) wines from the Barsac region of France. It was fascinating matching these 'gold' wines with food. The 2010 Opalie (\$107) set the scene with its freshness and palate weight while the 1998 Ch. Coutet (\$76/half bottle) sat well with the pork medallions main course. To finish, the dark-chocolate-dipped candied oranges were matched with the 2001 Ch. Coutet 'Cuvée Madame' (\$700). This is an amazing wine and only the 13th release since the first in 1943.

Exploring the Riverina will provide many opportunities to taste the 'home-grown' *Botrytis* wines. One of my favourites is De Bortoli Noble 1, a wine that has won many international prizes and trophies. The 2011 vintage is around \$30/half bottle while the outlay for the 2005 vintage is closer to \$50. Happy tasting!

honey, marmalade, citrus and vanilla, while the palate will be viscous with some acidity to balance the sweetness and great length.



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.

Tales of a sunburnt country

What do deodorants, baby wipes and bushfires have in common? It's not a trick question, or the start of a very funny joke. As I wrote in June (p. 40), the first two can be used as examples to illustrate the importance of exposure pathways in environmental and human health risk assessments. As it turns out, the recent bushfire experiences of the Victorian town of Morwell also give a good example of how exposure pathways are important.

Morwell, in the Latrobe Valley, lies adjacent to the Hazelwood power station and its open-cut coal mine. Many of the residents of Morwell are dependent on the electricity generation industry. In February and March of this year, Morwell was engulfed by dense smoke from a fire in the mine, which is currently the subject of an independent public enquiry. The fire, believed to have been deliberately lit, had started out as a bush and grass fire in early February, and entered the mine where there was an ample supply of solid fuel, and conditions favoured the generation of smoke. The EPA and public health authorities issued standard, general warnings about the smoke at first, advising vulnerable individuals to stay indoors, avoid exertion and, if possible, leave the area.

The concern was with the fine particles in the smoke (2.5 micrometres or less in diameter), which cause both chronic and acute respiratory effects. In this case, the sensitive receptors were being exposed directly to the hazard; the exposure pathway was through the air, the very medium that people need for life. As the fire continued and the smoke became more dense, the warnings were targeted at a much larger population, and anyone who could do so was advised to leave town.

There was some disquiet about the adequacy of the response from government agencies, particularly from those with limited mobility or nowhere else to go if they left home. There was also concern about the time taken to extinguish the fire (more than six weeks), although EPA staff and volunteer firefighters I have spoken with have mentioned the large number of resources that went into fighting it. Because of the scale of the task, stopping the hazard at the source was not a viable risk reduction option in the short term, and therefore moving the receptors (residents) became the only immediate means of managing the risk. Some TV images showed residents using face masks, but such protection was probably ineffective in this case, because a dust filter or face mask fine enough to trap the smoke particles of concern would have made it difficult to breathe. So, breaking the exposure pathway by moving residents away was probably the best advice that could be given at the time. The public enquiry will, no doubt, provide further comment on the suitability of the approaches adopted.

Direct exposure to bushfire smoke may pose an immediate environmental risk, but other environmental impacts can be felt long after a fire. The Black Saturday fires in Victoria occurred after a prolonged period of drought and, beyond the immediate



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catastrophic effects of the fire, the 'flooding rains' that followed towards the end of the ensuing winter also caused further impacts attributable to the fires. Vegetation, already sparse after the drought, was largely removed from affected areas, leaving the surface soils exposed. The rains that fell on Grand Final Day in 2009 were memorable for their intensity. Unfortunately, as there had been minimal regrowth of surface vegetation in the intervening months, the rainfall caused significant amounts of erosion. As a consequence, many farm dams and other water storage facilities were affected by deposition of sediments. The sedimentation caused a loss of storage capacity and, in some cases, had long-term impacts on water quality because of the fine particulate nature of the sediment.

Media coverage of the aftermath of bushfires frequently mentions losses of stock and fences. However, another environmental impact that can go unnoticed at the time is the arsenic-rich ash left over when treated pine fence posts are burned. Radiata pine is treated with copper chrome arsenate to prevent rot and insect attack. When fence posts are burned, the heavy metal content is concentrated in the ash, and the arsenic thereby becomes potentially more bioavailable. Left unattended, the ash could be eaten by grazing stock, wildlife or feral animals. Arsenic accumulation through the food chain, or immediate impacts on affected individuals, could then be expected. While it sounds like a difficult task, I am aware of landowners who have walked their fence lines after bushfires in an effort to remove the ash remaining where there had been fence posts.

When Dorothea Mackellar wrote of the beauty and the terror of her wide brown land, she probably didn't appreciate the half of it!



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Chemistry in capillaries

The *Transactions of the Chemical Society* are accessible online through the University of Melbourne library, but unlike the cases of many of the online journals, it's not possible to go straight to a specified paper. Instead, I have to select a year, then an issue, and then comb through the contents until I get to the paper I want. What a temptation to yield to reading a paper with an eye-catching title! Of course I succumbed, and that's how I came to read George Barger's 'A Microscopical Method of Determining Molecular Weights' in the 1904 volume.

I knew about Rast's method, which involves depression of the freezing point of camphor, but the accidentally encountered paper describes a solution method. Both depend, of course, on Raoult's law of dilute solutions. The Karl Rast method involves mixing camphor, which has an unusually high molar freezing-point depression constant, with a small quantity of the experimental substance and melting the mixture to see how much the melting point falls short of the camphor value, 177°C. Chemists, including me, have used this method since Rast devised it in 1922.

The alternative 'solution' methods are described by Glasstone: 'If two vessels containing different solutes in the same solvent are placed side by side in a close space, vapor will distill from the solution of higher vapor pressure and condense in the one having the lower pressure until, when equilibrium is attained, both solutions are exerting the same vapor pressure, that is to say, they are isopiestic.' The concentrations of the two solutions can then be measured, and if a concentration–vapour pressure relationship is established for one of them – potassium chloride and mannitol were popular solutes – then the molecular weight of the solute in the other solution can be estimated.

Barger described a variant on this procedure, in which drops of a standard solution and of one containing the unknown are introduced into a capillary tube and allowed to come to equilibrium. Measurement of the lengths of the liquid drops (I thought of them as slugs) under a microscope leads quickly to the molar concentration of the unknown and thence to its molecular weight. The experiment is usually performed with seven drops in a tube with diameter 1.5 millimetres and length 6–8 centimetres.

'The filling of the tubes requires a little practice', the author says, and he describes how this is done with the tube open at both ends. Capillary action is allowed to draw the first drop, of standard solution S, into the tube, which is closed with a thumb over the end when enough has been taken up. Tilting the capillary causes the drop to move along, and the procedure is then repeated with a drop of the experimental solution E, leaving a gap of about 3 millimetres between the drops. And so on, until the array S-E-S-E-S-E-S is in place, when the ends of the tube are sealed or plugged with wax. Equilibrium is reached quite quickly, usually in a few minutes and not over an hour. 'Before' and 'after' linear measurements show which drops have

increased and which have decreased, and since the measurements are proportional to molar concentrations, the final calculations are simple.

For measurements in aqueous solution, cane sugar and boric acid were useful standard substances, while in organic solvents the preferred standards were benzil and azobenzene, which had the advantage of yielding coloured solutions, yellow and brown respectively, which aided in distinguishing the standard and experimental drops. Benzene and light petroleum – it didn't seem to matter that the latter was a mixture – were popular solvents but low boiling points, like that of carbon disulfide, and higher, like that of xylene, could be tolerated.

Barger (1878–1939) was the son of an English mother and a Dutch engineer father. He studied in the Netherlands and at University College London and graduated in 1901 with first class honours in chemistry and botany from King's College, Cambridge. After working for a time as a botanist in Brussels, he then held a fellowship at Cambridge 1903–09. His main interest, however, was in alkaloids and other nitrogenous substances including ergot, thyroxine and vitamin B₁. He held several appointments in London before working for the medical research committee in the war years and then serving as professor of medical chemistry at Edinburgh (1919–37). He was Regius Professor at Glasgow for just a short time before his death in an accident on a Swiss lake.

His obituary notice for the Royal Society was written by Henry Dale, with whom Barger had collaborated on the ergot work that was his main claim to fame. 'Barger was in thought, as well as in speech and conduct', Dale records, 'a man of rigid and determined honesty', with a 'real thirst for experience' that found expression in travel, art and music, the latter despite his being tone deaf.

I conclude by going back to Rast, who in 1921 published some improvements on Barger's micro-method for determination of molecular weights, notably the better accuracy achieved by measuring only the inner five drops, neglecting the ones at each end. He also followed up Barger's observations about intermolecular association of polar solutes by observing that this was more prominent in pentane than in benzene solutions.

In contrast to Berger's well-documented life, Rast's is something of a mystery. I was unable to find much about him, not even his life dates and certainly not his professional appointments and achievements.



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 dispenses advice on chemical hazards and pollution.

events

Chemeca 2014

28 September – 1 October 2014, Perth, WA
www.icheme.org/chemeca2014

7th Asian Biological Inorganic Chemistry Conference (AsBIC-7)

30 November – 5 December 2014, Gold Coast, Qld
www.asbic7.org

11th Australasian Aluminium Smelting Technology Conference

6–11 December 2014, Dubai, United Arab Emirates
<http://11aastc.com>

RACI National Congress

7–12 December 2014, Adelaide, SA
www.raci.org.au/events-awards/raci-national-congress-2014
Early Bird registration closes 1 August 2014

Advanced Materials & Nanotechnology (AMN7)

8–12 February 2015, Nelson, New Zealand
www.amn-7.com

35th Australasian Polymer Symposium

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

Pacifichem 2015

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

RACI events are shown in blue.

istockphoto/estyan4



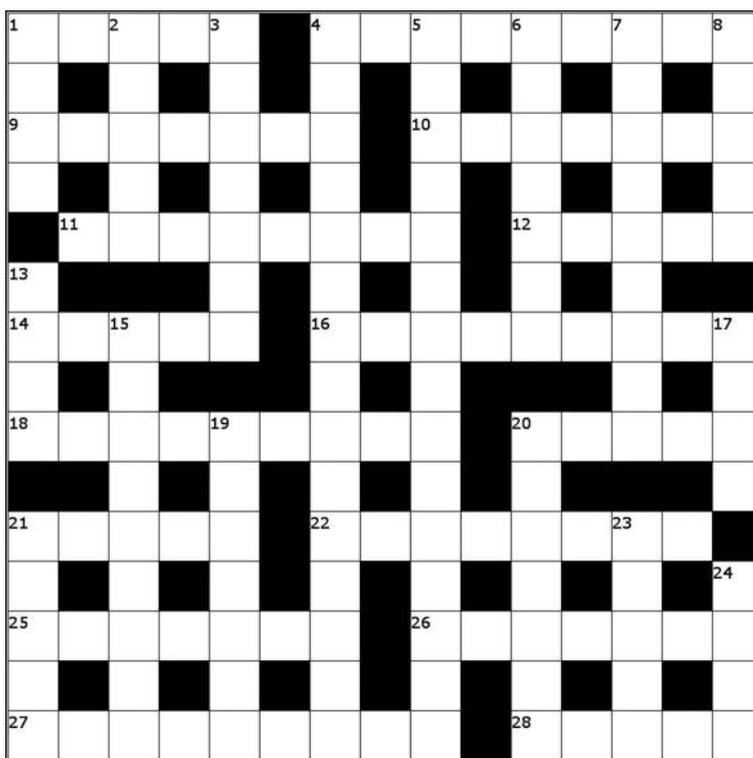
Coming up

Maritime archaeologist **GRAEME HENDERSON** and **IAN MACLEOD** at the Western Australian Museum trace a growing awareness of underwater cultural heritage, from the days of salvage law to a UNESCO convention.

Some new 2D nanomaterials are showing great promise as components in batteries, among other applications, says **MICHELLE SPENCER** at RMIT University.

RAY HODGES touches on three unique techniques that have led to Nobel Prizes.

cryptic chemistry



Across

- Meeting for speech filler. (5)
- Compounds containing two pyrrole rings linked through a methine group and IR spin-dry cycle! (9)
- Pressure for very big spasm over lip cover. (7)
- Welcome hug. (7)
- State function then play turnout. (8)
- Dress change. (5)
- Metal swings. (5)
- Fresh consultancy granted centres outcome. (9)
- Did racial abuse give rise to something reactive? (9)
- Oddly, Patty spies a semiconductor with positive free charge carriers. (1-4)
- Five elements demonstrated. (5)
- Reinsert, substituting one element for another, in reaction that transforms quinoline to quinaldic acid. (8)
- Sanguine about losing sulfur nucleobase. (7)
- Disinclination to move; still, first class. (7)
- Finally scarce yet clean burning C_2H_2 . (9)
- Blow jar. (5)

Down

- Arising out of 1 Across losing an element and rearranging. (4)
- Won a Nobel Prize in program analysis. (5)
- Pairs equals. (7)
- Oiled car bench or made CCl_2 . (15)
- Humpy field-lines around $R_2S=NPh$. (15)
- Radical altered by soil - the $C_5H_9O_4$ radical. (7)
- Fictitious ray aiming all over the place. (9)
- Covering the selenium mix-up. (5)
- Move restlessly about radical for 90% of a degree. (4)
- Six consumed an ion. (9)
- Subject them to the element. (4)
- Stupidity of m to V. (7)
- Have own. (7)
- A Greek commonly representing 19 Down. (5)
- Proportion of three elements. (5)
- Comes up in check calibration deficiency. (4)

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

Chemistry at the grassroots: a careers day at Marryatville Primary School

Increasing numbers of primary students are becoming interested in science, technology, engineering and maths (STEM) subjects, and schools are finding it necessary to add further classes to address the demand.

Marryatville Primary School in South Australia is helping its students to see how exciting chemistry can be and just where it can take them. During its recent careers day, the school harnessed the resources of local state government departments and invited representatives from the Fire Service, SA Pathology and the Department of Premier and Cabinet.

The format of the event was very simple. Small groups of students were arranged in a 'round robin' fashion, with presenters having a maximum 15 minutes in which to give a presentation about their occupation. The students came well prepared with ideas and some very probing questions of the presenters, before moving on to the next group.

One of my favourite experiments we conducted was when we collected different household liquids/detergents and mixed two of them together. After we mixed them together, we would observe it and identify if it was a solution or mixture. We did this with all the products and with one of the mixtures/solutions, it made a kind of a play dough mixture that we could play with.

Darren, year 7

Chris Embery, an OHS and Dangerous Goods Inspector with the South Australian Government, attended the school careers day event because he feels strongly about encouraging students and inspiring the next generation of scientists:

When you become successful, I believe that you have a duty to give back. Being at the grassroots, investing time in and potentially inspiring the next generation of chemists is a great way of doing this. Many of our most eminent scientists attribute their choice of career pathway to seemingly modest encounters, often becoming inspired after seeing a presentation or having a school teacher whose enthusiasm and love of learning inspired them to take up chemistry.

Particularly popular were the giveaways of pens, lanyards and posters provided by the RACI. 'If you want chemistry and science to be seen as "cool", you have to have avenues ready to prove it', Embery said. They also achieved this by using a

I enjoyed the practical science lessons because after we did the serious business with filling out the worksheets, we were allowed to mix up all different concoctions and doughy substances.

Ella, year 7

hands-on display of personal protective equipment (PPE) and several short, sharp videos of chemical reactions.

Jess Morelli, a teacher at Marryatville Primary School, said 'the kids found it very interesting to learn about the diverse range of jobs that use chemicals every day, and the engagement and interaction through Q&A, videos and props really opened their eyes as to how work and safety go hand in hand together.'

Today's primary school students are a lot more technologically savvy than we might give them credit for; with the wide availability of personal computers, they have seen all

The thing that I enjoyed most in this year was when the dangerous jobs people came to our school and talked about their job, I liked this because it was really enjoyable to see and learn about different jobs and how they were dangerous (I also enjoyed it because I got freebies).

Nicholas, year 7

the traditional software. They want information to be extensive and immediately available – if they are not engaged well enough or quickly enough, they will switch off.

Sadly, when students reach secondary level, they often lose interest in science. This is precisely why primary school curricula must be designed so that concepts are presented in ways that will excite, interest and motivate our young children to pursue secondary and tertiary studies, and then, hopefully, careers in science and technology.

Engaging primary school students in science learning is paramount to addressing looming skills shortages and minimising the follow-on impacts on Australia's future prosperity.

Dr Chris Embery MRACI CChem is a Senior OHS Inspector (Scientific) at SafeWorkSA, Department of Premier and Cabinet, Government of South Australia. **Jess Morelli** is a year 6/7 teacher at Marryatville Primary School, South Australia. Thank you to the RACI for donating the careers day giveaways.

Royal Australian Chemical Institute National Congress

Confirmed Plenary Speakers



**Associate Professor
Alán Aspuru-Guzik,**
Harvard University



Professor Phil Baran,
The Scripps
Research Institute



Dr Stacie Canan,
Global Health Division,
Celgene Corporation



Professor Makoto Fujita,
The University of Tokyo



Professor Hubert Girault,
Ecole Polytechnique Fédérale
de Lausanne



**Professor Katharina
Landfester,**
Max Planck Institute for
Polymer Research



Professor David Leigh,
University of Manchester



Professor Daniel Nocera,
Harvard University



Professor Greg Scholes,
University of Toronto

For the full biographies of confirmed speakers to the RACI 2014 National Congress please visit the Congress website at www.racicongress.com

Participating Divisions

- Analytical & Environmental Chemistry Division
- Biomolecular Chemistry Division
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- Organic Chemistry Division
- Physical Chemistry Division
- Polymer Chemistry Division
- Radiochemistry Division
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- Synthetic Chemistry
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- Advanced Materials
- Chemical Health and Safety
- Chemistry in Health
- Chemical Analysis and Sensing
- Community Engagement

**Early bird registration closing soon
Deadline: 1 August 2014**

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