

chemistry

October 2015

in Australia

Nicotine and the quest to control insect pests



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cover story

Nicotine as an insecticide in Australia: a short history

From its use from European settlement in Australia to today's neonicotinoids, nicotine has been a constant presence in insect control.

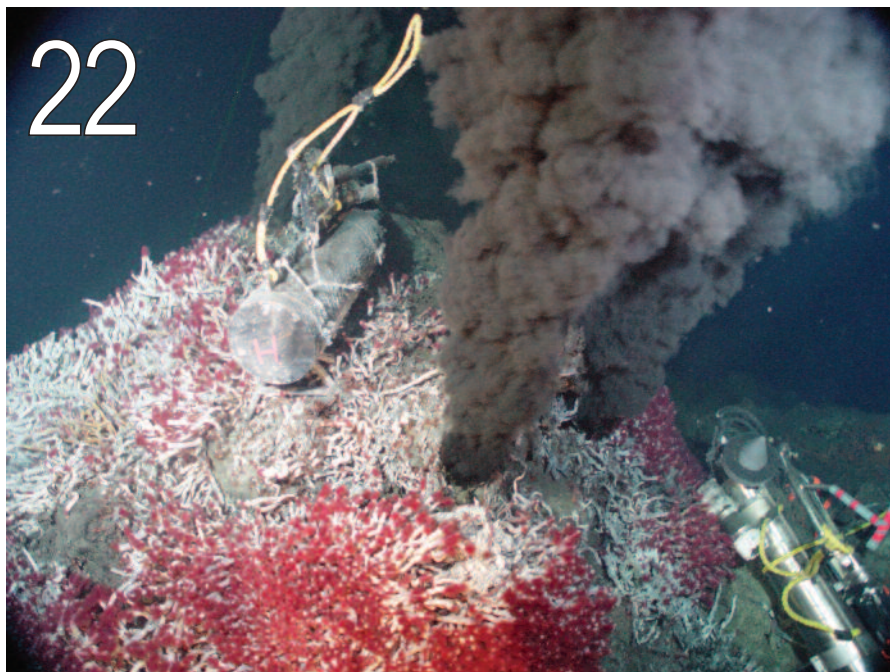
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Thinking outside the box – in places under the sea or outside the atmosphere – creates new paths into the metals cycle.

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Strengthening student engagement

The RACI, and scholarly societies around the world, are facing gradual but significant declines in membership numbers. They are therefore looking to particularly increase their student membership and engagement. According to Robert Harington of the American Mathematical Society, 'The emerging scholars we now see entering academia no longer view joining a society as key to their community role' (bit.ly/1K79h1z).

The New South Wales, Queensland and South Australian branches have already established active young chemists groups, arranging events such as careers workshops and murder mystery nights. The Western Australian and Tasmanian branches engage with the university-based young chemists groups.

As part of the Victorian Branch's strategy to engage with younger chemists, we have initiated a working group, focusing, to begin with, on engagement with postgraduate students. At a recent kick-off meeting with enthusiastic student representatives from most of the Victorian universities and research institutions, potential engagement with the RACI was positively received by the students, and we gained great insights and action points.

'Didn't feel invited', 'didn't know I could join', 'didn't realise the benefits' and 'not value for money' were common reasons for not joining the RACI, according to students at the meeting. Just two of the nine attending students were members. These reasons are echoed by students from other branches and the global scholarly community. A recent global survey of 14 000 highly educated and geographically diverse respondents (predominantly from scientific, technical, medical and scholarly communities) found that people are waiting to be invited: 15% of non-member respondents haven't joined a society because they haven't been invited, 12% said that 'it never occurred to them to join', and 9% 'never had a reason to join' (bit.ly/1Nm31nI). Baby Boomers (born 1945–65), Generation X (1965–80) and Generation Y, or Millennials (1980–2000), were represented equally among respondents. Sarah Sladek, author of several books about how organisations can engage with Gen X–Z, claims that 'Millennials are loyal to people, rather than institutions', so a personal invitation may resonate more with this group.

Free food + networking at students' doorstep + RACI representative = happy to join. With these simple ingredients I

joined the RACI at a sponsored barbecue nearly 20 years ago. Back then, with chemistry students all in the same building, it was easy to invite us all. Things have changed and, although food and convenience are still popular, we need to extend our mechanisms to enhance our visibility and reach students.

Taking a more personal approach to communication, and supporting peer-to-peer communication by word of mouth, social media and flyers in chemistry buildings, are certainly on our agenda, as are professional development and networking events. By student request, this year we have scheduled a trivia night and a 'speed-dating' career night. Students confirmed that they were very keen to host or attend career advice events, and students were particularly interested in meeting professionals, from a range of careers, who are not too long out of university themselves (see Brittany Howard's insightful article, July, p. 26).

The working group will host these two events, but we have every confidence that the young chemists will run their own independent group, and liaise with the other state/territory branches, in the near future.

At the Victorian Branch, we have also discussed facilitating a mentoring program, of value to both the mentor and the mentee. Many chemistry societies, for example in Puerto Rico and Germany, have mentoring in place. These programs are still in their early stages, and we will follow their progress with interest.

Director of the Royal Netherlands Chemical Society, Jan-Willem Toering, says, 'There is a lot of fuss about new generations X, Y and Z, and how they should behave and how to handle them. I think that chemistry is still a common language and that it is not the people that have changed, but just the tone of voice. We have all the different media at our fingertips to reach our members, but I am really convinced that the heart of the matter is to show yourself, to meet your members in person and try to connect them.' (bit.ly/1DWpYfi)

I'm looking forward to seeing more young chemists engaging with the RACI.



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Biodiesel in World War II

The article 'Biodiesel and by-products – glycerine' by D. Seddon (August 2015, p. 36) makes the point that trans-esterification of plant oils affects, advantageously, their viscosity and makes them more suitable for use as biodiesels. Of course, when esterification was first applied to biodiesel manufacture the primary aim was to raise the cetane number. This was in World War II Japan, where there were insufficient quantities of conventional fuels from the then Dutch East Indies (the sole source), and the Japanese Navy used plant oils. Without treatment, these plant oils did not perform adequately, and Japanese development chemists found a way of improving them by esterifying with methanol. The improvement could be expressed in terms of the cetane number. Japanese battleships including the *Yamato* used biodiesel prepared in this way.

Such usage did not continue into peace time. Instead, Japan built more and more oil refineries and the supertanker was developed so that crude oil could be exported to Japan in large quantities.

Clifford Jones FRACI CChem

Reflections after reading

'One man's meat is another man's poison' is attributed to the Roman poet and philosopher Lucretius. *Chemistry in Australia* August 2015 certainly raised a lot of related memories.

In recent editions Postdoc diary discussed how a continuous change in positions is the way to advancement, whereas in my younger days a professional future was best obtained through long-term placement with one employer.

In the 1960s, as a part-time RMIT chemistry student, I had several full-time jobs. Three of these were brought back into consciousness by the mention of 'diacetyl' in the article by Melinda Christophersen at CUB, where in 1965–6 mention of the detection of diacetyl almost created a panic. My main work was divided between QA (isohumulone levels and haze measurements) and R&D (hop extraction and consequent analysis of various humulone-related compounds – all connected with the hop extract project).

Prior, in 1963–4, I worked at Russell Grimwade Biochemistry School at Melbourne University for Dr Richard Jago and Robin Anders, during the final stages of his PhD project (now Emeritus Professor at La Trobe University) and where the relationship of acetoin and diacetyl was an important component of the flavour formation in dairy products.

Subsequently in 1969, I joined Bush Boake Allen, a leading flavour house, working in QA, flavour development/application, where diacetyl was vital to many flavours. However, there is a rare but severe lung disease, called colloquially 'popcorn workers lung', sometimes caused by inhalation of diacetyl in butter flavours.

CUB provided a one-third pint milk bottle for my daily sampling from the 'bright beer' tanks. Why this container was designated is still a mystery to me, especially at one of the

most-modern, best-equipped industrial laboratories. Perhaps it was more robust than fragile glass or more available than rare plastic beakers. Inevitably the mandatory pre-sampling rinse/dispose procedure provided me with a forbidden (instant dismissal) heart-starter.

These bottles were previously used to provide daily milk to school children in the 1940 and 50s which was always 'sunstruck' and very unpleasant. With high sunlight hours, Australian beverages can become 'light-struck', resulting in undesirable flavours and other detrimental effects, particularly during transport and storage.

Research into reducing light-strike by RACI stalwarts Dr Keith Farrer and John Harvey (see June and August Your say) respectively, resulted in milk being over-packaged in opaque plastic containers and beer, already in ubiquitous brown bottles, also being packaged in cardboard. The author also assisted in establishing the rapid deterioration of sunlight-exposed soft drinks.

Anthony F. Zipper FRACI CChem

F. Albert Cotton

There are a number of factual inaccuracies in the review by Franz Wimmer of the book *My life in the golden age of chemistry*, by F.A. Cotton (August 2015, p. 28).

First, E.O. Fischer worked at the Technische Universität, Munich, not in Berlin. Independently of Woodward and Wilkinson, he deduced the correct structure for ferrocene, though the name he gave it (Doppelkegel or double cone structure) has not survived in the chemical literature.

Second, although Cotton undoubtedly made many fundamental contributions to the renaissance of inorganic chemistry, he was not the *first*, for example, to apply crystal field theory to coordination chemistry, a development that can be traced back to the physicists H. Bethe and J.H. van Vleck and others in the 1930s. Many others, including Carl Ballhausen and Klixbull Jorgensen in Copenhagen, J.S. Griffith and Leslie Orgel in

Got something to say?

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Send your contributions (approx. 400 words) to the Editor at editor@raci.org.au.



Cambridge, and the Australians Brian Figgis and Tom Dunn at University College London, continued the development after World War II.

Likewise, although Cotton certainly instituted the first systematic studies of fluxional *organometallic* molecules by dynamic NMR spectroscopy, he was not the *first* to employ the technique to study fluxional molecules in general, such as cyclohexanes and bullvalene.

The term *agostic* (not *agnostic*!) interactions, referring to the interaction of saturated C–H bonds with electronically unsaturated transition metal centres, was coined by Malcolm Green (University of Oxford) and Maurice Brookhart (University of North Carolina), who first recognised the generality of the phenomenon.

Finally, FAC was *never* known as Frank A. Cotton, and that name never appears in his books and publications. Anybody who referred to him in that way was likely to receive a blast of typical invective.

Martin Bennett FRACI CChem

Detection limits

Chemistry in Australia continues to be even more interesting to read as the years progress. The August 2015 issue had a nice blend of old, current and future problems covered.

In atomic spectroscopy, one can use either absorption or emission to analyse elements but the sensitivity of the two techniques varies with the position in the periodic table. Atomic absorption is less troubled by matrix effects in complex samples but does not always give the lowest detection limit. Analysis of alkali earth elements such as Mg and Ca is more sensitive by flame absorption than by flame emission, but the reverse is true for alkali elements such as Li or K.

High-temperature emission using ICP (inductively coupled plasma), where most elements are present as ions, reverses these trends. The low ionisation potential of alkali elements leaves few neutral atoms in the plasma for their optimum emission lines. Similarly, the plasma produces high concentrations of Mg⁺ and Ca⁺ where the single electron in the outer shell gives exceptional sensitivity at their optimum ion spectra wavelengths.

I found the determination of Li in straight seawater to be an ideal lab exercise for highlighting such problems when teaching students. By flame atomic absorption, the low lithium level of about 100 ppb is essentially undetectable above noise, but with the same flame and spectrometer, flame emission using a chopper (to match the amplifier needs) gives a well-defined peak when the 680 nm spectral region is scanned. Scanning allows the background light level to be noted each side of the

Li emission line, and by increasing the power to the photomultiplier this peak can be enhanced at will to give lowest detection limits. Usually one takes this limit as a peak three times the noise of the background. If one uses pure water for the calibration series, then the result for peak above background calculated is double the accepted value. This is due to the enhancement effect of the Na present, which like Cs additions provides an excess of electrons to the flame and ensures most Li atoms are in the ground state (a procedure originally called 'radiation buffering'). One could attempt to matrix match by adding AR grade NaCl to the calibration standards, but as one approaches detection limits, even AR grade chemicals can be insufficiently pure.

The usual way of avoiding enhancement (or suppression) effects on sensitivity by the matrix of complex samples is to use a method of spiking the samples themselves. For the seawater samples, the Li peak is scanned to give the height above background and then a known amount of Li is added with a micropipette from a concentrated standard and the sample is rescanned. This ensures the matrix modifies the sensitivity of the standard to that of the sample and then the ratios of peaks above background allows the true value in the unknowns to be calculated.

There are only about 80 stable elements and their atomic spectra are very specific. Thus despite potential errors of actual level present, at least the analyst is reasonably sure the correct element is being reported. Not so with molecular analysis. There are infinite numbers of compounds from simple to complex biomolecular, and all have broad band spectra. Avoiding errors here relies upon the selectivity of the prior separation method for the target species.

Ray Hodges FRACI CChem

'Your say' guidelines

We will consider letters of up to 400 words in response to material published in *Chemistry in Australia* or about novel or topical issues relevant to chemistry. Letters accepted for publication will be edited for clarity, space or legal reasons and published in print and online. Full name and RACI membership status will be published. Please supply a daytime contact telephone number (not for publication).

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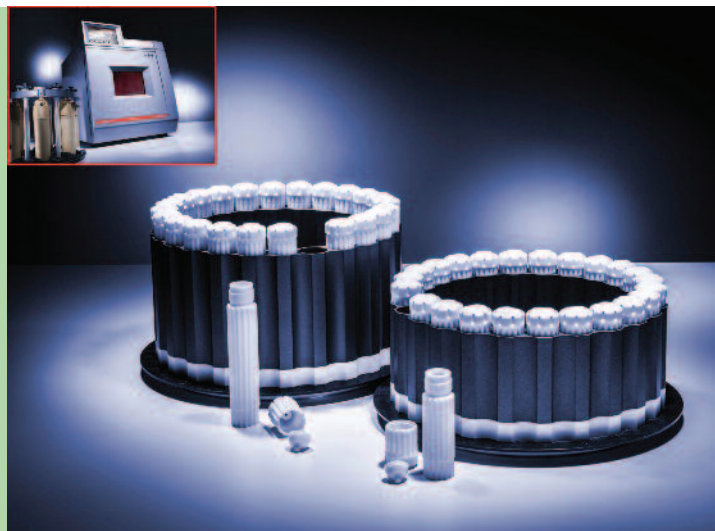
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Latest five-year plan for CSIRO released

CSIRO has released its masterplan to improve Australia's record in innovation and help the country respond to global changes and digital disruption.

In its strategy for 2015 to 2020, Australia's Innovation Catalyst, CSIRO outlines how the organisation will become a global collaboration hub and help boost the country's innovation performance.

'Australia currently ranks 81st in the world when it comes to innovation efficiency – the bang for our buck we get when we transform innovation investment into results,' CSIRO Chief Executive Dr Larry Marshall said.

'If that was a team sport ranking, we'd be outraged. As a country, we need to work together to improve this result.'

'Australia's prosperity, health and sustainability is closely bound to our capacity for innovation – and CSIRO has a key role to play here.'

'CSIRO is Australia's largest patent holder. We're the people behind fast wi-fi, part of the global team which developed extended-wear contact lenses, designer polymers using RAFT technology and the Hendra vaccine – but this is the tip of the iceberg when it comes to the value we offer the Australian people.'

In a novel approach for the 90-year-old science body, it crowd-sourced ideas and suggestions from more than 7000 people, including its research partners, other collaborators, its own staff and the public to help determine the direction of the strategy.

'For CSIRO the question is really, what does Australia need?' Marshall said.

'The crowd-sourcing helped answer this question by asking people to consider a range of challenges and opportunities

ahead and asking how we should respond.'

The organisation's new strategy has been shared with staff, and represents a new era for the national science agency.

'At the core of the strategy is the need for CSIRO to be a catalyst for change and growth in the innovation system in Australia. Innovation is a team sport,' Marshall said.

'We must form new bonds and collaborate across disciplines, sectors, science and business. That is where profound innovation happens – at the intersection of these areas.'

'We must also be asking who our customers are and if we're creating the value that they need. We work with businesses, industry, governments and communities and we need to find ways to benefit every Australian.'

One of the greatest challenges for Australia has been the difficult road for inventions and technology to go from an idea to then being in the hands of the public.

'To help, we have formed the CSIRO ON program – an initiative to fast track CSIRO technology and ideas into the market and to get it into people's hands more quickly,' Marshall said.

'This is what we call "breakthrough innovation" where we will help reinvent existing industries and create new ones.'

Part of the push for greater collaboration and co-ordination by CSIRO will be increased co-location with universities and other research organisations and a greater emphasis on international connections.

Download the plan at www.csiro.au/en/About/Strategy-structure/Strategy.
CSIRO



Caught on camera: first glimpse of powerful nanoparticles

Good things come in small packages – and metallic nanoparticles are some of the smallest. Although their dimensions are measured in nanometres, with each nanometre being one-millionth of a millimetre, scientists believe that these tiny particles could be used to fight cancer, collect renewable energy and mitigate pollution. The problem is that it is difficult to know how they work, since they are so small that their structure is impossible to see.

Until now, that is. An international team featuring contributors from leading institutions in the US and Korea and co-led by an Imaging CoE scientist has recently discovered a solution to this problem. Their discoveries will allow researchers to investigate the 3D structure of these miniscule particles for the first time.

In a paper published in *Science* (doi: 10.1126/science.aab1343), Monash Associate Professor Hans Elmlund and collaborators from Princeton, Berkeley and Harvard reveal the details of a novel imaging method and show how it can be used to characterise the 3D structures of platinum nanoparticles.

The new method, which is called 3D Structure Identification of Nanoparticles by Graphene Liquid Cell EM (SINGLE), exceeds previous techniques by combining three recently developed components. The first is the graphene liquid cell, a bag one molecule thick that can hold liquid inside it without obscuring it from the electron microscope. The second is the direct electron detector, which is even more sensitive than traditional camera film and can be used to capture movies of the nanoparticles as they spin around in solution. Finally, a 3D modelling approach known as PRIME allows the scientists to use the movies to create 3D computer models of individual nanoparticles.

Although platinum nanocrystals have

many different applications, they are mostly based on one attribute of the material: it is an excellent catalyst. This is part of the reason that Elmlund and his colleagues chose to work with platinum nanocrystals in particular; the detailed atomic structure of each particle determines, to a large degree, how effective it is as a catalyst.

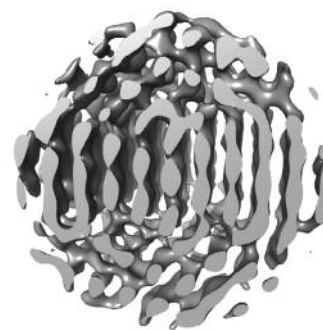
The differences in structure between individual nanocrystals are pronounced, because the crystals are created by aggregation. They are effectively built up atom by atom, leading to highly complex and unpredictable structures that could not be determined – until now.

In their new article, Elmlund and his collaborators demonstrate the power of their innovative system by describing in detail the structure of two platinum nanoparticles, which were also captured in the movie clips that accompany the publication. ‘It was very exciting, because seeing the movie I knew that there was a possibility that we could extract 3D information from the image series’, said Elmlund.

But the value of the paper extends beyond the demonstration of a novel method. Because the platinum nanoparticles described have never been seen in such detail before, at the level of individual atoms, Elmlund and his colleagues got the opportunity to draw new conclusions about how these highly useful particles grow – and their discoveries have surprised the scientific community.

‘I think everybody in the field had anticipated cubical or at least highly symmetrical platinum nanocrystals’, said Elmlund. ‘It was surprising to learn that they form asymmetrical multi-domain structures.’

For the imaging scientists involved, next steps will include investigating the formation and evolution of nanoparticles



Slab through the 3D reconstruction of particle 1 along the vertical plane with tentative atomic positions indicated. ABC repeats of {111} planes are visible.

and characterising the transitions they go through to reach their final form. ‘It is important for us to understand this, so that we can design new materials, for example, to build better or more efficient solar cells, or make better and more economical use of fossil fuels’, said Elmlund. Their new method will undoubtedly help them to shed new light on these areas, and may lead to further revelations; after all, as Elmlund reflected, ‘Making discoveries is one of the great privileges of being a scientist.’

The new SINGLE method devised by Elmlund and his collaborators relies, in part, on the recently discovered wonder material graphene. First isolated in the laboratory in 2003, this strong but light substance has many intriguing properties.

Each sheet of graphene is only one atom thick, and is made up of carbon atoms with bonds linking them to three of their neighbours. Seen under a microscope, the atoms and their bonds form a honeycomb lattice that resembles chicken wire.

Most of graphene’s exciting properties are derived from these extraordinary proportions. For Elmlund’s purposes, what was required was a material envelope to hold a liquid as it was examined by a microscope. Graphene, being extremely thin and disproportionately strong, fit the bill perfectly.

CENTRE FOR ADVANCED MOLECULAR IMAGING

In search of the heaviest element

Like absolute zero on the temperature scale, what is the heaviest element that could possibly exist? That's the question 2015 Rutherford Lecturer Distinguished Professor Peter Schwerdtfeger, Director of the Centre of Theoretical Chemistry and Physics at Massey University, Albany, would love to know the answer to.

'I'm really curious where the periodic table really ends. It may be that we cannot create elements beyond 119 or 120. But we can still simulate these on computers using quantum theory. There is speculation – though it is sheer speculation – that the periodic table has to finish at around 170 protons,' Schwerdtfeger said.

The heaviest elements that are known to occur naturally are uranium (atomic number 92), with plutonium in trace amounts. Heavier elements are increasingly unstable, decaying almost instantly, although there has been some speculation that there may be an 'island of stability' where super heavy elements can exist for longer periods.

Are there some super heavy elements lurking under rocks or trapped in ice

somewhere? Schwerdtfeger thinks this is highly unlikely.

The lack of naturally occurring super heavy elements means that in order to study them, scientists have to first make them, and this is problematic. 'Experimenters need to know the exact conditions required to produce each new element, and theoreticians have had to catch up. When you attempt to produce the next element up now, you're missing more than a dozen neutrons to stabilise the nucleus. And you're working with products that decay within a millisecond.'

Even so, the super heavy elements livermorium, ununoctium, ununtrium, ununpentium and ununseptium have been made in recent years and the quest to make heavier elements continues.

Once we understand the fundamentals about how progressively heavier elements are generated in the universe, it may help us search for life outside Earth, according to Schwerdtfeger. 'It is clear that for life to exist on planet Earth, carbon and oxygen, for example, must be produced and subsequently accumulated and we need the right conditions for this



Distinguished Professor Peter Schwerdtfeger

to happen. Once we have a more complete picture, we can better understand the formation of other planets in other solar systems and whether they can sustain other life forms.'

Schwerdtfeger was awarded the 2014 Rutherford Medal, the Royal Society of New Zealand's top research medal, for his world-leading contribution to fundamental aspects of chemical and physical phenomena in atoms, molecules and condensed matter (see March issue, p. 10).

MASSEY UNIVERSITY

IChemE Global Awards 2015 shortlists announced

The shortlists for the IChemE Global Awards 2015 have been announced with over 100 entries making the final stages of the awards in November.

The Awards, in association with Aramco, celebrate excellence, innovation and achievement in the chemical, process and biochemical industries.

Successful organisations shortlisted include Air Products, Atkins, BP, Costain, Dow Chemical Company, Johnson Matthey, Universiti Teknologi Malaysia, GSK, Saudi Arabian Oil Company, McGill University, University of Liverpool, United Utilities, University of Bath, Pfizer, Seoul National University, PETRONAS and Sellafield Ltd.

The winners of the global awards will be announced on 5 November 2015. The ceremony in Birmingham, UK, is just one of several international events organised by IChemE to

celebrate the achievements of the chemical engineering profession. Other events include the IChemE Singapore Awards (22 October 2015) and the IChemE Malaysia Awards (26 October 2015).

Shortlisted individuals and organisations in Australia include:

- Christopher Jansen, WorleyParsons (Young Chemical Engineer in Industry Award)
- Biao Kong, University of Melbourne (Young Chemical Engineer in Research Award)
- CSIRO and Monash University (with University of Sussex) for 'Drosophila smell receptors for industrial applications' (Research Project of the Year Award).

INSTITUTION OF CHEMICAL ENGINEERS

Core library project backs national exploration

A \$7.3 million project will transform a vital resource for national offshore petroleum exploration and the search for new onshore mineral resources in Western Australia.

Australian Industry and Science Minister Ian Macfarlane and WA Mines and Petroleum Minister Bill Marmion have announced an additional \$2.5 million in joint Commonwealth (\$1.2 million) and State (\$1.3 million) funding to expand the Perth Core Library in Carlisle.

'The federal government appreciates the importance of this library and has committed funds through the National Offshore Petroleum Titles Administrator (NOPTA),' Macfarlane said.

'The Perth Core Library already boasts more than 400 kilometres of core and will store two-thirds of all Commonwealth-managed petroleum core derived from offshore drilling.

'This world-class facility has helped identify major potential shale gas deposits and is in constant use by companies and prospectors working to find the mines and petroleum fields of tomorrow.'

The expansion will create extra viewing space for geologists to examine drill core and a conference room, and extend the area housing a sophisticated rapid spectroscopic logging and imaging system known as a HyLogger core scanner.

HyLogger information is being processed to create a growing

online core library accessible worldwide.

'The core library archives State and Commonwealth drill samples crucial to new exploration research,' Marmion said.

'The additional funding comes on top of \$4.8 million committed in last year's WA State Budget to enlarge the library's warehouse for drill core samples by about 50%, or 3500 square metres.

'The core library storage area is filling up rapidly, thanks to increased exploration activity generated by the State Government's Exploration Incentive Scheme, so it is gratifying to be able to get this project under way.'

Macfarlane said the library was one of the most important resources in Australia for petroleum companies to do pre-competitive analysis before going to the considerable expense of drilling.

'When the work is finished, the core library is expected to satisfy the combined needs of the State and Commonwealth for the next 20 years, he said.

Concept plans have been prepared for the core library project, with construction expected to start later this year and be finished by the end of 2016.

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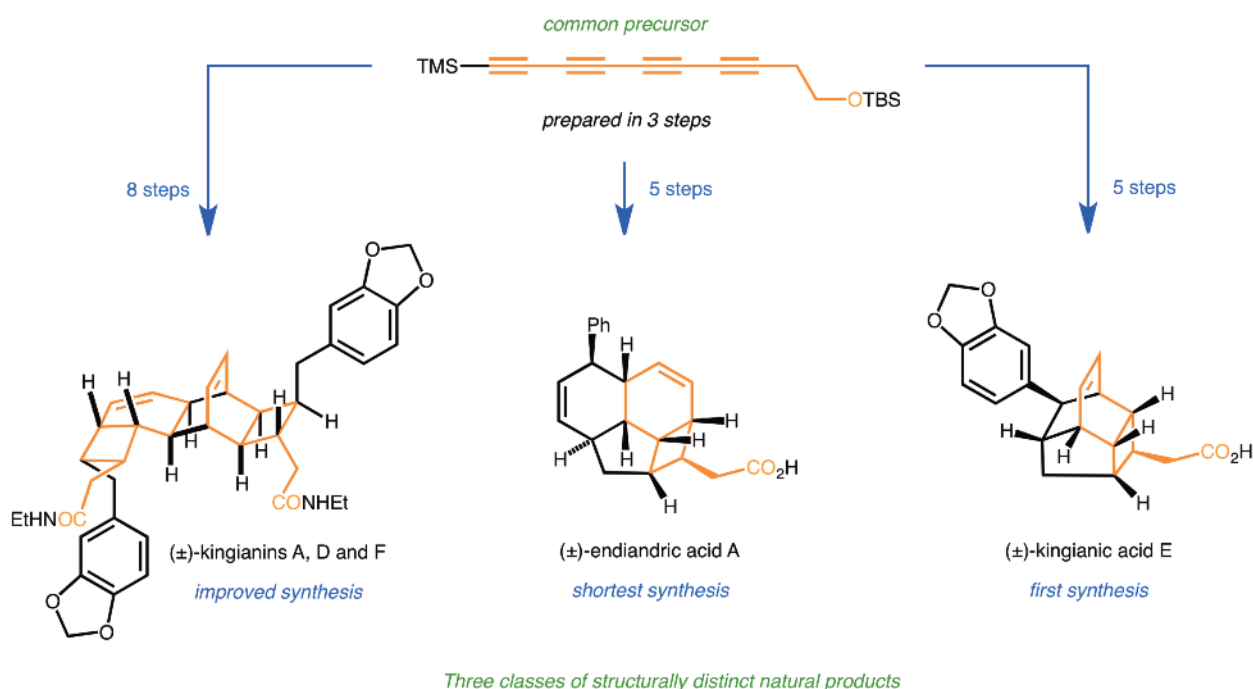
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Versatile route to polycyclic natural product family

The caged polycyclic natural products of the *Endiandra* genus have intrigued – and challenged – synthetic chemists for 35 years, since the proposal of the spectacular pericyclic biomimetic cascade by Black, Banfield and coworkers. Until recently, synthetic approaches to these natural products (which include the endiandric acids, the dimeric kingianins and the kingianic acids) have been designed with a specific subfamily in mind, with starting materials transitioning into products of a single

structural type, over a number of steps. Believing there was potential for a more versatile and efficient strategy, chemists at the Australian National University made the bold decision to target endiandric, kingianin and kingianic natural products from a common tetrayne Grignard reagent, via a series of alkylation reactions (Drew S.L., Lawrence A.L., Sherburn M.S. *Chem. Sci.* 2015, **6**, 3886–90). The research team, consisting of PhD student Sam Drew and group leaders Professor Mick Sherburn

and Dr Andrew Lawrence, used their expertise in stereoselective alkyne partial reduction to transform three conjugated tetraynes into all-*Z*-tetraenes, which were perfectly primed for domino electrocycloisat-ion-Diels–Alder reactions. This powerful strategy significantly shortened the step count required for the total synthesis of endiandric acid A (eight steps) and represents the first unified approach for the synthesis of structurally distinct natural products of the *Endiandra* genus.



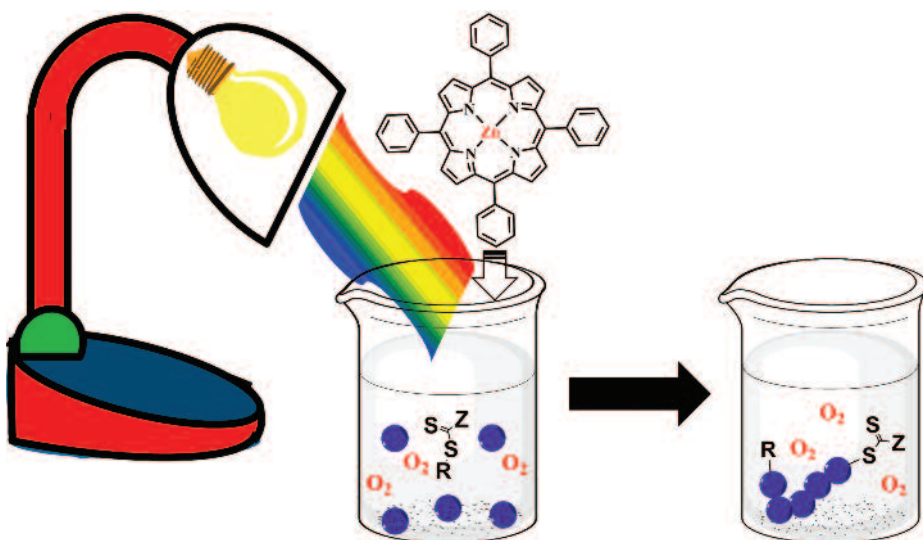
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Harnessing natural pigments and light to drive living radical polymerisation

Natural porphyrin-based compounds, such as chlorophyll and haem, are essential ingredients of life as they play critical roles as intermediates in various biosynthetic pathways. Inspired by nature, researchers have explored synthetic porphyrins with various metal cores for photodynamic therapy to treat cancer and for solar energy harvesting. Realising the potential of porphyrin frameworks, Associate Professor Cyrille Boyer and co-workers at the University of New South Wales have used metallocporphyrins to generate functional polymers with a variety of applications (Shanmugam S., Xu J., Boyer C. *J. Am. Chem. Soc.* 2015, **137**, 9174–85). Zinc porphyrin, which has been employed as a sensitizer for both photodynamic therapy and solar energy harvesting, was used to promote photo-induced electron transfer to activate living polymerisation over a broad range of wavelengths (435–655 nm). An interesting feature of



the zinc porphyrin-activated polymerisation is the ability to tune polymerisation rates by simply varying the wavelength and intensity of the visible light, which could be exploited to build 3D materials. Furthermore, this

technique overcomes a major limitation of radical polymerisation, namely sensitivity to oxygen, by making possible polymerisation in an open vessel with excellent control over molecular weight and dispersity.

Demonstration of pH-dependent electrostatic catalysis in radical reactions

It is normally assumed that the ability to use electric fields to accelerate chemical reactions is limited to redox processes occurring at electrode surfaces. However, electric fields should theoretically be able to catalyse non-electrochemical reactions by electrostatically stabilising high-energy charge-separated resonance contributors to the reaction's transition state. In practice, the challenge is orienting the field relative to the reaction centre. One solution is to use charged functional groups within the substrate, auxiliary or catalyst whose electric field is relatively localised but can be precisely aligned with respect to the reaction centre. If the charged functional group is an acid/base group, this approach has the added advantage of incorporating a pH switch for the catalytic effects. Researchers from the Australian National University have now provided a proof-of-concept of pH-dependent electrostatic catalysis by demonstrating a pH switch of up to two orders of magnitude on the rate and equilibrium constant for hydrogen atom transfer between a hydroxylamine bearing a non-conjugated carboxylic acid and a reference profluorescent nitroxide radical (Klinska M., Smith L.M., Gryn'ova G., Banwell M.G., Coote M.L., *Chem. Sci.* 2015, doi: 10.1039/C5SC01307K). Deprotonation of the carboxylic acid stabilises the resulting nitroxide radical anion, favouring the forward reaction. This ability to manipulate nitroxide stability via a simple pH switch opens the way to the possible use of this effect in synthetic and polymerisation processes.



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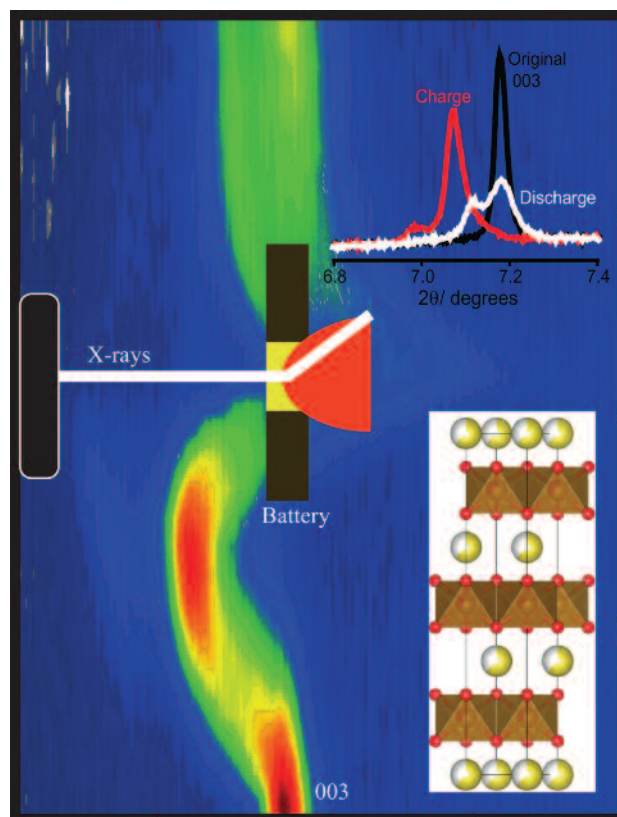
April 15	Abstract submission closes
June 25 - Oct. 15	Early registration
October 16	Standard registration begins
November 13	Housing closes
December 20	Registration closes





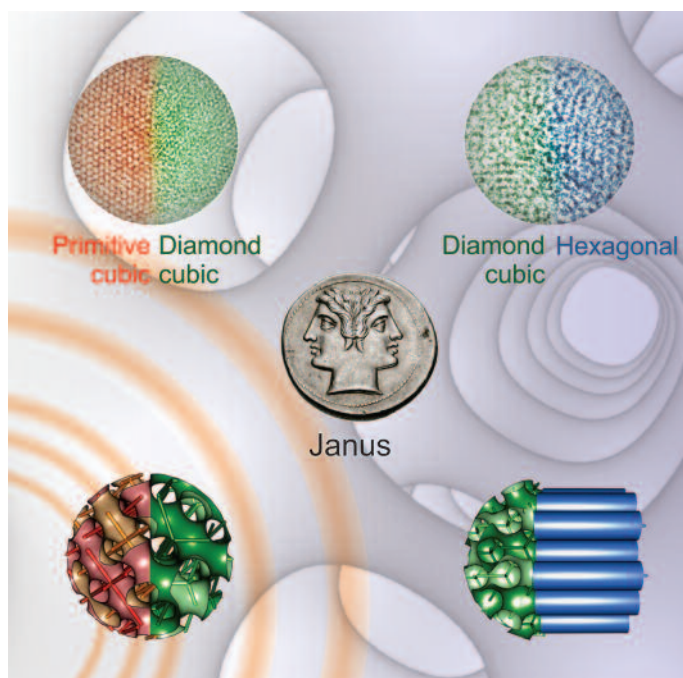



Watching microscopic structural changes in battery electrodes in real time



Making a sodium-ion battery equivalent to a lithium-ion battery is advantageous due to the potential reduction in cost. The majority of lithium-ion batteries function by inserting/extracting lithium ions into/from the electrodes during charge/discharge. Therefore, minimising the crystallographic consequences of inserting and removing a larger ion – sodium relative to lithium – from a host electrode is a key challenge faced by researchers. A team led by Dr Neeraj Sharma from the University of New South Wales and Professor Teófilo Rojo from CICenergigune in Spain, working with colleagues from the University of Wollongong, ANSTO and the Australian Synchrotron, has been able to determine the structural evolution of the O3-phase of the $\text{Na}_{2/3}\text{Fe}_{2/3}\text{Mn}_{1/3}\text{O}_2$ positive electrode material during battery operation (Sharma N., Gonzalo E., Pramudita J.C., Han M.H., Brand H.E.A., Hart J.N., Pang W.K., Guo Z., Rojo T. *Adv. Funct. Mater.* 2015, **25**, 4994–5005). The overall structural motif of the material was maintained during charge and discharge, in marked contrast to the changes observed with other O3 polymorphs with different compositions of transition metals. This may explain why O3- $\text{Na}_{2/3}\text{Fe}_{2/3}\text{Mn}_{1/3}\text{O}_2$ features similar performance to its P2-phase counterpart while other O3 compositions typically show inferior performance compared with their P2 counterparts.

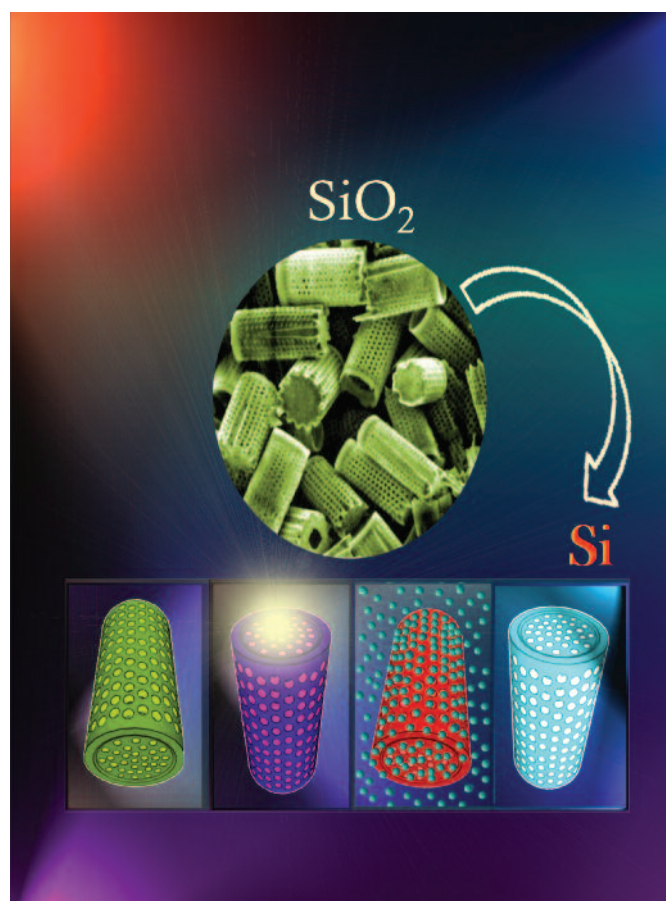
Two-faced self-assembled lipid nanoparticles



Self-assembled lipid nanoparticles have been widely studied as delivery vehicles for drugs, genes and in vivo imaging agents. The amphipathic nature of lipid materials and their controllable internal nanostructures may offer several advantages, including enhanced solubility of hydrophobic drugs, controlled release, and protection against hydrolysis and enzymatic degradation. The research group of Professor Calum Drummond at RMIT aims to develop advanced multi-functional lipid materials by achieving fine control of self-assembled nanoscale structures. A recent study led by Professor Drummond and Dr Nhiem Tran of the CSIRO has reported the first observation of Janus nanoparticles consisting of stable co-existing ordered mesophases created by lipid self-assembly (Tran N., Mulet X., Hawley A.M., Conn C.E., Zhai J., Waddington L.J., Drummond C.J. *Nano Lett.* 2015, **15**, 4229–33). Janus nanoparticles, with dual co-existing phases, have been engineered in the past for inorganic and polymeric materials, but stable lipid-based Janus nanoparticles had not been reported until now. The study used a combination of synchrotron small-angle X-ray scattering and cryogenic transmission electron microscopy to confirm the presence of mixed cubic phases and mixed cubic/hexagonal phases within individual lipid nanoparticles. The study also proposed a theoretical model of the interface between the co-existing nanostructured domains within a nanoparticle. The development of smart nanomaterials such as Janus lipid nanoparticles may satisfy the need for more complex, biomimetic, multicompartment and multifunctional nanoparticle systems in the future.

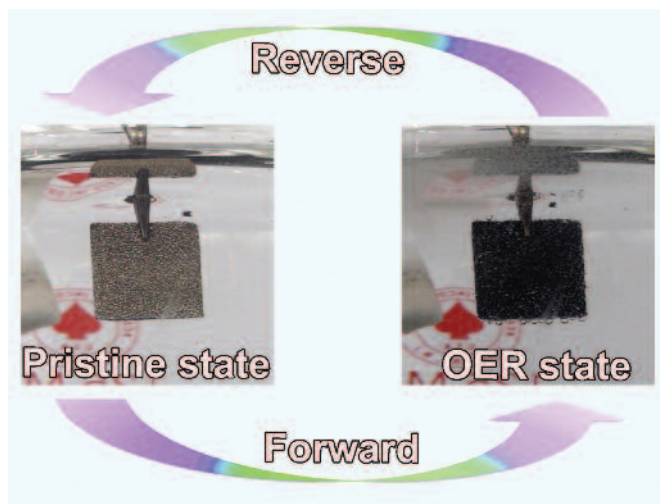
Replicating nature in drug carriers

Researchers in the School of Chemical Engineering at the University of Adelaide have used a simple reduction process to make silicon replicas of the silica exoskeletons of unicellular microorganisms called diatoms for use in drug delivery (Maher S., Alsawat M., Kumeria T., Fathalla D., Fetih G., Santos A., Habib F., Losic D. *Adv. Funct. Mater.* 2015, **25**, 5107–16). These silicon diatoms exhibit interesting 3D morphologies that are biologically optimised for movement in complex biological environments and were shown to act as degradable drug carriers for sustained delivery of therapeutics. Their hollow microcapsule structure with micro- and mesopores, high surface area, large drug-loading capacity, rapid biodegradability, and self-reporting capabilities due to intrinsic luminescence make them ideal for drug-delivery applications. The study's findings indicate that these silicon-based drug carriers could be used in place of current therapies for a broad range of intraocular diseases, including proliferative vitreoretinopathy and choroidal neovascularisation in age-related macular degeneration. They were prepared from inexpensive and readily available natural resources (diatomaceous earth) using a scalable conversion process and represent a promising low-cost alternative to existing synthetic silica and polymeric materials.



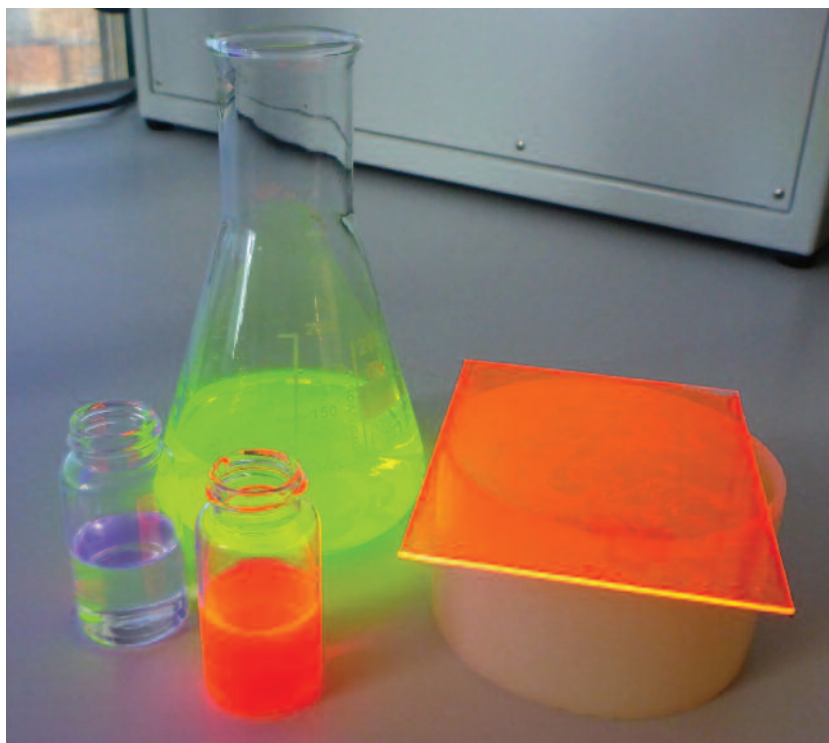
Smart catalyst electrode for oxygen evolution

Increasing energy needs and environmental concerns have stimulated extensive research into renewable energy technologies such as metal–air batteries, water splitting, fuel cells, and CO₂ conversion. Electrochemical reactions such as the oxygen evolution, hydrogen evolution, oxygen reduction and CO₂ reduction reactions are fundamental to these technologies. Recently, there has been great interest in using multifunctional catalyst electrodes that catalyse the electrochemical reaction of interest with high efficiency while possessing additional functionalities, such as high catalytic activity to another electrochemical reaction or mechanical flexibility, to meet the requirements of the desired application. Inspired by the stimuli–response functionality of natural organisms, Professor Shizhang Qiao and co-workers at the University of Adelaide have developed a smart catalyst electrode by the in situ growth of nitrogen-doped NiFe double-layered hydroxide (NiFe LDH) nanolayers on a nickel foam substrate (Chen S., Duan J., Bian P., Tang Y., Zheng R., Qiao S.-Z. *Adv. Energy Mater.* 2015, doi: 10.1002/aenm.201500936). The electrode not only exhibits excellent performance towards the oxygen evolution reaction, but also dynamically changes colour when oxygen evolution occurs, thus permitting in situ visual monitoring of the catalytic reaction. A potential application of this colour-changing property as an indicator of the charging and discharging processes during electrochemical cycling was demonstrated in a Zn–air battery.



Light concentration through heavy aggregation

Researchers from the University of Melbourne have developed an air-stable transparent luminescent solar concentrator (LSC) that takes advantage of the unique photophysics of pyrene aggregates (Banal J.L., White J.M., Lam T.W., Blakers A.W., Ghiggino K.P., Wong W.W.H. *Adv. Energy Mater.* 2015, doi: 10.1002/aenm.201500818). LSCs are light-harvesting devices that consist of photoluminescent materials integrated with a waveguide. A simple device configuration comprises a luminescent material deposited on top of a glass panel. Light is absorbed by the luminescent material and the resulting emission is trapped by total internal reflection and waveguided to the edge of the glass panel, where the energy can be used for photovoltaic conversion. The Melbourne team has been developing a class of organic fluorophores that show large Stokes shifts and high photoluminescence quantum yields in the solid state. In this latest contribution, a sterically congested *gem*-pyrene ethene fluorophore was found to display a Stokes shift in excess of 1.0 eV while maintaining high emission efficiency. Resulting transparent LSCs showed comparable performance to inorganic phosphor devices with good stability in air without encapsulation. Optimisation of such a device could lead to transparent building-integrated photovoltaics or power sources for the Internet of Things.

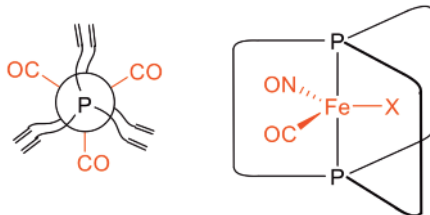


Compiled by **David Huang** MRACI CChem (david.huang@adelaide.edu.au). This section showcases the very best research carried out primarily in Australia. RACI members whose recent work has been published in high impact journals (e.g. *Nature*, *J. Am. Chem. Soc.*, *Angew. Chem. Int. Ed.*) are encouraged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

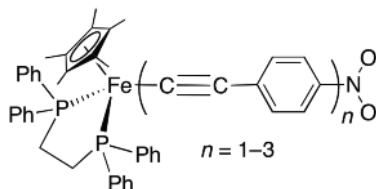
Aust J Chem

The September issue contains several papers authored by speakers at the RACI National Congress held in Adelaide, 7–12 December 2014.

John A. Gladysz and coworkers (Texas A&M University) report the syntheses of three series of trigonal bipyramidal *trans*-bis(phosphine) complexes, which can potentially undergo threefold intramolecular ring closing metatheses to yield gyroscope-like complexes as indicated in the figure.



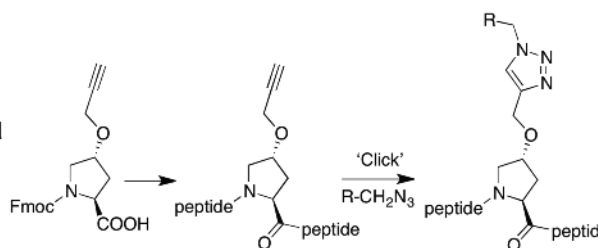
Frédéric Paul, Jean-François Halet and their coworkers (Université de Rennes 1, France) have prepared phenylalkynyl iron complexes, $\text{Fe}(\text{dppe})(\eta^5\text{-C}_5\text{Me}_5)$ and report an analysis of their properties, including an unexpected hypsochromic shift of the long-wavelength UV-vis absorption bands – up to 700 nm – as a function of carbon chain lengthening.



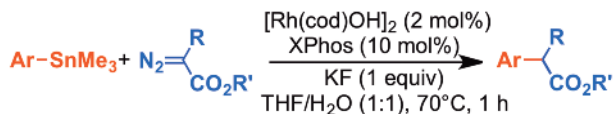
Click chemistry – the addition of an azide to an acetylene to produce a triazole – is a popular method for producing bio-conjugates.

P.E. Thompson and co-workers at the

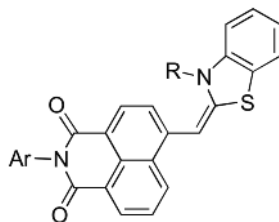
Monash Institute of Pharmaceutical Sciences used this method to prepare linear and cyclic peptide conjugates derived from Fmoc-propargyloxypyrrolines. These conjugates retain the binding affinity and conformation of the original peptide.



Jianbo Wang et al. (Peking University, China) report the first examples of Stille coupling using diazo compounds in the Rh^{I} -catalysed cross coupling reaction of arylstannanes with diazoesters. This operationally simple reaction proceeds under mild conditions and will undoubtedly prove to be useful in the synthesis of α -aryl esters.



Nitro groups can sometimes be used advantageously as leaving groups in $\text{S}_{\text{N}}\text{-Ar}$ nucleophilic substitution reactions as alternatives to the more common halides. Katharina Landfester (Max Planck Institute for Polymer Research in Mainz, Germany) and co-workers report the use of such a reaction to assemble several 'two-in-one' merocyanine chromophores derived from 1,8-naphthalimides, including the structure shown.



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

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as an insecticide in Australia

BY **ROBERTO FUSETTO** AND
RICHARD A.J. O'HAIR

A short history

From its use from European settlement in Australia to today's neonicotinoids, nicotine has been a constant presence in insect control.

The protection of crops and livestock from harmful insects has been and continues to be a major concern of the agricultural industry in Australia. The beginning of European agriculture in Australia occurred in the winter of 1789, when members of the First Fleet planted their crops in the settlement made at Parramatta.

The early years of agriculture were tenuous, with the settlers grappling to adapt British agricultural practices in a foreign landscape with constant

threats. Apart from crop failures due to bad weather conditions (drought or flood), insect pests were recorded as an early problem. One of the earliest reports of insect damage to crops appeared in the *Sydney Gazette*, Sunday 28 October 1804:

SYDNEY. We are concerned to state, that the Caterpillar and Grub continue very numerous and destructive at the Hawkesbury, where they are doing much damage to the very promising crops in that quarter. The wheat in every other district is clear of those insects. The wheat on the Five Hundred Acres at the

Government Grounds about Castle Hill is nearly ready for reaping, and promises an abundant Increase. Owing to Some severe blights it is singular that there is not a single early Peach to be found on the numerous trees of that kind which in former years produced so great an abundance of fruit.

Several months later, the same newspaper published a recipe for an insecticide:

A liquor thus compounded will destroy caterpillars, ants and other insects – namely, soap, flower of sulphur, and champignons, equal quantities, dissolved by a gentle heat in twenty times their united weight of water. – Insects sprinkled by this liquor die immediately.

Finding ways to combat insects was a rather hit and miss affair, although the *Sydney Gazette* regularly published articles on agricultural successes and recipes for the control of insects. An article, also published in 1804, highlighted successful efforts at growing turnips and how to protect turnips from fly attacks:

Among the Receipts published for preventing the fly taking turnips are the following, which have been tried with much success. The first is, to steep the seeds in water with flower of brimstone mixed, so as to make it strong of the brimstone; another, steeping the seed in water with a quantity of the juice of horse aloes mixed. The sowing of soot or tobacco dust over the young plants as soon as they appear above ground, has also been found very serviceable; and indeed, whatever will add vigour to the young plants will prevent their being destroyed by the fly, which never attacks them until they are stunted in growth.

This early report on an unconventional use of the tobacco plant, *Nicotiana tabacum*, a native of South America first brought to Europe in 1490s, is not the first. Indeed, the first English report on the use of extracts of tobacco as an insecticide appears to have been the recommendation of tobacco juice to kill lice on children's heads in the 1681 version of Nicholas Culpeper's *The English physician enlarged*. A review of

In Victorian times, as crop production spread to other Australian colonies and local production of tobacco took hold, many newspapers, magazines and books recommended the use of tobacco as an effective insecticide.

the literature identified a number of other early reports on the use of tobacco extracts in the fight against insects in Europe.

It seems unlikely that tobacco was widely used as an insecticide in the early colony, since tobacco, like rum, was a precious commodity distributed as rations to the British troops and had to be imported due to Governor Philip setting a priority to grow crops for food by prohibiting the local cultivation of tobacco in April 1791.

There is evidence that Australian Aborigines used the native tobacco plant *Duboisia hopwoodii* as both a human narcotic and an animal poison. In 1882, Kempe observed that 'the leaves of this shrub are used by the natives to poison emus' around the Hermannsburg area of Central

Australia, while Spencer and Gillen's 1899 classic study on Aboriginal practices noted the:

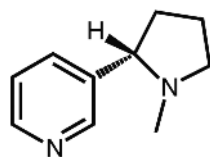
leaves of the pituri plant (Duboisia Hopwoodii) are used to stupefy the emu. The plan... is to make a decoction in some small waterhole at which the animal is accustomed to drink. After drinking the water the bird becomes stupefied, and easily falls a prey to the ... spear.

Work by various botanists and chemists in Australia and in England established the presence of two alkaloids within the leaves of *Duboisia hopwoodii*: nicotine and nornicotine. Their levels varied according to soil composition (pH and salt content) and rainfalls, offering a potential explanation as to why the Aborigines used different species of 'pituri' as either mild narcotic or strong poison, depending on the levels of nornicotine present.

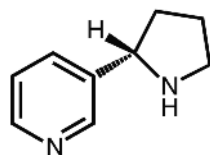
In Victorian times, as crop production spread to other Australian colonies and local production of tobacco took hold, many newspapers, magazines and books recommended the use of tobacco as an effective insecticide. For example, in 1857, *The Victorian Agricultural and Horticultural Gazette* suggested 'Fumigate Greenhouses with tobacco smoke now and then, to keep down the insect tribe.'



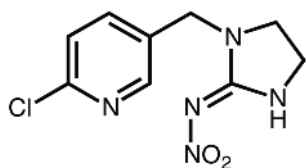
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nicotine

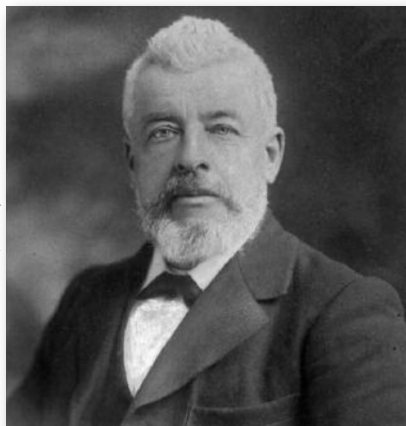


nornicotine



imidacloprid

Chemical structures of nicotine, nornicotine and the neonicotinoid imidacloprid widely used in commercial insecticides (e.g. in formulations with the trade names Confidor and Gaucho).



Charles French, government entomologist for the Colony of Victoria, who wrote widely on insect pests and their control.

By the late 1880s, it was recognised that native and introduced insects were an increasing economic burden in Australia. In *Elements of Australian agriculture*, MacKay discussed a series of recipes to fight insect pests and plant and animal parasites. To combat sheep scab he reported:

There are a number of remedies for scab – tobacco, sulphur, arsenic, mercurial ointment, oil of tar, corrosive sublimate, and others. The old Australian remedy is 5 oz., good tobacco infused in 1 gallon of boiling water, and 3 oz. sulphur. Mr Randall, an American authority on sheep, recommends the occasional addition of a little spirits of turpentine, which, of course, does not mix with the infusion but floats on top. Two or three dippings in the above, as a rule, insure a cure.

In 1889, Charles French was made government entomologist for the Colony of Victoria, with a remit to investigate the ravages of native and introduced insects. His job entailed fieldwork, including identification of insects and inspections of properties. His major contribution was the *Handbook of the destructive insects of Victoria*, Volumes I–V, which were published in 1891–1911.

French's handbook of 1891 discussed the use of tobacco as an insecticide. For example, to prevent woolly aphids or American blight, French recommended: 'When young trees have to be planted, and there is reason to believe that the plants are infested, it is a very good plan to immerse the bundles of trees in tobacco water.' p. 40 (plate 1, p. 34).

French's son, Charles Hamilton French, followed in his father's footsteps. In 1896, he was appointed to the Department of Agriculture as an inspector under the Vegetation Diseases Act. When this work morphed into insect control, he became assistant government entomologist. Over a 20-year span, he contributed 31 papers on entomological studies to the monthly *Journal of Agriculture*. Tobacco sprays appear to have been one of his

favourite weapons to combat insect pests, including the potato thrip, the red spider and the Rutherglen bug.

By the 1900s, nicotine isolates entered worldwide markets as an insecticide. Sold in different forms (oil soap, free base solution or dust), nicotine sulfate, one of the most stable derivatives of nicotine, was commercialised as Black Leaf 40. In the US (1912), Black Leaf 40 revealed its potency in controlling the spread of *Phytophthora infestans*. One of the first Australian reports on nicotine as a pure extract highlighted its use to control pests in crops in combination with other pesticides (e.g. lime-sulfur, lead arsenate and Bordeaux mixture). In the early 1930s Black Leaf 40 entered the Australian market, replacing previous mixtures due to its more stable form and better insecticide action. This method of pest control was commonly used in Australia until the introduction of DDT in 1947, which then became the most widely used insecticide due to low cost, reduced dose and higher efficiency.

By the 1950s, a variety of chemicals and solutions was readily available in Australia to control pests in agricultural fields or in the home garden. Indeed, an anonymous writer with the nom de plume 'Mardella' provided a humorous take on the arsenal available to the home gardener in the article 'Gardening These Days is Mainly Pest-Chasing' (see cartoon):

Ranged along the whole other side of the shed are my pest-blitzing chemicals – two great shelves of them – a mute testimony to the war I wage against the 'creepies and crawlies' (as my wife calls them) that frustrate me in my determination to have a garden. To recall a few of the labels of the bottles and tins that confront me: there are DDT concentrated (one gallon); white oil; red oil; DDT powder, snail killer; Bordeaux mixture; black leaf 40; anti-wilt powder; benzene hexachloride; fruitfly bait; lime sulphur; gam mexane; soil fumigant; spraying sulphur; bulb disinfecting fluid and bluestone.



Cartoon 'Preparing for one more season of entomological gardening'. (*The West Australian*, 1950, 17 June, p. 21.)

Nowadays, the mode of action of nicotine is reasonably well understood. This psychoactive alkaloid is an agonist of the ionotropic nicotine acetylcholine receptors (nAChRs), which upon activation lead to an increase in signalling along the neuronal network. The exposure of pests to nicotine for a prolonged time or at high doses leads to the activation and desensitisation of the nAChRs in the brain, ultimately causing death. However, nicotine resistance has arisen in insects due to the expression

of altered nAChRs with a different affinity for the alkaloid. Other mechanisms of resistance remain to be established. Human neurotoxicity to nicotine is not uncommon as proven by the overuse of transdermal nicotine patches or the consequences of long-term nicotine exposure during gestation.

The growing number of pests developing resistance to nicotine and the more serious problems caused by nicotine to human health, has opened the way to the use of new pesticides

Agricultural Gazette of N.S.W., November 1, 1933.

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The Neptune Oil Company in Sydney advertises for its insecticidal mixture Neptune Sprays, which contain Black Leaf 40 (*Agric. Gaz. NSW*, 1933, vol. 31, p. 80. Reproduced with permission from the National Library of Australia).

termed 'neonicotinoids', which have been inspired by, and are often structurally related to nicotine (see diagram). Although nicotine is no longer used as an insecticide in Australia, synthetic neonicotinoids are now widely employed in Australia for the treatment of different plants and soil and for protection of seeds and timber.

Roberto Fusetto and **Richard A.J. O'Hair** FRACI
CChem are at the School of Chemistry, University of Melbourne. A full list of references is available from the authors.



Groundbreaking work

Smart ways to seek metals

PART II

National Oceanic and Atmospheric Administration Earth–Ocean Interactions Program

Sully Vent in the Main Endeavour Vent Field, north-east Pacific. Hydrothermal vents occur where tectonic plates are drawing apart, and in some cases where subduction is creating weaknesses in the crust. They're the underwater equivalent of land features that we find more familiar: hot springs, fumaroles and geysers.

Thinking outside the box – in places under the sea or outside the atmosphere – creates new paths into the metals cycle.

BY **DAVE SAMMUT**

The Earth has a problem. It's really not that big a space to support more than seven billion humans, especially when that population is growing at more than 200 000 per day (and accelerating), especially when our global average intensity of use of every kind of resource is growing and especially when all of these resources are held within a band about 12 kilometres thick (a couple of kilometres in the crust and the rest in the atmosphere).

Within that infinitesimally small percentage of the world's volume, the vast majority of the resources we need currently come from the land, which itself is less than 30% of the surface

area. Ultimately, while the mathematics might play out on a vast scale, the conclusions are inevitable: we need to maximise the efficiency with which we extract, process, transport and utilise our finite resources, and then we must ensure that every practical scrap is returned to the beginning of that cycle.

In the first part of this series (September, p. 20), I wrote about some really interesting initiatives being undertaken within the land-based metals cycles, with a particular emphasis on 'above ground resources' – metalliferous materials that offer excellent opportunities for recycling, up-cycling, industrial ecology and every other term that might apply.

From 'urban mines' (landfill) to

sewage sludge residues, those present-day opportunities are emerging as realistic, incremental improvements to efficiency in the global metals cycles. But what about the really interesting ideas for tomorrow, and what of the questions and challenges these raise?

Seabed mining

Fortunately for most people, the majority of geological activity from plate tectonics occurs where nobody wants to live. While I'd be willing to extend that statement to include Los Angeles, I am of course mostly referring to the ocean floor. In the past 50 years, we have made exotic and fascinating discoveries about what was for a long time considered a lifeless wasteland.

The ocean floor is on average higher in iron and nickel content than the land, which is higher in aluminium and silicon. In a gross oversimplification, one of the factors that makes 'land' land is that the lighter elements 'float' higher on the molten magma of the Earth, and the ocean floor 'hangs' between the stretches of land. Occasionally, as in parts of Newfoundland and Labrador, the subduction of one tectonic plate will push an area of seabed up, and so Labrador is now host to one of the world's biggest nickel mines.

In the 1960s, it was discovered that nickel- and manganese-rich balls were just lying on the abyssal plains of the Pacific Ocean. There was a flurry of news just this year, when huge versions of the same were found in the Atlantic. Measuring from golfball to bowling ball size, these grow incredibly slowly – at a rate of just millimetres per million years. The discovery (then and now) sparked serious investigations and expenditure into the possibility of their recovery.

The other big discovery of the 1960s was 'black smokers', or hydrothermal vents. Superheated water emerges from these vents heavily laden with dissolved minerals – copper, zinc, lead, nickel, silver and

gold. On contact with the near-freezing water at the deep oceanic floor, these minerals immediately precipitate. The typical depth at which active sites are being found is around 2100 metres, but black smokers have been found as deep as 5000 metres, for example in the Cayman Trough.

In fast-growing, active areas, black smokers can reach 40–60 metres in height, growing at up to 30 centimetres per day. However, it has more recently been found that some of the largest 'massive sulfide' deposits may actually form from slower-growing sites. The substantial Mount Isa ore body is actually an example of a formerly seafloor massive sulfide mineral deposit.

A combination of economic and technical factors means that the seabed mining of minerals is an idea whose time has come, 'ready or not'. High-grade land-based mineral resources in politically stable areas are becoming less common. Even with incremental efficiencies in mining and minerals processing techniques, metals prices creep inexorably upwards. Decades of petroleum experience have honed deep-sea technologies. Inevitably, companies have started seriously looking at the opportunities afforded by offshore resources.

The most successful to date is diamond mining. De Beers already has multiple dedicated vessels that effectively suction diamonds from the shallow seabed, typically in the alluvial zones where rivers passing through land-based diamond fields empty into the sea (for example off the west coast of South Africa). Its vessel *MV Mafuta* (formerly the *Peace in Africa*, as seen in the Discovery Channel's documentary series *Mighty Ships*) mines 10 000 m³ of water and gravel per hour, to produce roughly 240 000 carats (~48 kg) of diamonds annually.

The emerging entrants into the seabed mining of massive sulfides are Nautilus Minerals and Neptune Metals. Of these, Nautilus is closer to production, having recently settled a

A combination of economic and technical factors means that the seabed mining of minerals is an idea whose time has come, 'ready or not'.

long-running dispute with the government of Papua New Guinea over costs. The mineral grades in Nautilus' primary site, Solwara 1 in the Bismarck Archipelago, are roughly ten times the typical grade of a land-based copper deposit: 6.8% Cu, as compared to 0.7%.

Proponents argue that there are many advantages to seabed mining: less tonnage to be mined per unit metal recovered, no impact on food production, surface freshwater or groundwater, pollination, soil formation or erosion, historic or cultural values, and 'no significant risk of disaster', such as mine tailings collapse.

However, there are justifiable reservations about the concept of seabed mining. The third big discovery in ocean geology was the astounding presence and diversity of life surrounding these active smokers. Far from light and oxygen, entire ecologies of previously unsuspected organisms exist, as chemosynthetic bacteria and archaea form the basis of a food chain supporting diverse higher organisms, including giant tube worms, clams, limpets and shrimp.

The effects of seabed mining on these ecologies is largely unknown. It is possible that each site may be unique, and their mining creates multiple risks: disturbance or destruction of species and the balance of species; the effects of stirred-up sediments on filter feeder populations;



Close-up image, taken by NASA's Near Earth Asteroid Rendezvous mission in 2000, of Eros, an S-type asteroid with an orbit that takes it somewhat close to Earth.

NASA/JHUAPL

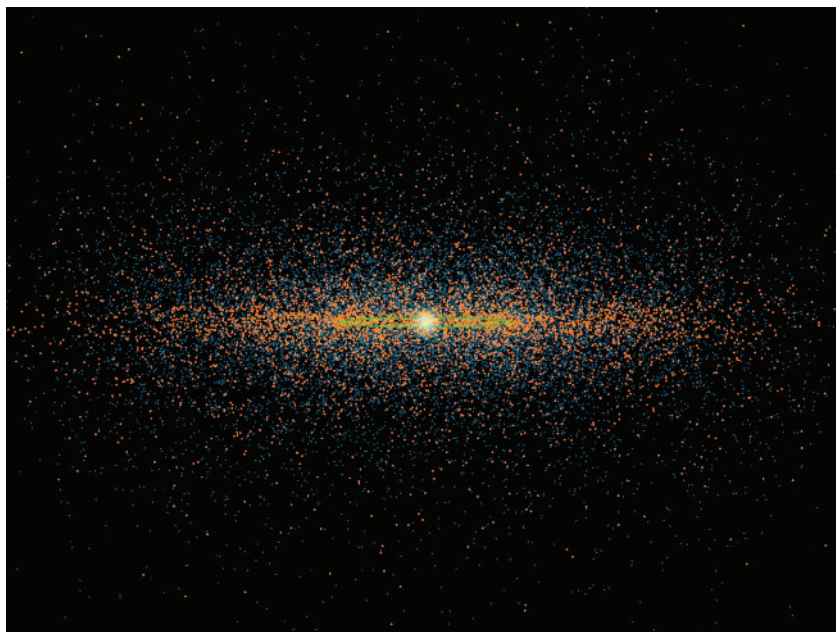


Diagram showing an edge-on view of our solar system. The dots represent a snapshot of the population of near-Earth asteroids (blue) and potentially hazardous asteroids (orange) that scientists think are likely to exist on a typical day based on the asteroid-hunting portion of the Wide-field Infrared Survey Explorer (WISE) mission. Earth's orbit is green.

NeoWISE

methane clathrate release; the potential for sub-oceanic landslides; acidification of the water; and more.

To address these concerns, a three-year research project involving 25 European research institutions kicked off in January this year. Among its studies, the EU Joint Program healthy and Productive Seas (JPI Oceans) initiative will visit a seafloor area in the Peru Basin that was disturbed by ploughing in 1989 to investigate the scale of recovery, the ecosystem status and the biogeochemical situation after 26 years.

While I think the science is fascinating, I agree with project coordinator Dr Matthias Haeckl of GEOMAR: 'We should get to know the deep sea better before we start to change it on [a] potentially large scale'.

Asteroid mining

An avid reader of science fiction from a young age, I have grown up with the excitement, adventure and challenges of life in space. And after a decade or more of relative dormancy in space exploration, the news as I write this article is filled with space. The New Horizons flyby has transformed poor, unloved Pluto from a fuzzy dot to a treasure trove of new information. The European Space Agency's Rosetta mission soft-landed its Philae probe on comet 67P carrying alpha-particle X-ray and IR-vis spectrometers, and a GC-MS. And in July, private company Planetary Resources has successfully launched its Arkyd 3 spacecraft on a test mission to the International Space Station.

Planetary Resources is one of two US companies that are currently vying to be the first to mine economic resources from asteroids. Both have ambitions to be doing so within the next ten years. This is particularly interesting because asteroid mining has implications both for returning metals to Earth, and for supplying further space-based missions.

Approximately 70–75% of objects in the asteroid belt beyond Mars' orbit

are expected to be carbonaceous 'C-type' asteroids, rich in organic compounds, ammonia and water, as well as potentially useful isotopes of hydrogen and helium. The material is expected to be extremely friable, able to be crushed between thumb and forefinger, making it readily recoverable. And it could be critical to supplying further space missions, where each tonne lifted from Earth's gravity well into low orbit currently costs more than \$20 million.

The other two types of asteroids identified in spectral studies are silicate 'S-type' and metal-rich 'M-type'. Both are considered to be relatively rich in metals, particularly valuable and useful metals: Au, Ir, Ag, Os, Pd, Pt, Rh, Ru, W, Fe, Co, Mn, Mo, Ni, Al and Ti. And these metals are likely to be distributed quite evenly through the asteroid, making them readily accessible.

Some scientists have advanced the theory that while Earth's gravity would have pulled the siderophilic (iron-loving) elements to the molten core of the planet during its formation roughly 4.5 billion years ago, much of the available near-surface resources that we now mine actually came to Earth during the subsequent period of asteroid bombardment after the Earth had largely cooled.

Astronomysource.com estimates that a single 1-kilometre-diameter M-type asteroid could alone contain roughly 7000 tonnes of platinum, with a value of more than \$200 billion at today's prices. Given that this is more than 50 times the annual global consumption, a single asteroid would be enough to significantly disrupt global markets. Successfully mining asteroids on a commercial scale could potentially affect markets in much the way that the invention of the Bayer and Hall-Heroult processes catastrophically devalued aluminium in the late 19th century. But then, the sudden change in the cost of aluminium created entire new uses that ultimately revolutionised a range of

Possession is nine tenths of the law

For both seabed and asteroid mining, the law is scrambling to catch up with technology. With substantial expenditure from private companies to recovering resources from non-territorial areas, there is a huge question mark over how value is to be shared.

A 1994 United Nations Convention on the Law of the Sea yielded the International Seabed Authority, which notionally polices and licenses the seabed (but not the waters above it). In principle, the value of resources falling outside the exclusive economic zones of individual nations is to be shared globally, including with developing and landlocked nations. However, even with 159 member nations, there is one prominent holdout (a country that has perfected the 'self' in 'self-interest'), contenting itself with 'observer' status.

Space is even more of a cowboy paradise. While the Outer Space Treaty was signed in 1967, which declares the moon and other celestial bodies as the 'Common Heritage of Mankind', there are multiple ambiguities in the practice of the law. The US refused to join more than 100 other countries in ratifying the 1984 Moon Agreement, and more recently its Congress passed the *Asteroid Act*, granting ownership of any resources extracted from asteroids to the company that mined them. This sort of unilateral declaration is strongly akin to America's 1856 Guano Islands Act, and it might be expected to cause the same sort of legal trouble.

Ultimately, these issues probably won't be tested at law until long after mining has begun. Until then, asteroids are likely to be a big game of 'finders keepers'.

industries, including food and construction. What opportunities would a change in the cost of platinum group metals have on our industries?

There are plenty of challenges in the concept of mining asteroids. With little or no gravity, you don't so much 'land' on an asteroid as 'dock' with it. Means will have to be found to securely anchor the mining equipment to the surface, or Newton's third law will make the job pretty difficult. For C-type and S-type asteroids, a simple scoop or something akin to a snowblower – technologies that exist already – should serve admirably, and some target metals might be magnetically separable from the regolith. However, new cutting technologies might be needed for denser M-type asteroids. That remains an unknown at this stage.

The extreme temperature gradients in space are another major challenge. In a July 2015 proposal funded by NASA's Emerging Space office, NexGen Space LLC posed a novel solution for moon colonisation. The short description is that large

robotically controlled mirrors will reflect the sun's rays into a crater, where it will create a less hostile micro-environment for a small army of other terraforming robots that will mine water and minerals from the moon's surface, while fixed equipment will hydrolyse the water for fuel and air for future colonists.

Other NASA-funded technologies are examining 3D printing of metal components in situ, and the repurposing of a host of other current technologies for real advancement of space-based development.

However, the *Nostramo* of Hollywood's 1979 classic *Aliens* was a mining ship returning from an asteroid. While the possibility of life on an asteroid is unlikely to be quite as scary, the seabed experience tells us that life can exist where we least expect. We may need to literally tread carefully in our progress.

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



Understanding public perceptions of chemistry

The Royal Society of Chemistry looks at the findings from their research on public attitudes to chemistry in the UK.

Last year at the Royal Society of Chemistry we announced that we were undertaking research to try to understand public attitudes to chemistry in the UK (*RSC News*, October 2014) and since then hundreds of members have been involved in interviews, surveys and workshops.

We are now very excited to present the findings of the first national, in-depth study of how the UK public thinks and feels about chemistry, chemists and chemicals.

The first study of its kind

Much research has been conducted into public attitudes towards science but there is relatively little data about

attitudes towards chemistry. Anecdotal evidence suggests that there is low public awareness and recognition of what chemists do. Our study provides robust data on the public's relationship with chemistry in the UK, and an insight on how it could be improved.

The research was conducted on our behalf by the social research company TNS BMRB. It included several stages of qualitative and quantitative research, including a national public survey, with 2104 face-to-face interviews with UK adults (16+).

Here we present the key findings, along with infographics. You can read the full report and see other supporting materials at our project page (rsc.li/pac).

Good news

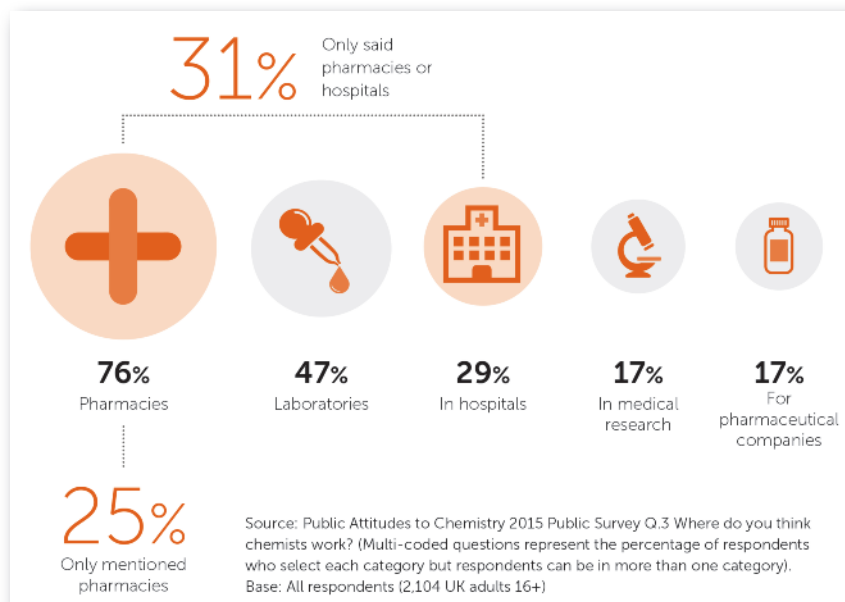
The public perception of chemistry, chemists and chemicals is more positive than we expected. We asked our members to take part in an online survey to find out how they thought the public would answer some of the questions. When we compared what we thought people would have said with what they actually said, we saw that members painted a significantly more negative picture than the one that emerged from the public survey.

For example, only 25% of the UK public agreed that 'school put them off chemistry' but 96% of the members we polled thought that more people would have agreed with that statement. Also, 60% of the UK public agreed that 'everything is made of chemicals' but only 25% of the members we polled thought more than half the public would have said so. So our negative prediction has not been confirmed; far from it. Overall, people in the UK are positive about chemistry's impact on society.

Strong neutrality

Despite this general acclaim for chemistry, people lacked specific examples of how chemistry makes a positive impact, instead finding it easier to specify and visualise negatives or stereotypes. People lacked personally relevant and concrete examples and, for many, the word 'chemistry' activated memories, symbols and feelings of their school experience. In the absence of other associations, this was the predominant driver of responses. In general most people lack an emotional connection: half (51%) of our survey respondents said they felt 'neutral' about chemistry.

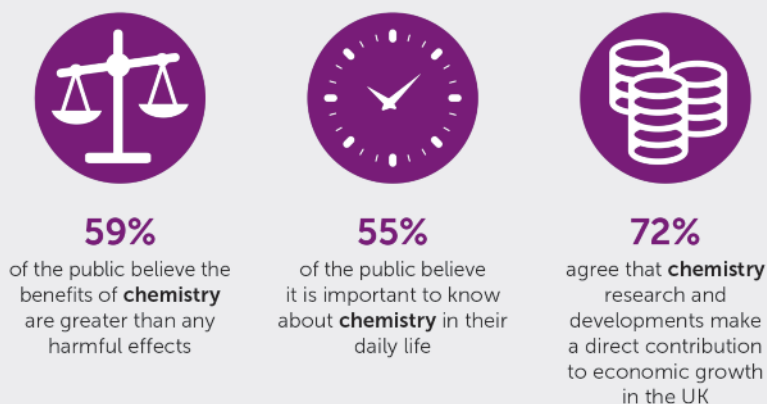
The lack of association and emotional neutrality is indicative of a void in people's engagement with chemistry. Their views are vulnerable to stereotypes and are influenced strongly by the only thing most people can link back to chemistry: their school experiences. Workshop participants described their negative or neutral experience at school



When prompted, people recognise that not all chemists work in pharmacies and, as with all scientists, they are held in high regard.

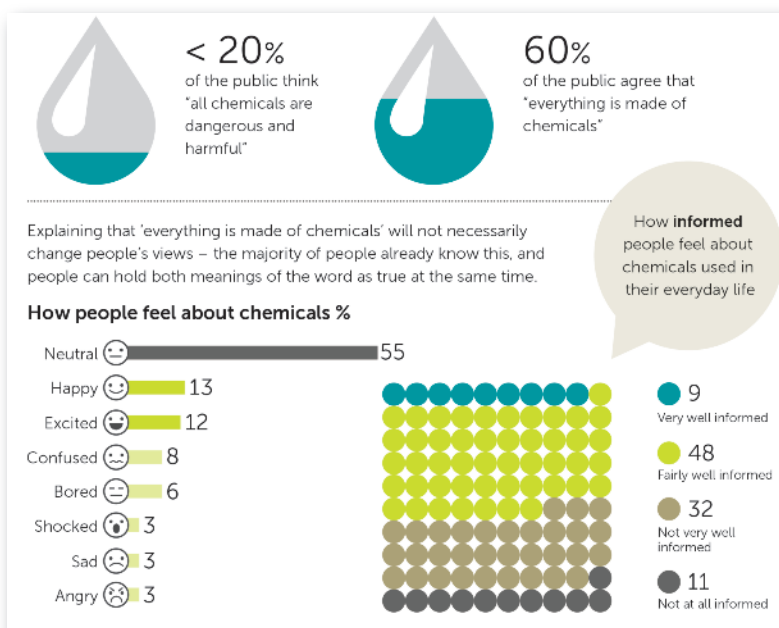


People are positive about chemistry's contribution to society



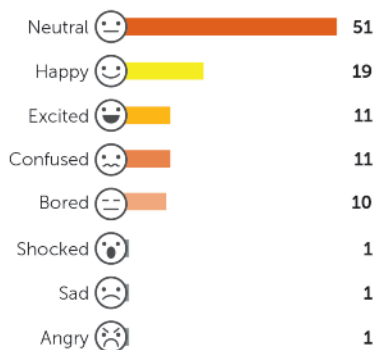
leading them to feel indifferent, but for some it elicited feelings of fear and insecurity. This translated into a general lack of confidence about the

subject. Over half (52%) of survey respondents agreed that they did not feel confident enough to talk about chemistry.



Public perceptions of chemistry are more positive than chemists expected

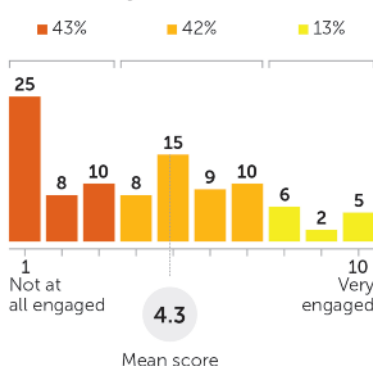
How do you feel about chemistry? (%)**



People don't have an emotional connection with chemistry

Royal Society of Chemistry

How engaged or interested are you with chemistry? (%)



Overall engagement is fairly low

dangerous substances. Though this is the principal meaning, it is not the only meaning, and respondents showed their definitions were multiple and context-dependent. In general, people scored quite well in all the questions about chemicals:

- 75% disagreed that all chemicals are dangerous and harmful.
- 70% agreed that everything including water and oxygen can be toxic at a certain dose.
- 60% also said that everything is made of chemicals.

Just as for chemistry, people were relatively neutral about chemicals (55%) and just under one in five (19%) reported feeling positive. People's views of chemicals were nuanced and multifaceted, and they were seen to possess positive, neutral and negative attributes.

A clear finding of this research was the associative separation that existed between chemicals and chemistry. People's views and feelings about chemicals were not attributed to chemistry or chemists.

Challenges and opportunities for public communication of chemistry

Current public attitudes to chemistry are fairly neutral and in general the picture is more positive than we expected. There are few actively negative views to overcome, and there are some inherent challenges involved in engaging people with a subject in which they have limited interest.

This research offers us new insights into people's view on chemistry, chemists and chemicals. We hope the findings will inspire our community to think about the results.

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Views on chemists

Most people associate chemists with pharmacists, as they lack other examples of the kinds of industries chemists work in. While this is probably not a big surprise, as many chemists know about this issue in the UK, the scale of this is certainly not to be underestimated. Initial survey responses to the word 'chemist' showed an overwhelming and strong association with pharmacists (26%), medication (22%) and the chemist's shop (13%). When asked where a chemist might work, three-quarters

(76%) of respondents said a pharmacy, with one in four (25%) mentioning only pharmacies.

When we asked about chemists as scientists, people's views were positive, with 95% saying they thought chemists made a difference in the world, 93% saying they were honest, and 88% that they were approachable.

The double meaning of 'chemicals'

The word 'chemicals' is used in everyday language as short-hand to refer to harmful or potentially

Justin Gooding appointed inaugural editor-in-chief of ACS Sensors

The Publications Division of the American Chemical Society (ACS) has announced the forthcoming 2016 publication of *ACS Sensors*, a peer-reviewed, interdisciplinary research journal to be devoted to the dissemination of original research findings from across all areas of modern sensor science. Justin Gooding FRACI CChem, Scientia Professor and founding co-director of the Australian Centre for NanoMedicine at the University of New South Wales, will serve as the journal's inaugural editor-in-chief.

Sensors research encompasses the study of miniaturised devices that can detect specific biological, chemical or physical processes; compounds; or ions in complex samples and that transmit real-time information. With the global sensors market estimated to reach over \$110 billion by 2019, the foreseen impact of various sensors is significant. As sensors continue to shrink in size, decrease in cost and require less power, the need for sustained innovation is paramount, and fundamental chemistry research forms the basis for diverse applications.

ACS Sensors will provide a needed forum for scientific interchange among members of this globally dispersed and scientifically diverse community of researchers. The journal will publish seminal advances related to all aspects of sensor research, including but not limited to biosensors, chemical sensors, gas sensors, intracellular sensors, single molecule sensors, cell chips, arrays and microfluidic devices.

'This is an exciting time for studies on sensors, with progress being propelled by incredible fundamental, as well as technological, advances,' says Gooding. 'Sensors are important to many aspects of our daily lives, from assessing whether our water is safe to drink to probing and understanding the inner workings of the cells of our bodies – and yet there are many scientific innovations still to come as researchers craft new sensors tailored to a wide range of analytical and other transformative applications. My goal is to establish *ACS Sensors* as the foremost interdisciplinary journal in the field, by featuring novel discoveries drawn from both basic academic and commercial research sectors, as well as ground-breaking engineering applications.'

Gooding is internationally recognised for his work in surface modification, biosensors, functional nanomaterials, cell-based diagnostic devices and electroanalysis, and he is the first ACS Publications editor-in-chief based in the Asia-Pacific region. In addition to his roles as deputy head of the School of Chemistry at the University of New South Wales and founding co-director of the Australian Centre for NanoMedicine, Gooding is the node leader for the Australian Research Council Centre of Excellence in Convergent Bio-Nano Science and Technology. The recent recipient of the prestigious Australian Laureate Fellowship,

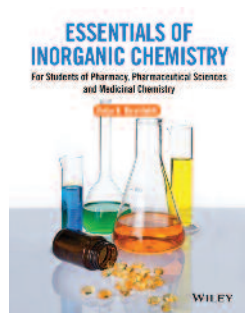


Gooding has authored or co-authored nearly 300 publications and holds 11 patents.

ACS Sensors began accepting research submissions for consideration in early August 2015 and will publish its first issue online in January 2016. It will include flexible open-access publishing options for authors, but otherwise will be free from any required author publishing charges.

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Essentials of inorganic chemistry: for students of pharmacy, pharmaceutical sciences, and medicinal chemistry

Strohfeldt K.A., Wiley, 2015, paperback, ISBN 9780470665589, 286 pp., \$89.95

This conveniently sized volume gives the reader a wealth of information about the historical and current pharmaceutical uses of compounds and the *in vivo* roles of various elements, stories that were sufficiently interesting to encourage me to read the book in one sitting. The book is at its best recounting the discovery and subsequent development of drugs such as Salvarsan (first of many modern arsenic-based drugs) and cisplatin (the well-known anticancer drug).

At the outset, Strohfeldt states two goals for *Essentials of inorganic chemistry*. The first is 'to interest students from pharmacy, pharmaceutical sciences, and related subjects to the area of inorganic chemistry'; the second is 'to teach basic inorganic chemistry, including general chemical principles, organometallic chemistry and radiochemistry, by using pharmacy-relevant examples'.

It should be possible to meet both these goals, but it is a big ask. They often oppose one another, especially early in the book where Strohfeldt often ducks away from some interesting descriptive passage to discuss an essential concept in physical chemistry. These excursions on topics such as osmotic pressure and the Nernst equation work against the goal of stirring students' interest in inorganic chemistry. Readers with some familiarity with physical chemistry are likely to skip or pedantically nit-pick these parts, and for readers without such familiarity they seem too concise to be of great help. Similarly, the very general chemistry content of the introductory chapter is likely to bore most target students with a potential interest in inorganic chemistry, while the copious organic nomenclature and structures introduced later in the text without explanation are likely to baffle students for whom this information is new and useful.

After the introductory chapter, *Essentials of inorganic chemistry* is sensibly structured as a bit of a tour of the periodic table. Strohfeldt considers each group in turn in its own chapter, but after group 15 skips to the d-block and unaccountably never returns to discuss the pharmaceutical roles of members of groups 16–18. From the d-block, Strohfeldt goes on to the lanthanides and radiochemistry, before concluding with a chapter on chelation for heavy metal poisoning, but selenium nutritional supplements, non-radioactive roles of iodine, and the anaesthetic properties of xenon are omitted.

Questions and case studies are given for each chapter, which are welcome; in my experience with one physical chemistry textbook (which will here go nameless), pharmacy students bitterly resent textbooks without end-of-chapter questions.

These questions could, however, be more numerous and are somewhat repetitive; almost every case study begins 'your pharmaceutical company has been contacted by an important client ...' Answers to the questions are given on the book's companion website, but I could not find a password to access the site in my review copy.

All in all, I believe *Essentials of inorganic chemistry* has a good chance of meeting its author's first stated goal, to help interest students in inorganic chemistry. It would be a useful adjunct to more general chemistry texts for students in first and second years of study in pharmacy, pharmaceutical sciences, and medicinal chemistry, providing a framework to structure the more detailed but less contextualised information on inorganic pharmaceuticals they will doubtless be looking up on the internet.

Chris Fellows FRACI CChem

The chemistry of molecular imaging

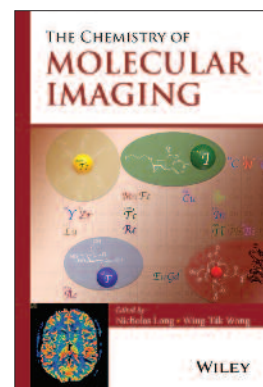
Long N., Wong W.-T. (Eds), Wiley, 2014, hardback, ISBN 9781118093276, 408 pp., \$213.95 (Amazon.com price US\$117.60), online access options available at bit.ly/1SZevPb

The editors of *The chemistry of molecular imaging* claim it's the first such book 'written from a chemist's point of view about the chemistry of novel biological probes' rather than a focus on the mathematical and physical principles behind techniques such as MRI and CAT scans. I think they just might be right.

It should be stressed that the form of molecular imaging in this book relates almost exclusively to biomedical imaging methods; indeed it might better have been called *The chemistry of molecular bio-imaging*. The medical focus is not so unexpected given the important role molecular imaging will likely play in unscrambling the molecular mechanisms of disease in years to come. However, if you are thinking of images such as those presented in the 2009 work of Gross and colleagues using atomic force microscopy (bit.ly/1FFYKL2), then I'm afraid you will need to look elsewhere.

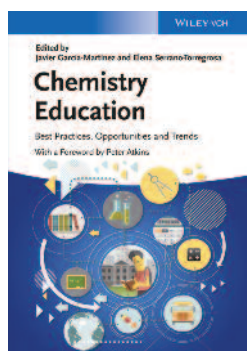
Notwithstanding the above, what the book does cover it covers very well. There are no less than 16 chapters, each written by high-quality researchers and with a good range of examples and illustrations of all the important points. Chapter 1 provides the reader with a good grounding of the basics of topics such as PET and NMR. This is followed by chapters on the chemistry of a very comprehensive range of contrast and imaging agents. The book ends with chapters on topical subjects such as microbubbles for ultrasound and MRI and imaging probes using nanoparticles (the buzzword of the moment).

The chemistry of molecular imaging is very well written and



for the most part easy to read - with the proviso you have some background in chemistry and/or imaging techniques. If you don't have the latter, then you might struggle with some sections. You can, however, dip in and out of chapters of interest. If you have an interest in any form of bio-molecular imaging, then I think you will find something here that will appeal to you.

Oliver Jones MRACI CChem



Chemistry education: best practices, opportunities and trends

Garcia-Martinez J., Serrano-Torregrosa E. (Eds), Wiley-VCH, 2015, hardcover, ISBN 9783527336050, 792 pp., \$347.95

I remember learning to light a Bunsen burner and what an Erlenmeyer flask looks like. This is the sum total of my retained knowledge from high school chemistry. It

seems things have changed – a lot and for the better.

Chemistry is an odd subject. On the surface so accessible, such *fun*. Who isn't delighted by giant soap bubbles, invisible ink and the Mentos candy soda fountain? But then, to understand the hydrophilic and hydrophobic nature of molecules, the process of oxidation and the interaction between carbon dioxide and nucleation sites requires a long struggle with abstract concepts and the acquisition of complex cognitive skills.

Alleviating this struggle is the focus of *Chemistry education* (*Chem ed* for short). First, a quick overview of its three parts, 28 chapters and 46 contributors from 14 countries on four continents.

Part 1, 'Chemistry education as a global endeavor', focuses on making connections between students and teachers and between chemistry and 'real-life'. Here you will find fresh perspectives on curriculum design, empowering teachers and lifelong learning, all illustrated with examples from ongoing practice. This isn't about half-day 'field trips' to a local factory. In one of many examples, learners solved an emissions problem for the owners of a pulp mill and saved them millions of dollars in fines. That's 'real-life'.

Part 2 is a showcase of best practices and innovative strategies for problem solving, flipped classrooms, project-based learning, making laboratories work better and microscale experiments. Part 3 illustrates the role of new technologies. Even the technically adept may be surprised at just how many new technologies there are in use now and on the horizon.

Throughout the book, chapter authors introduce readers to new knowledge and understandings of the cognitive processes

underlying teaching and learning and reflect on the various goals and aims of chemistry education. The chapter on the role of language in teaching and learning is particularly insightful and a topic too seldom addressed in discussions of pedagogy.


New technologies are exciting, but without the focus on process and intentions that runs throughout *Chem ed*, technology is just more bells and whistles. What is new since I was in school is this deeper understanding of the cognitive processes underlying teaching and learning and the recognition that teaching a science must serve multiple needs that run from immediate in-the-classroom-today to the long-term competitive advantage of nations.

Yes, we want Nobel Prize-winning chemists on our team, but we also want a well-trained work force of lab technicians and support staff. We want doctors and nurses and vets and fire fighters and police officers and printers and food service staff who know exactly as much as they need to know about chemistry to perform their jobs well – and who are also not afraid to learn what they need to know as the job changes. Finally, we want an informed citizenry, people who can read a news article with a critical eye, people who can attend a town hall meeting on a development proposal and ask intelligent questions about potential chemical hazards.

Chem ed is about how committed and innovative educators are achieving these goals. A comprehensive assessment like *Chem ed* is a seminal work, one scholars are likely to be citing for decades. It is a snapshot of the early days of a fundamental transformation in education. The content of *Chem ed* is of a part with the explosive growth of massive open online courses, the vigorous debates about the future of certification and the future of learning in general. Connect these dots and it begins to look like the long-promised and much-hyped 'revolution in education' is finally here.

I have been ready for the revolution since about grade six. If you are too, then get a copy of *Chemistry education* and share it with your colleagues.


Terry Clayton



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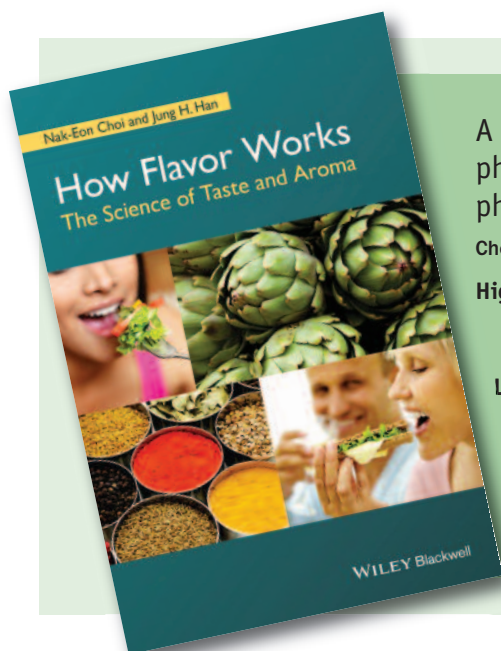
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A curious blend of evolution, chemistry, biochemistry, physiology, psychology, neurology, history, sociology and philosophy relating to the science of taste and aroma.

Choi N.-E., Han J.H., Wiley, 2015, softcover, 223 pp., ISBN 9781118865477, \$59.95

High point: a very accessible, compact text providing the reader with a very comprehensive picture of taste and aroma fundamentals. Willing to demystify and debunk some popular nutritional myths.

Low point: a tendency for repetition and incomplete referencing.

Audience: anyone with even a passing interest in how we elucidate taste and smell.

Fascinating fact: how flavours are produced by cooking a steak (Maillard reaction).

... the author is keen to demystify or dispel a number of popularly held notions pertaining to particular foodstuffs and the nature of food itself. Monosodium glutamate (MSG, the sodium salt of glutamic acid), often cast as the villain, is the author's personal bugbear.

Jung H. Han has produced a very accessible English translation of Nak-Eon Choi's 2013 Korean language text *What is taste?* Both are accomplished food scientists and have either authored (Choi) or edited (Han) a number of nutrition-related books. Choi is also a self-declared 'super blogger'.

The text is a curious blend of evolution, chemistry, biochemistry, physiology, psychology, neurology, history, sociology and philosophy relating to the science of taste and aroma. When we begin to analyse precisely how taste and aroma work, the roles of these 'ingredients' in the mix rapidly become evident.

One cannot understand or gain an appreciation for taste and aroma without a firm grasp of the underlying (evolutionary) origins of taste. So the author devotes a considerable portion of the book to describe and explain the biological, chemical, neurological and physiological fundamentals of taste and 'smell'. A refreshing aspect of Choi's work is his point, made on several occasions throughout the book, that the constituents of foods, drinks and other substances are not inherently 'good' or 'evil' or possess special powers. In Choi's world, it is how our body's systems interact with various chemical components that is truly remarkable.

Early in the book, it also becomes clear the author is keen to demystify or dispel a number of popularly held notions pertaining to particular foodstuffs and the nature of food itself. Monosodium glutamate (MSG, the sodium salt of glutamic acid), often cast as the villain, is the author's personal bugbear. By book's end, however, the reader can be in no doubt about glutamic acid's (and by association MSG's) biochemical virtues. Choi also attempts to dissect and 're-balance' the debate about natural versus synthetic flavours (e.g. in terms of safety, efficacy), obesity, alcohol consumption and the media and its portrayal of nutritional issues. To a large extent, Choi succeeds in drawing or showing the link to these issues and the science of taste and aroma. What's more, he also manages to achieve his goal of 'righting some wrongs'.

The book comprises ten chapters (the last being 'concluding remarks'). Each is subdivided into multiple sections of varying length, often just one-third of a page. Formatting chapters into 'bite-sized' pieces helps Choi hold your attention (no 'visual fatigue' here!)* and also allows him to explore a great variety

*Olfactory fatigue' is the temporary, normal inability to distinguish a particular odour after a prolonged exposure to the given aroma. It is a brain-regulated phenomenon to sustain our sensitivity to new odorants.

of taste and flavour aspects and curiosities.

So just how exactly do taste and aroma work? It's complicated; the factors that influence our ultimate perception of the taste of foods include the nature of the food itself (e.g. its form, shape, texture, colour), variables such as temperature, price and pH, marketing, dining environment,* our emotional state, previous encounters with the substance and age to name a few (figure 3.1 provides a neat summary of the key factors). In spite of the complexity, Choi manages to convey the fundamentals of the taste and olfactory components, systems and connections in the initial chapters to good effect.

Of the human senses, the olfactory was developed first and is highly integrated with the limbic system, the body's survival and emotion circuit. This direct link to the limbic system (where memories of flavours and odorants are stored) explains why our taste and aroma response is not only rapid but contextually rich. You remember not only the olfactory but emotional, spatial and time information as well. And if the aroma-induced memories are of a pleasant nature, then the limbic system may even reward us with a 'shot' of dopamine!

The key cells that detect odorant molecules (and initiate a 'cascade' of enzymatic reactions and nerve transmissions) are G-protein coupled receptors, or G-receptors for short.† Humans used to have a reasonable swag of these odorant detectors but over time their number has degenerated to around 400. This 'loss of sensation' has been compensated for largely by refinement and enlarging of our brain, which by

Choi's estimates accounts for more than 50% of cognitive reactions to tastes and flavours. Humans no longer rely on olfaction but on the visual sense to locate and procure food. Chapters 4 and 8 explore G-receptors and the neurology of taste and olfaction in more detail.

Choi reminds us on more than one occasion that flavours and odorants were not synthesised with humans in mind. What we consider as flavours and odorants (desirable or not) overwhelmingly have been purposed largely to protect (e.g. phytoncides), prolong and perpetuate the life of their producers – primarily plants. Plants (particularly the angiosperms) are the planet's primary chemical factories. Interestingly, while the number of known plants exceeds 300 000, '... more than 90% of the odorants are obtained from less than 20 breeds of plant'. And Choi estimates the '... tens of thousands of tastes, flavours and colours of food ingredients are characterised by ... remaining 2%, which have very low molecular weights.'

Chapter 6 is where Choi's taste and aroma training come to the fore. It's here Choi can explore and relate the wonderful world of perfumers, sommeliers and others engaged in the business of formulating and testing new or 'improved' tastes, flavours (and odours). It was pleasing to discover neither a love of cigarettes or garlic nor being of advanced years precludes one from becoming (and indeed succeeding as) a 'trained nose'. As Choi reminds us, discerning and describing particular odours (as a career) is all about training and experience, to develop and enhance parts of our brain involved in high-level cognitive processes, such as the prefrontal cortex and orbito-frontal cortex. To become a perfumer or sommelier 'you must not learn how to smell but how to think'.

There is a light but pertinent sprinkling of figures. My favourites include the Maillard reaction (fig. 5.3), an amino acid-reducing sugar play which occurs during cooking and gives 'browned' foods (e.g. steak, breads) their desirable flavours; a schematic of

manufacturing processes for compound aromas (fig. 6.1) and a schematic of sensorial perception pathways of the brain, as activated by foods (fig. 8.1). From a quick glance of the latter, one gets a clear and strong appreciation for how critical the brain is to integrating, interpreting, memorising (providing future motivation) and responding to flavour/odorant stimuli. As Choi states, taste is truly illusory – it '... does not exist in the chemical substance, but ... how it is perceived by our brains'.

The book is not without its foibles. Choi is prone to repetition; an already slim (barely above 200 pages) volume could have been trimmed further without detriment. For example, he duplicates the 1920's story concerning how many odours humans might be able to discriminate and remember (a 'neat' but debatable 10 000) – an intriguing anecdote but repeated nonetheless. At other times, Choi does not substantiate his conclusions with evidence or makes either rather bold or glib assertions. For example, Choi cites a study about resveratrol (which dismisses its alleged life-prolonging effects) but does not provide the reference. Similarly in a section about aromachology (the scientific study of the psychological effects of fragrances), Choi makes several assertions about the healing effects of various terpenes without stating any references. On another occasion he concludes (after discussing properties of a handful of natural pigments) '... there are not any ideal pigments in nature'. And I was left totally bemused by this remark about 'supernormal stimuli': 'All women are becoming identical in their appearance and body shape ...' Really?

These minor quibbles aside, translator Han and author Choi on the whole deserve considerable credit for producing a readily 'digestible' and rather fascinating insight into the complex 'science' of taste and aroma. Anyone with an interest in foods, flavours or fragrances (dare I say most of us!) will definitely 'sniff out' something of value from this book.

Damien Blackwell MRACI CChem

*One of my favourite contrasting images concerning dining environment is 'Enjoying dinner with loved ones in a high class restaurant ... sweet music ... and fabulously decorated food is *completely different* from eating the same food in a dark dungeon filled with screams after being kidnapped by a rugged looking man!'

†Richard Axel and Linda Buck were awarded the Nobel Prize (Physiology or Medicine) in 2004 for discovering that G-receptors identify odorants in olfactory cells.



Scientific Babel: how science was done before and after global English

Gordin M.D., University of Chicago Press, 2015, 415 pp. ISBN 9780226000299 (hardback) \$40 approx.; 9781847659583 (ebook) \$25 approx.

Scientific Babel by Michael Gordin is a magnificent book about the language of science. It is a very erudite, scholarly work and simultaneously makes engaging and fascinating reading. The title alludes to the

Tower of Babel, described in Genesis, where the mono-linguistic but 'uppity' lot of the times got punished for their folly by suddenly finding themselves in a poly-linguistic morass.

Communication has been a problem ever since! Recently I attended a church service where the congregation was split roughly 50:50 between English and Mandarin speakers. When a hymn was announced, the 'Anglos' sang lustily in English and the 'Mandos' sang lustily in Mandarin. Cacophony indeed! Babel revisited?

Well, it certainly reinforced just how important communication is, particularly in science, and, as an aside, just how lucky many of us are that English has emerged as the international language of scientific communication. Mind you, there can still be major discord between the message given and the message received. Years ago a message from my wife, relayed to me via switchboard and secretary, saying 'The baby is OK' turned out to be 'The lounge is being delivered today'!

Gordin traces the development of scientific communication from the times when all educated (essentially European) people could read, write and, frequently, speak Latin,* and thus science had a universal *lingua franca*, through the emergence of a dominant triumvirate (German, French and English) surrounded by numbers of major national groups publishing work in their mother tongues. Inevitably, this created obstacles to information transfer/propagation as well as mistranslations, misinterpretations and misunderstandings. For example, mistranslation of the terminology of Mendeleev's original Russian paper into the more widely understood German almost cost him the honour of acknowledgement as the 'inventor' of periodicity. Perhaps inevitably, all the babble and confusion spurred efforts to invent a new, universal (artificial) language for scientific communication. The Nobel laureate Ostwald (he of dilution law and ripening fame) was a significant driving force for this, strongly advocating for a modified version of Esperanto and later for another artificial language, 'Ido'.

The Great War really killed off, or at the very least presented a significant distraction from, these ideas. German scientists emerged from this conflict to find themselves shunned by their international confreres. While this in no way impeded award of the first post-war Nobel Prize in Chemistry to Fritz Haber,

famous for fixation of nitrogen and infamous as the inventor of chemical warfare, it did somewhat dampen enthusiasm for all things German, particularly in the US where the strong tradition of young scientists pursuing postdoctoral research in Germany dwindled (despite German dominance of Nobel awards in chemistry in the inter-war years) and many legislatures proscribed both the teaching of German in schools and universities and the very speaking of the language. With the rise of the National Socialist (Nazi) Party in Germany throughout the 1930s, its dismissal of Jews and Communists from the public service (which included universities), its doctrines of hyper-nationalism, racial purity and superiority, coupled with its systematic murder of European Jewry during World War II, it is probably not too surprising that German fell off the platform of dominant scientific languages.

Meanwhile, the US was emerging as an industrial and scientific powerhouse. Not only was German unpopular, but other foreign languages were as well. Besides which, French was just too darned complicated, with all the stuff about genders and declensions of verbs, not to mention the whole shebang being vetted by a central (French) authority. English is much more straightforward! (Though try telling this to someone struggling to learn it!) Anyhow, English won. It is the *lingua franca* of 21st century science.

Gordin will reveal this intriguing story far better than I ever can. It is a complex book on a complex subject. You read a chapter, and then pause to reflect. Overall, I found it a thoughtful and thought-provoking work, filled with insights into how the language of science got us to where we now find ourselves. This is an important story, but not necessarily the full story. There is an implicit assumption that science is, as it were, an invention of the European Renaissance. That may be so. God may, in fact be an Englishman! Alternatively, to get a full picture, it may also be necessary to look at, for instance, scientific communication over history in China, India, or Persia or in an Islamic tradition. How were the problems of communication resolved in other societies? 'If you want to understand just one life, you must swallow the world' (Salman Rushdie). Well, *Scientific Babel* might not be everything, but it is a damned fine bite! Everyone should buy it and read it.

R. John Casey FRACI CChem

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*With tongue firmly in my cheek, isn't this still the case?

Astringency, polysaccharides and ethanol

Two additional factors can impact on astringency perception in wine, which I will outline here to bring this series to a close. One is the role of polysaccharides in moderating the tannin–protein interaction that was first described for foods and beverages in 1987 and reviewed in 2012 by Le Bourvellec and Renard (*Crit. Rev. Food Sci. Nutr.*, vol. 52, pp. 213–48), although the focus was generally on beverages other than wine.

For wine, Victor de Freitas with Nuno Mateus and co-workers from the University of Porto in Portugal proposed in 2004 two models for what they called ‘the disruption effect of carbohydrates [polysaccharides] on protein–tannin aggregates’ (*Anal. Chim. Acta*, vol. 513, pp. 135–40). One model involves the formation of a ternary complex involving tannin, protein and a charged polysaccharide, while the other is based on the concept of the polysaccharide encapsulating or sequestering the tannin, thereby limiting the tannin–protein interaction.

Perhaps not surprisingly, studies appear to support both mechanisms. Essentially all studies have been carried out using model systems and the model design would appear to impact on the results that are obtained. Some approaches have used the three-component models using tannins in combination with proteins and polysaccharides, while others have used only polysaccharides and tannins. To add to the complexity of the studies, not all have used proteins that are, or model, salivary protein and in some cases, the polysaccharides are not wine-derived. Drawing robust conclusions on the impact of polysaccharides on the astringent response remains a challenge.

The research objective now is to relate the various model studies using the three-component systems to the actual wine matrix. Stéphane Vidal and colleagues noted in 2004 (*Food Qual. Pref.*, vol. 15, pp. 209–17) that ‘mouthfeel is a highly complex process’. It depends, they proposed, on not only ‘the presence of each individual component but also on interactions between components and on the structure of the resulting molecular assemblies’. This, to me, opens up the possibility of some good physical chemistry to examine particle dynamics or molecular assembly processes that occur in the wine matrix and link these to sensory studies on astringency. This research activity could also provide a better understanding of wine fining where protein is added to red wine to soften the astringent response.

The ethanol concentration of wine and its impact on astringency perception has received only limited attention until recently. While there is general agreement that the astringent response decreases with increasing ethanol concentration, there is at least one study that suggests the opposite. Part of the issue again relates to experimental design. Ethanol itself can have a dominating effect on mouthfeel, especially in model systems, so several studies have used low (5%) ethanol in the model matrix, while others have used more ‘wine-like’ concentrations.

In our 2012 review on astringency (*Trends Food Sci. Technol.*, vol. 27, see p. 31), we argued that there was a need to examine the effect of ethanol on the molecular aggregation processes occurring in wine and the consequent effect of changes in aggregation on astringency perception. A step towards this has recently been published by researchers from the Australian Wine Research Institute and the University of Queensland (McRae et al., *J. Agric. Food Chem.*, 2015, vol. 63, pp. 4345–52). Using isothermal titration calorimetry, the researchers examined the interaction between poly-L-proline (a model for salivary protein) and various tannin fractions extracted from wine at different ethanol concentrations. Polysaccharides were not part of the solutions used for the titration experiments. The results indicated a change in tannin–protein binding occurred from a combination of hydrophobic and hydrogen bonding to only hydrogen bonding as the ethanol concentration increased from 10% to 15%. The paper became a ‘media hit’, first in *Vitisynth* (bit.ly/1NcbBTM) and then in several other media outlets including that of wine writer, Jancis Robinson (bit.ly/1KSJgBt). It’s great to see chemistry getting positive media coverage.

Some basic physical chemistry may well be important when considering mouthfeel changes and their association with different ethanol concentrations. The viscosity of ethanol–water mixtures actually increases with the proportion of ethanol in the mixture until around 30 mole per cent ethanol (Tanaka et al., *Rev. Phys. Chem. Jpn*, 1977, vol. 47, pp. 12–24). The increase in viscosity and its impact on the various interactions in a wine matrix, especially hydrogen bonding interactions remains to be examined.

I am aware of some new research that will provide more insight into the role played by polysaccharides on tannin–protein interactions. I will discuss it in a follow-up column once the research is published.

To conclude this current quartet on astringency, I will comment on the relationship between saliva flow and astringency, in response to questions on how to measure saliva flow. Imagine being in the dentist’s chair and having the suction tube placed in your mouth while the dentist drills happily away. It is much the same with measuring saliva flow, without the pain of the drill! A saliva stimulant is placed in the mouth and the saliva is collected by suction over a given period and then measured. My dental hygienist tells me that people on antidepressant medication have markedly reduced saliva flow, to the extent that artificial saliva may be sprayed or rubbed in the mouth to enhance lubrication. I am not sure, however, if a research project on the effect of artificial saliva on wine astringency would be funded.



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.

Are LNG exports more valuable than the chemical industry?

At the time of writing, there is political consensus that Australia's 2030 emissions of carbon dioxide should be significantly lower than the emissions level of 2005. The present government's target is for a 26% reduction while that of the opposition is over 30%.

Since 2030 is only 15 years away, it is worthwhile to consider the amount of carbon dioxide emission *increases* that are locked into the economy and consider the impact of this on the chemical and other process industries.

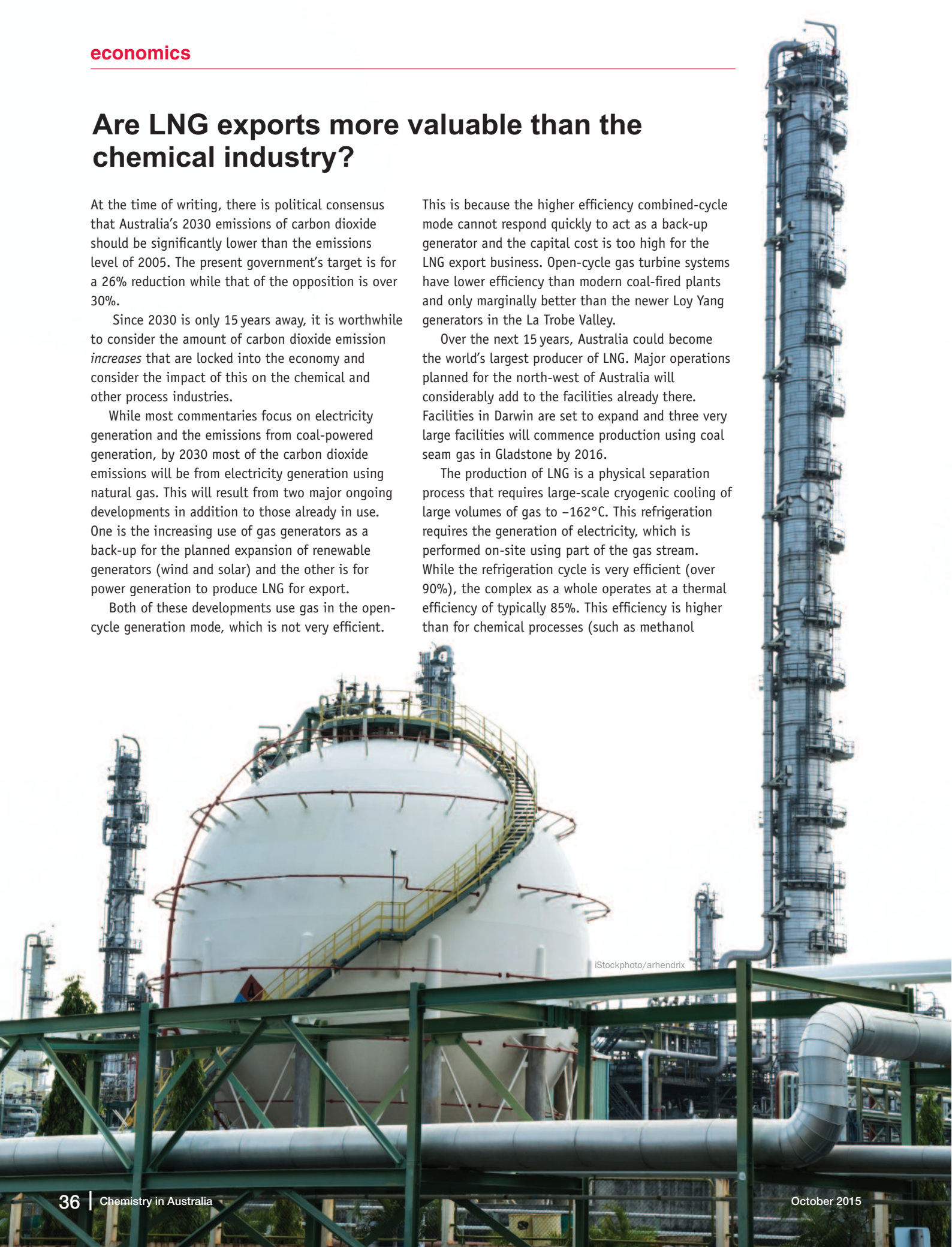
While most commentaries focus on electricity generation and the emissions from coal-powered generation, by 2030 most of the carbon dioxide emissions will be from electricity generation using natural gas. This will result from two major ongoing developments in addition to those already in use. One is the increasing use of gas generators as a back-up for the planned expansion of renewable generators (wind and solar) and the other is for power generation to produce LNG for export.

Both of these developments use gas in the open-cycle generation mode, which is not very efficient.

This is because the higher efficiency combined-cycle mode cannot respond quickly to act as a back-up generator and the capital cost is too high for the LNG export business. Open-cycle gas turbine systems have lower efficiency than modern coal-fired plants and only marginally better than the newer Loy Yang generators in the La Trobe Valley.

Over the next 15 years, Australia could become the world's largest producer of LNG. Major operations planned for the north-west of Australia will considerably add to the facilities already there. Facilities in Darwin are set to expand and three very large facilities will commence production using coal seam gas in Gladstone by 2016.

The production of LNG is a physical separation process that requires large-scale cryogenic cooling of large volumes of gas to -162°C . This refrigeration requires the generation of electricity, which is performed on-site using part of the gas stream. While the refrigeration cycle is very efficient (over 90%), the complex as a whole operates at a thermal efficiency of typically 85%. This efficiency is higher than for chemical processes (such as methanol



Australian LNG projects and estimated carbon emissions from associated power generation

Project	Company	Site	Start	2020 (Mt/year)	2030 (Mt/year)
North West Shelf JV	Woodside and JV Partners	Burrup Peninsula	1998	18.98	18.98
Pluto Train 1	Woodside Energy	Burrup Peninsula	2012	4.3	4.3
Darwin LNG	ConocoPhillips, INPEX	Darwin, Bayu Udan	2006	3.2	3.2
Gorgon LNG	Chevron, Shell, ExxonMobil	Barrow Island	2016	15	30
Ichthys gasfield	INPEX Holdings	Browse Basin, Darwin	2016	8	8
Wheatstone LNG	Chevron, Apache, KUFPEC, Tokyo Electric	Carnarvon Basin, Dampier	2016	8.6	25
QCLNG	BG Group	Gladstone	2014	8.5	12
Gladstone LNG	Santos, Petronas, Total, Kogas	Gladstone	2016	3.9	10
Australia Pacific LNG	Origin, ConocoPhillips, Sinopec	Gladstone	2016	4.5	18
TOTAL LNG				74.98	129.48
CO ₂ EMISSIONS (0.462 tonne CO ₂ /tonne LNG)				34.61	59.77

production), which are typically 75% efficient for the process and 65% for the facility as a whole.

Despite this relatively high efficiency, the enormous scale of the LNG facilities will generate and emit large volumes of carbon dioxide from the power generation required. For most LNG operations, this emission is supplemented by emissions resulting from producing and cleaning the gas prior to LNG production. This principally involves removing carbon dioxide from raw natural gas. In most cases, this carbon dioxide is emitted to the atmosphere. For the Gorgon project (which contains 15% (v) carbon dioxide in the raw gas), this carbon dioxide is captured and injected in deep strata below Barrow Island. For coal seam gas, further emissions arise from fugitive emissions of methane (which has 22 times the greenhouse potential of carbon dioxide) and, because the gas is produced at low pressure, the compression of the gas for piping to the LNG facilities at Gladstone.

Current and upcoming LNG projects are given in the table. Using a value of 0.462 tonnes carbon dioxide per tonne of LNG for the emission from the power generation to make LNG shows that these projects, when completed in 2020, will emit in the region 35 million tonnes of carbon dioxide (MtCO₂e) and by 2030 this emission could be 60 MtCO₂e.

Australia's 2005 total carbon dioxide emissions was about 535 MtCO₂e. If this is to be reduced by 25%, then the target total emissions will be about 400 MtCO₂e. If in 2030, LNG development goes as planned, then this will result in emissions of at least 15% of the total. In order to achieve the target, the non-LNG part of the economy will have to cut CO₂ emissions by 36% based on a national target of 25% reduction on 2005 levels. For a 30% target, the reduction required would be over 40%.

The requirement for gas generators for back-up power in the electricity generation sector will increase as the penetration of wind and solar generation increases. Furthermore, there is a widespread view in the industry that the gas required for this

duty is just not available, so that many of the coal-fired generators will still be required in 2030 to ensure an enduring electricity supply. It is highly unlikely that there will be significant cuts to emissions in the transport sector in the next 15 years, especially the fastest growing part of air travel. The upshot is that a large portion of the emission reduction will have to come from other sectors, including the chemical process industries.

This can be achieved in two ways. The first would require the closure of a significant portion of the chemical process industry, ending domestic production of fuels, polymers, fertiliser and other energy-intensive industries. To date there has been no economic analysis to show that the overall result will be beneficial.

The second method is to allow the purchase of carbon emission credits from developing nations that have generated credits under the UN Clean Development Mechanism (CDM) or a similar carbon-trading scheme.

Whether or not international trading of CDMs and the like would be allowed in any new international protocol is a moot point. If the purchase of these credits is allowed, then those industries that could afford them could still continue to operate. Ideally this should also apply to the LNG export industry but this industry has been very successful in arguing that it should be exempt from carbon emission restrictions.

One aspect of carbon permit trading that has not been addressed is that since China (a developing centrally planned economy) generates a substantial number of CDM certificates, then companies owned by China could have a ready access to CDMs not available to their competitors in Australia. How the politics of this would pan out is anybody's guess.



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

Stopping to smell the flowers

I do not have to stop to smell the flowers because I have been able to do that while I work, as both a flower-grower and a chemist.

'Natural products chemists are conspicuous when they are wandering in the bush. They habitually break pieces from plants, rub them between their fingers, and smell them.' I once wrote this sentence in a paper summarising some interesting things I had read about the mysteries of odours, animals and plants.

Olfaction is an interesting and ancient phenomenon. It is thought to have evolved from the way individual cells in many different situations sense their environment and follow what we loosely term a 'chemical gradient'.

There have been various theories about how the olfactory receptors recognise an odorant molecule. I became sceptical of the simple lock and key hypothesis promoted in student practical exercises when I realised that both cyanide and benzaldehyde have the same smell. We are doing students a disservice about how science works if we keep perpetuating the difference in odour of *R*- and *S*-carvone as the only olfactory mechanism. Other theories include the effects of bond vibrations (which has been partially disproved) and various ideas about 'electronic' interactions, similar to those mentioned in Dave Sammut's article on bees (June issue, p. 18). I echo Dave's comment that there is unlikely to be one simple mechanism for olfaction.

Linda Buck and Richard Axel won a Nobel Prize in 2004 for elucidating that each olfactory receptor can detect several related odorants, and each odorant can stimulate more than one receptor. An odorant pattern, or 'fingerprint', of each smelly molecule stimulates the necessary set of nerves, which send the resultant signals to the brain for decoding. Enzymes can also modify some of the molecules during this process. There is amazing chemistry going on in your nose (where nobody knows).

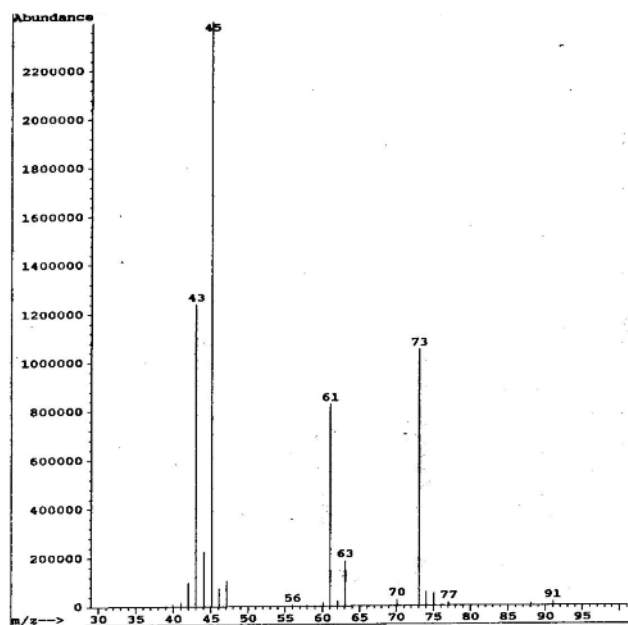
My curiosity was piqued by the very unusual odour of the eastern Australian banksias in my flower plantation. When they are at the point of anthesis (presenting the pollen) and concomitantly producing lots of nectar, some (but not all) have a peculiar and almost addictive smell. I decided to 'grow my own research project' and find out what it was.

Banksias are said to have a generalist pollination syndrome, unlike some other plants such as orchids that rely on a particular animal or insect, although smell may be only one of several attractive features in these cases. Birds are now known to have a sense of smell suited to their environmental niche although once they were assumed to be smell-blind (e.g. bit.ly/1TstDIB). I saw legions of birds visiting the nectar-dripping flowers. Professor Rob Whelan's team at the University of Wollongong has shown that small animals such as gliders and antechinus do as much pollinating at night as birds do during the day, so one of my early hypotheses was that the banksias might produce a smell that attracts birds during the day, and a different one to attract marsupials during the night. But no, the

My curiosity was piqued by the very unusual odour of the eastern Australian banksias in my flower plantation ... I decided to 'grow my own research project' and find out what it was.



Banksia robur. Some of the little flowers have undergone anthesis, and the pollen is presented on the end of the stigma. This is when the odour is most intense.

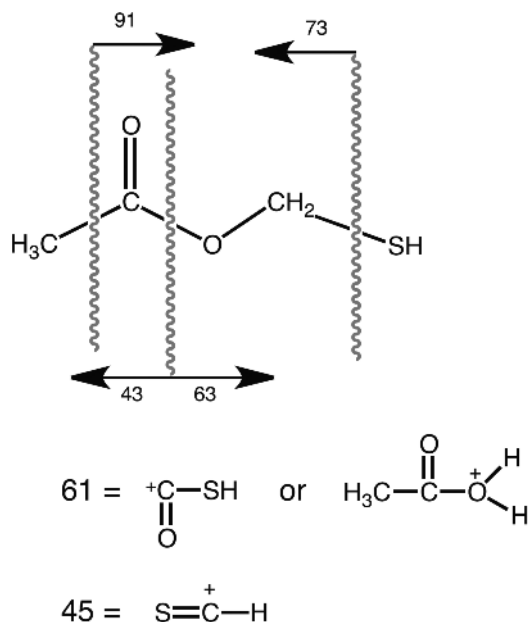


Mass spectrum of 'unknown peak 6' present in all the banksias with the funny smell. Possibly mercaptomethyl-*O*-acetate, if we are not seeing the molecular ion.

smell of half-opened banksias is the same in my paddock on a still night, on a warm day, or in an enclosed space. The chromatograms from environmentally appropriate dynamic headspace analyses are similar too.

I slowly learnt that biology does not follow a chemist's idea of reductionist logic. Animals, birds and insects can learn to associate particular smells with any food source, particularly if it contains sugar. All these creatures can be trained to find food in artificial flowers that have smells and colours that would not be encountered in nature (as mentioned in Dave Sammut's article on bees). So they are not necessarily hard-wired to follow one particular odour to a food source.

In any attempt to isolate the volatile compounds, my first methods involved heating the banksia flowers. I then found a homologous series of aliphatic aldehydes and not a lot else. It is known that some aldehydes are important components of many natural odours. They are possibly formed by degradation of fatty acids such as linoleic acid in the cell membrane by lipoxidase enzymes (LOX), which are released when the cells are damaged. This response of the plant to wounding has parallels in our own primary immune response – the production of prostaglandins. However, these breakdown products can also be produced when the enzymes are released after mechanical damage, and since these heated extracts smelled nothing like banksias, and these aliphatic aldehydes did not show up when I used more gentle dynamic headspace analysis at ambient temperature, I decided they were laboratory artefacts. After all, steam-distilled eucalyptus oil smells nothing like fresh eucalyptus leaves, tea-tree oil smells nothing like fresh *Melaleuca alternifolia* leaves, and dried bay leaves and frozen coriander leaves don't smell or taste like the fresh ones. Just sayin'.



Possible fragments of mercaptomethyl-*O*-acetate (or sulfanylmethyl acetate or thiomethylacetate) that correspond to peaks in the mass spectrum (E.S. Elmore and D. Mottram, pers. comm.).

Eventually, using headspace techniques more like the natural environment of the flowers in the paddock, I found an 'unknown compound 6' (the peak number from a particular chromatographic method), whose mass spectrum did not match anything else we could find. It was there in the flowers who had the peculiar smell, and absent in those that didn't. So, after spending a long time dreaming about fragments flying through the mass spectrometer columns and waking up at all hours to sketch their possible structures, I phoned a friend (actually, a colleague of a colleague of a colleague), who came up with a potential structure that fitted – more or less. It is possibly mercaptomethyl-*O*-acetate (which does have a Chemical Abstracts number). Unfortunately, I got no further in the complete identification of this very flighty molecule (volatile from 'volare' – to fly) due to being a Lone Ranger researcher with only an occasional Tonto and no Silver, and my earlier-than-anticipated retirement.

Recently, again using *Chemistry in Australia* resources, I checked the mass spectra of the sulfur compounds that Geoff Scollary told us have been found in wines, but none of them look anything like my 'compound 6'.

If anyone has any suggestions, or if research has moved forward since my retirement and it is now a known compound, please drop me a line at *Chemistry in Australia*. My curiosity about this compound is not yet satisfied.



Dr Deidre Tronson FRACI CChem used to be a mad scientist, but is now the Good Little Banksia Lady who, in retirement, is an enthusiastic member of Scientists and Mathematicians in Schools at a local primary school. She has proudly raised three science graduates. She has had separate careers in research and teaching, culminating in a position as part-time senior lecturer at the University of Western Sydney, Hawkesbury campus.

Droning on and on

In 1989, Bob Hawke promised that his government would plant a billion trees. The program was to be conducted in cooperation with Landcare, and was intended mainly as a land rehabilitation exercise. Nowadays, a politician making a similar announcement would also make a statement about how much carbon dioxide would be sequestered in all the trees as they grew.

I have never seen any reporting of the success of the program, so its efficacy may turn out to be one of the great unknowns. Hawke's plan was that this task would take several years to complete, but that there would be great environmental, social and employment benefits. Now, a British company, BioCarbon Engineering, has announced its plan to plant one billion trees in one year, using drones to speed up the process. The initial phase would see 1000 trees a day planted in deforested areas, which is a long way from a billion in a year, but it sounds like an innovative approach to tackling an environmental issue.

I first heard of this when a magazine article was posted in an online environmental discussion forum. However, what truly surprised me was the negative tone of many of the comments posted in response, most of which missed the point of the article. Concerns were expressed that genetically modified seeds might be used, or that non-indigenous species might be planted, and a range of other misdirected fears. It seemed to me that the proposal opened up all sorts of opportunities to address some of the downsides of tree planting programs, yet the commenters had missed the upside of the idea.

Other commenters referred to using a drone to complete an aerial survey of the replanting zone before actually spreading seeds. So, using digitised maps from the survey, and GPS positioning, it should be possible to establish a randomised pattern of points at which seeds would be distributed. Using multiple passes over the same area, with different random patterns, and different seed types on each pass, it should also be possible to approximate a natural distribution of new growth of multiple species, without all the effort of having planters walk over what may be difficult terrain.

In other publications reporting on this story, comments have been made about the low rates of germination of seeds distributed in aerial plantings, using planes. One experienced operator suggested that 30% was the best rate of germination and tree growth he had experienced. I'm no expert in silviculture, but a 30% germination rate sounds a lot better than what I'd expect trees to achieve in their natural state. However, for reforestation it might be a low rate of maturation that inhibits success, when compared to humans marching over the terrain, planting seedlings.

Most likely because of the larger areas covered in plantation timber, the use of aircraft for a range of operations is relatively commonplace. One of my recent clients was a plantation company that had lost a large area of plantation forests during the 2009 Black Saturday bushfires in the central highlands of Victoria. I became involved when neighbouring farms complained about overspray with an atrazine herbicide during the process of re-establishing the plantation. Simazine was applied before replanting, to prevent the emergent regrowth of undesirable species (i.e. weeds). The efficiency with which the herbicide could be applied over a large area had to be balanced against the inaccuracy induced by unpredictable winds and the need to fly at minimum heights to stay away from existing trees.

Aerial spraying of agricultural chemicals has been around almost as long as aviation itself. Many World War II pilots began flying as cropduster pilots. One of the best known cinematic images is of Cary Grant being pursued through a corn field in Hitchcock's *North by Northwest*. Grant emerges from the corn field encounter unscathed. Even his stylish suit seems little the worse for wear. However, not all encounters between humans and agricultural spraying have such a benign outcome.

In 2004, EPA Victoria successfully prosecuted a company and individual involved in land-based (not aerial) spraying of vineyards near Robinvale, Victoria. The spray operator commenced operations with a tractor-mounted sprayer near the edge of one property, while vineyard workers were tending vines close by on an adjoining property. The spray drifted across to the vineyard workers, affecting them severely. One was hospitalised, and the treating ambulance paramedics also required medical treatment, due to exposure to contaminated clothing on the affected workers. Additionally, other members of the public were affected by the residues on the workers' clothes as they sat in a medical centre waiting room. A more precise method of applying the pesticide, such as a low flying drone (if available at that time), might have avoided the ill effects.

Perhaps the moral of the story is that while we might be wary and suspicious of new approaches to some activity, it is also important to remember that the established practices can also have their pitfalls.



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The hot breath of a cow

Cellulose, being a glucose polymer, should be an excellent foodstuff but we humans can't digest it, or at least not very much of it, so it passes through our gut unchanged. We can digest the other glucose polymer, starch, but yeasts can't handle either of these large molecules. In beverage production, it's necessary to break down the starch in a 'malting' process so the smaller molecules can be taken into the yeast cells and converted to ethanol and carbon dioxide.

Many other animals are also unable to digest cellulose completely even though many of them grind the grass exceedingly fine. You only have to look at horse droppings to see how successful the internal processes are. Recommending this piece of citizen science brings to mind the work of a Monash colleague who spent a field trip in Africa turning over elephant droppings to see how well the beasts ground up their food. In contrast, you won't see much grass in what comes out of a ruminant animal like a cow, goat or sheep. Such animals have a special digestive compartment, the rumen, in which cellulose is broken down to glucose, or at least glucose oligomers such as cellobiose and cellotriose that the digestive enzymes can handle. The changes are achieved by friendly gut flora that thrive on such food. The mass balance requires us also to acknowledge that some of the carbonaceous material flows down other metabolic pathways, and there is also a fair bit of methane produced. Since, mole for mole, methane produces much more global warming than CO_2 , Australia's cow burps (but, curiously, not cow farts) make a significant contribution to our greenhouse gas inventory.

Listening to lectures about the beautiful organic chemistry that enabled researchers to synthesise the polyether antibiotic monensin, first isolated from *Streptomyces cinnamonensis*, I also learned that its major use was as an additive to ruminant animal feed where it served to suppress the formation of methane, which was, in a sense, a wasted nutrient. Another way to reduce methane emissions is to flood the digestive system with a methane-lookalike, so the last stage of the methane-producing enzyme sequence sees plenty of its 'product' and simply doesn't produce any of the real stuff. Halogenated methanes are believed to play this role, with bromochloromethane (BCM, CH_2ClBr , halon 1011), a compound formerly used in fire extinguishers, a possible antimethanogen.

The global warming potential of BCM has not been calculated, but it's probably not much different from that of dichloromethane, 8.7 (100-year basis). The lack of attention to BCM could be because in the late 1990s it was added to the list of controlled substances under the Montreal Protocol on substances that deplete the ozone layer, and a phase-out date of 2002 was agreed. Its ozone-depleting potential (ODP) is quite modest, only 0.12, and much lower than that of CFCs (ODP = 1) that were the main targets of the Montreal Protocol. Under the Montreal Protocol, feedstock uses of controlled substances are still permitted, on the understanding that the substance would thus be destroyed or irreversibly transformed.



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Although it worked in laboratory glassware, treating whole animals with gaseous BCM (it boils at 68°C) was an exercise that could not be countenanced in the field. There the matter rested for some years until CSIRO researchers took up the vogue for encapsulation and tried BCM (10–12%) encapsulated with α -cyclodextrin, a polysaccharide in which the molecules consist of six glucose units linked head to tail. Tried in Brahman steers, it greatly reduced methane production but the animals did not gain weight so the carbon had not been redirected into protein production. Other antimethanogens investigated by other groups had produced similarly disappointing results. All this was reported by CSIRO researchers in 1997 in the *Australian Journal of Agricultural Research* and the intellectual property so generated is protected by a series of patents granted over the next few years. Japanese researchers have been active in this area, too, with their latest paper being published in the *British Journal of Nutrition* in 2012.

No information is available about the fate of the BCM in these procedures. Is it destroyed, or is it released to the atmosphere in the same way that the methane it supplanted would have been?

Feedstock uses of BCM in the chemical industry usually rely on differential nucleophilic displacement of the halogens by different nucleophiles that consequently become linked via methylene groups. Thus, nucleophile Nu_1 displaces bromine to give (by careful control of stoichiometry) $\text{Nu}_1\text{-CH}_2\text{-Cl}$, which then reacts with nucleophile Nu_2 to give $\text{Nu}_1\text{-CH}_2\text{-Nu}_2$. There is also a provision in the Montreal Protocol for solvent uses of certain controlled substances provided the use was begun before 30 June 1996. Under this provision, the use of BCM as solvent for the bromination of polystyrene is sanctioned. The product, bearing bromine substituents on benzene rings, is used as a flame retardant additive for plastic materials.

But to end with the cows – the front end, of course – I read recently that scientists in Victoria, collaborating with colleagues in the US, were having success with the use of 3-nitrooxypropanol (NOP, $\text{HO-CH}_2\text{-CH}_2\text{-CH}_2\text{-O-NO}_2$), a methane suppressor developed by Swiss company DSM Nutritional products. A single gram added to the cow's daily feed ration cut methane emissions by 30%. A good start, but it seems there is still some way to go with this problem.



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

4th Federation of Asian Polymer Societies – International Polymer Congress

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

2015 Sustainable Industrial Processing Summit and Exhibition

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

HAZOP Study for Team Leaders and Team Members

20–22 October 2015, Perth, WA
www.icheme.org/hazoppertth#.Va22kEW8Kfc

7th International Conference on Recent Progress in Graphene and Two-dimensional Materials Research Conference

25–29 October 2015, Lorne, Vic.
<http://rpgr.physics.monash.edu.au>

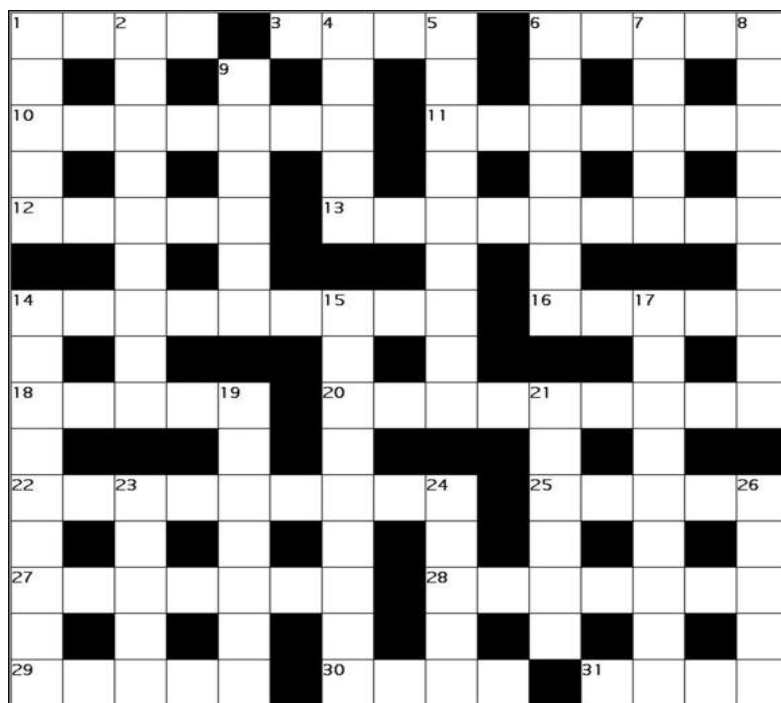
Australia and New Zealand Magnetic Resonance Society Conference

29 November – 3 December 2015, Bay of Islands, NZ
<http://anzmag2015.co.nz>

Pacificchem 2015

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

RACI events are shown in blue.



Across

- 1 Money for assurance, so we hear, a big bundle! (4)
- 3 Starts symmetry axis (rotary inversion) for garment. (4)
- 6 Metal behind collection. (5)
- 10 A carbon abandons discharges. (7)
- 11 Attempt late addition in a serine protease. (7)
- 12 Electron in decay went way up. (5)
- 13 Vibration might run last spectrum around. (9)
- 14 Muckraker lands around 68. 68! (9)
- 16 Drink over 18 Across description. (5)
- 18 Antique English document contains reference to ruler. (5)
- 20 Centres of minuted algorithmic drivers are alimantal. (9)
- 22 Warning! Flame on right switch. (9)
- 25 Gets back to VIP for balance on the central point. (5)
- 27 Mineral concretions composed of lutetium, lithium, calcium and carbon. (7)
- 28 Hotel sing along ends when ten players are put out. (7)
- 29 Plant sulfur tip. (5)
- 30 Bear master. (4)
- 31 Two element insects. (4)

Down

- 1 Crafts four elements. (5)
- 2 One important state dined on kill. (9)
- 4 Arsenic fixed advantage. (5)
- 5 Make sense of reaction of triterpene losing an electron. (9)
- 6 Hopelessly bad? That's deep! (7)
- 7 The first woman to hold a university chair in a scientific field of studies: 561614. (5)
- 8 Males strangely agree to include iodine in diverse collection. (9)
- 9 Cared for washed denim and finally ironed. (6)
- 14 Orders fermented 18 Across in cess pool. (9)
- 15 Offensive smell? Try in acid mixture. (9)
- 17 Unhappiness around nice grave. (9)
- 19 Bring up food. (7)
- 21 Threaten iodine melting point goal. (6)
- 23 Perforated 67 and went ahead. (5)
- 24 Active bell over iodine. (5)
- 26 States, after time, potassium and sulfur become ivory. (5)



Coming up

- Salmon and their strontium signatures
- Looking forward: where is chemistry headed?
- The hidden battle over e-cigarettes
- Some great science board games
- Simple tabletop chemistry for kids

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

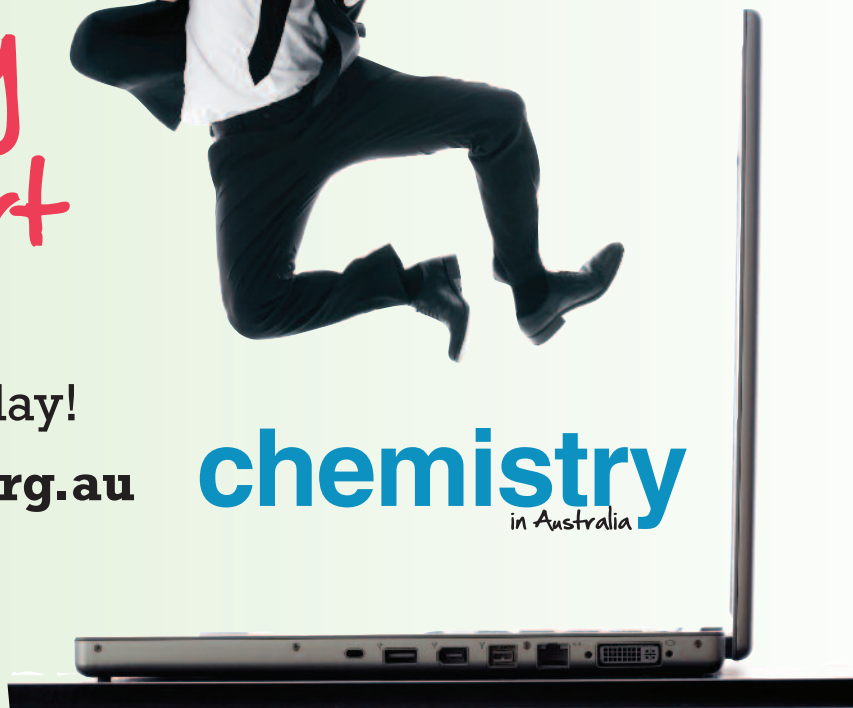
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