

# chemistry

September/October 2019

in Australia

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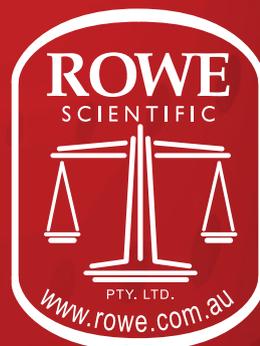


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## Learning beyond chemistry

Fifty years ago, American medical researchers Daniel Carleton Gajdusek and Clarence J. Gibbs, Jr published 'Infection as the etiology of spongiform encephalopathy (Creutzfeldt-Jakob disease)' in *Science* (<https://doi.org/10.1126/science.165.3897.1023>). Their paper described inoculation and disease transmission between chimpanzees of fatal spongiform encephalopathy from suspensions of brain, and retransmission of the disease to another chimp with an inoculum stored for more than two years. It was part of a body of work that would earn Gajdusek and geneticist Barum S. Blumberg the Nobel Prize in Physiology or Medicine in 1976 for their discoveries concerning 'new mechanisms for the origin and dissemination of infectious diseases'.

In the 1950s, Gajdusek worked as a visiting investigator at the Walter and Eliza Hall Institute of Medical Research in Melbourne, and it was here that he began the work that led to his Nobel Prize. He realised that Creutzfeldt-Jakob disease and others like it had their origins in an as-yet unidentified infectious agent.

Twenty-one years after Gajdusek's laureate honour, American biochemist and neurologist Stanley B. Prusiner received the Nobel Prize in the same discipline for his discovery of that infectious agent: 'prions – a new biological principle of infection'. His work followed on from that of Gajdusek, after one of Prusiner's patients died of Creutzfeldt-Jakob disease-induced dementia.

Prusiner's work has sparked the interest of RACI fellow Alan J. Jones, who wrote about his self-education on prions in the July/August issue (p. 32) and reviewed a recent book edited by Prusiner (p. 34). Alan's piece in that issue is the first in our 'Beyond chemistry' series, where contributors write on a subject they've been learning about outside their main area of expertise. In his work before retirement, Alan used NMR spectroscopy to probe the structure of scientifically significant hydrocarbons and the 'molecules of life'.

Alan, who says 'I have educated myself about prions mainly through reading and watching video lectures', intends to keep up with the prion literature, and would like to discuss his interest with like-minded people ([alanjjones@netspeed.com.au](mailto:alanjjones@netspeed.com.au)).

I have been doing some extracurricular exploration of my own, and, like Alan's, my interest stems from a 'fundamental curiosity' that is distinctly scientific. A recent learning of mine is on the topic of 'Women making history: ten objects, many stories', a course delivered by Harvard University via the online open course organisation edX. I've long been interested in the curation of objects or ideas to tell a bigger story, and this course fits the bill. It begins with an online guided visual exploration of an unknown object. The lecturer asks participants to 'be curious'. On the 'tour', we begin to get a sense of the object's size, weight, age, construction, texture and parts.

The object, we later learn, is a camera that was owned by the first published female photojournalist in the US, Jessie Tarbox Beals, which is now housed at Harvard's Arthur and Elizabeth Schlesinger Library on the History of Women in America.

Please contact me if you'd like to share your story of learning beyond chemistry.



Biljana Cvetanovic

### Sally's resource list

edX, *Women making history: ten objects, many stories*, [edx.org/course/women-making-history-ten-objects-many-stories](https://edx.org/course/women-making-history-ten-objects-many-stories)

*New Philosopher*, [newphilosopher.com](http://newphilosopher.com)

Radcliffe Institute for Advanced Study, Harvard University, *Schlesinger Library*, [radcliffe.harvard.edu/schlesinger-library](http://radcliffe.harvard.edu/schlesinger-library)

Trustees of the British Museum, *A history of the world in 100 objects from the British Museum*, National Museum of Australia Press, 2016

Wikipedia, *Jessie Tarbox Beals*, [en.wikipedia.org/wiki/Jessie\\_Tarbox\\_Beals](https://en.wikipedia.org/wiki/Jessie_Tarbox_Beals)



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## Glyphosate instructions

When the doctor prescribes ‘take one pill three times a day after meals’, should one decide ‘couldn’t be bothered, will take 21 for the week on Monday morning before brekkie instead?’ Late for work, need to run a few red lights when it looks as though it will be OK?

Instructions are for real and that also applies when using herbicides such as glyphosate.

But aren’t the instructions on the bottle really a bit over the top and that’s because the regulators are trying cover their rear ends? If this stuff is sooo safe, why these worrying instructions?

The instructions certainly seem over the top but not for that reason. The real reason is that one size generally has to fit all types of users. The regular (using significant amounts for a long time), the occasional domestic home gardener, and then one who also needs to worry about pets and small children running over the area sprayed.

We occasionally miss taking a prescribed pill or may take two to catch up. Equally, we tend to ‘relax’ spray instructions, given our circumstances.

Just as well instructions have margins of safety built in.

Given the litigation regarding glyphosate (Roundup) and cancer, beware the political expediency that pushes replacing a known known with a known unknown (a lesser used product).

We need more common sense and that, sadly, isn’t common.

Ben Selinger FRACI CChem

## Periodic table art and literature

Like many *Chemistry in Australia* readers, I’m sure, I was impressed by the article ‘The art of the periodic table’ (July/August, p. 6).

I looked at the website [www.periodictable.ga](http://www.periodictable.ga) (beautiful) and clicked on the link that connects to one of the artists (Damon Kowarsky, [damon@fastmail.net](mailto:damon@fastmail.net)). He advised me that you can purchase:

- limited edition prints in sizes from A3 upwards, printed with archival inks on 100% cotton paper. The A3 versions are \$120 each, including postage
- larger sizes (including up to a metre across)
- the original drawings for \$1200 unframed/\$1500 framed.

I have purchased some of my favourite elements – for work and home.

And on a related periodic table note, Alf Larcher’s article ‘A mother’s love: Maria Dmitrievna Mendeleeva’ (p. 14) was fantastic. It was extremely well researched and beautifully written. I enjoyed it immensely. Inspired, I immediately passed it on to my semi-chemist wife (a medical doctor) in a hopefully not too vain attempt to show her that we chemists, as well as being almost perfect, do have a literary and romantic quality that comes to the fore every now and then.

Stephen Grocott FRACI CChem

## Science German

It is a remarkable coincidence that the term ‘Science German’ appears twice in the July/August issue. On page 5, I state that it was an optional course in my day as a student in England, and on page 41 Ian Rae states that it was a compulsory course in his day as a student in Australia. I always thought that the primary reason for such courses was that so much information and wisdom in organic chemistry was contained in a journal set up partly by the pioneering organic chemist Justus von Liebig (1803–73) and called *Justus Liebigs* [note the absence of the possessive apostrophe] *Annalen der Chemie*, which was in the German language. The journal was in existence from 1832 until 1997 when it merged with a number of other journals to form *European Journal of Organic Chemistry*. It was often referred to by English speakers simply as *Liebig’s Annalen*.

*Zeitschrift für Physikalische Chemie* began in 1887 and *Zeitschrift für anorganische und allgemeine* [inorganic and general] *Chemie* in 1892. Both were in the German language, so Science German courses would also have made these accessible to students. I raised the matter of Science German (July/August, p. 5) because of a statement in an earlier issue (May/June, p. 14) that John Cornforth, while an undergraduate student at the University of Sydney, had consulted the original German research literature. Cornforth graduated from the University of Sydney in 1937. R.S. (later Sir Ronald) Nyholm, of whom I have written previously (July 2013, p. 39), graduated there the following year. That he at that early career stage benefited from one or more of the journals referred to in this piece is a most plausible conjecture. Cornforth and Nyholm went to Oxford and London respectively to do PhDs.

One could take this roll call of young Australian chemists seeking a PhD in England about 70 years ago further; for example, by mentioning A.T. Austin, of whom also I have written previously, and M.F.R. Mulcahy. Their supervisors were Sir Robert Robinson (Cornforth), Sir Christopher Ingold (Nyholm and Austin) and Sir Cyril Hinshelwood (Mulcahy). Robinson and Hinshelwood became Nobel laureates. Why Ingold did not has been the subject of a recent publication (Ridd J.H. *ACS Symposium Series* 2017, vol. 1262, pp. 207–18).

Clifford Jones FRACI CChem



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## Acrylics and waste

With reference to the article on particulate plastics in the July/August issue (p. 18), I worked for 14 years as a chemist in the manufacture of acrylics and I feel the following comments may be of note. First, acrylics are not manufactured from acrylic acid  $\text{CH}_2=\text{CHCOOH}$  but from acrylonitrile  $\text{CH}_2=\text{CHCN}$ , and its alternative name of vinyl cyanide has never been used probably because of the connotation with cyanide. Poly-acrylonitrile is very brittle and is therefore always used with a co-monomer such as methyl acrylate, which usually is added between 5 and 10% of the total monomers. This produces a fibre that withstands the rigours of the textile processing without fibre breakage because short fibres cause imperfections in the final fabrics.

I used to handle customer complaints and used to identify the fibre source by dissolving the fibre in an aqueous solution containing a high concentration of an inorganic salt. The polymer was then precipitated in water as a film, dried, and scanned using infrared spectroscopy, which gave a trace from which the nitrile/acrylate ratio could be calculated and gave a fingerprint that showed if the fibre originated from our plant. The plant also used to make the precursor fibres for the manufacture of carbon fibres, which at the time in the 1970s were in their infancy.

Technically, I believe the process of redissolving acrylics for reprocessing could be feasible especially as the solvent can be recovered and reused, and with carbon fibres gaining more applications in vehicles it could be a win-win situation in reusing a waste product and saving fossil fuels currently used to manufacture acrylonitrile. I do not know if the process is still under patent, which is why I have not identified the salt used, but as it is almost 40 years since I left the factory and it is no longer in operation, I suspect the patents would have expired.

Colin Wheatley FRACI CChem

## Russian connections

The July/August issue featured Russia – Mendeleev's family support by Alf Larcher and Ian Rae's visit there. These articles prompted me to think about links in my research with Russia.

Elements of the periodic table most influential in my career were chromium (see submission in RACI's *Stories from the periodic table* ([bit.ly/2ABHUGP](http://bit.ly/2ABHUGP))) and platinum. Catalysis studies of platinum involving aromatics (PhD, University of New South Wales, late 1960s) were followed by studies with alkanes (postdoc, UK, early 1970s). This latter work came about when the Russian A.E. Shilov noted that our platinum cocktail would only activate methane when benzene was also present. My replacing of benzene with pyrene greatly enhanced stability for alkanes. Although I didn't ever visit Russia, Shilov did make my findings the topic of chapters in his books in 1984, 1986 and 2000.



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Send your contributions (approx. 400 words) to the Editor at [wools@westnet.com.au](mailto:wools@westnet.com.au).

However, one did not have to go to Russia to find tough suburban environments ... Travelling with two young children, we found it similar in New York in 1986 when visiting my wife's (Delma's) first cousins. They (Ross and Val Stretton) were lead ballet dancers in a Russian troupe (under Rudolf Nureyev) and lived in Park Slope (Brooklyn). Our plane arrived late evening, and taxi drivers refused to drive us to their home. As in Russia, cars parked in the street necessitated batteries to be removed overnight. This was an onerous job because all cars also had to swap sides of the street every other day to permit council trucks to clean gutters.

Travelling from there to Manhattan Island by the Triplex underground was also enlightening. Another surprise was the four of us walking in completely deserted streets on a weekend from the south side of the Twin Towers down to nearby Pier 1. On glancing to the north, I noted the next block had throngs of pedestrians and when I looked again at the map, it showed their avenue was lightly coloured yellow and referred to as 'safe'.

After New York, we went to the state of Nebraska to visit my aviation fuel partner (Todd Petersen) who was marketing the portable volatility tester I had developed in 1979 (more than 3000 were sold and we still supply approvals for use of autofuel in light aircraft). Security there was not a concern as they didn't lock anything up.

Ray Hodges FRACI CChem

## Turning waste water into a billion-dollar export

A West Australian project to produce high-value magnesium carbonate utilising existing wastewater streams from salt production in the Pilbara has the potential to establish a lucrative new export industry in the region, modelling has shown.

Emerging Australian specialty chemicals producer EcoMag Ltd plans to recycle wastewater streams (known as bitterns) generated by Pilbara sea-salt producer Dampier Salt to extract valuable hydrated magnesium carbonate – a high-purity, high-value magnesium product with multiple applications, including in smartphones and as a flame retardant, and which currently fetches about US\$1250/tonne.

EcoMag's proposed processing facility at Karratha is expected to initially produce approximately 80 000 tonnes of hydrated magnesium carbonate per year. Construction will cost approximately \$130 million, according to feasibility study estimates.

Modelling undertaken as part of a recently completed study by EcoMag has confirmed the volume of bitterns available for processing is much larger than initially considered and could potentially support vastly higher production levels.

As part of the ongoing regulatory approval process, EcoMag is providing bitterns dispersal modelling to the WA Department of Water and Environmental Regulation, taking into account 45 years of data for evaporation rates, rainfall patterns, tides and extreme weather events, such as the cyclones that occasionally strike the area.

EcoMag Chief Executive Officer Tony Crimmins said that even at the initial proposed plant capacity, the project would add significantly to Karratha's manufacturing output, generating around \$130 million of revenue per year, almost all of it from exports.

EcoMag

## Rapid cross-resistance bringing cockroaches closer to invincibility



A German cockroach feeds on an insecticide in the laboratory portion of a Purdue University study that determined the insects are gaining cross-resistance to multiple insecticides at one time. John Obermeyer/Purdue Entomology

Cockroaches are serious threats to human health. They carry dozens of types of bacteria, such as *E. coli* and salmonella, that can make people ill. And their saliva, faeces and body parts not only trigger allergies and asthma but could cause the condition in some children.

In the US, a Purdue University study (published in *Scientific Reports* (article 8292)) led by Professor Michael Scharf found evidence that German cockroaches (*Blattella germanica* L.) are becoming more difficult to eliminate as they develop cross-resistance to insecticides.

Each class of insecticide works in a different way to kill cockroaches. Exterminators will often use a mixture of multiple classes or change classes from treatment to treatment. The hope is that even if a small percentage of cockroaches is resistant to one class, insecticides from other classes will eliminate them.

In one treatment, Scharf and his co-authors rotated three insecticides from different classes into use each month for three months and then repeated this. In the second, they used a mixture of two insecticides from different classes for six months. In the third, they chose an insecticide to which cockroaches had low-level starting resistance and used it the entire time.

By rotating three insecticides, the researchers were able to keep cockroach populations constant over a six-month period, but they could not reduce them. The two-insecticide mixture did not work,

and cockroach populations flourished.

In one of the single-insecticide experiments, the researchers found that there was little starting resistance to the chosen insecticide, and they were able to all but eliminate the cockroach population. In the other, there was about 10% starting resistance. In that experiment, populations grew.

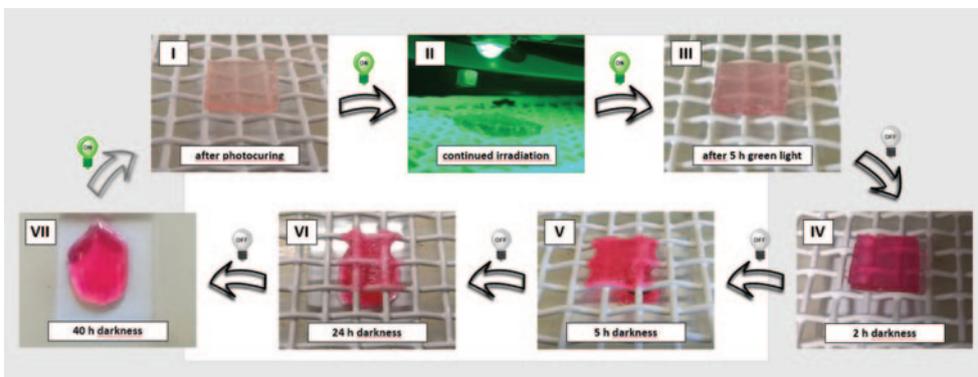
In later lab tests, the team found that cross-resistance likely played a significant role. A certain percentage of cockroaches would be resistant to a particular class of pesticide. Those that survived a treatment and their offspring would be essentially immune to that insecticide in the future. But they also gained resistance to other classes of insecticide, even if they hadn't been exposed to them and had not had previous resistance.

Female cockroaches have a three-month reproductive cycle during which they can have up to 50 offspring. If even a small percentage of cockroaches is resistant to an insecticide, and those cockroaches gain cross-resistance, a population knocked down by a single treatment could explode again within months.

That's why an integrated pest management approach is critical, Scharf said. He recommends combining chemical treatments with traps, improved sanitation and vacuums that can remove cockroaches.

Purdue University

## Green light for new generation of dynamic materials



Demonstration of naphthalene-TAD material light-stabilised dynamic behaviour.

Developing synthetic materials that are as dynamic as those found in nature, with reversibly changing properties and which could be used in manufacturing, recycling and other applications, is a strong focus for scientists.

In a world-first, researchers from QUT, Belgium's Ghent University (UGent) and Germany's Karlsruhe Institute of Technology (KIT) have pioneered a novel, dynamic, reprogrammable material – by using green LED light and, remarkably, darkness as the switches to change the material's polymer structure, and using only two inexpensive chemical compounds. One of these compounds, naphthalene, is a well-known ingredient in moth repellents.

The new dynamic material could potentially be used as a 3D printing ink to print temporary, easy-to-remove support scaffolds. This would overcome one of the current limitations of the 3D process to print free-hanging structures.

The research is part of an ongoing international collaboration between macromolecular chemist and Australian Research Council Laureate Fellow Professor Christopher Barner-Kowollik FRACI CChem (QUT), Dr Hannes Houck, who recently completed his PhD across QUT, UGent and KIT, Professor Filip Du Prez (UGent) and Dr Eva Blasco (KIT). Their findings have been published in the *Journal of the American Chemical Society* (<https://doi.org/10.1021/jacs.9b05092>).

Barner-Kowollik said what makes the discovery unique is that light is used as the trigger to stabilise, rather than destroy, chemical bonds – so the researchers have coined a new term – 'light-stabilised dynamic materials' (LSDMs).

The researchers said what they have achieved is the opposite of what is usually done in chemistry and 'many people didn't think it could be done'.

'Typically, you use different wavelengths of light or additional heat or harsh chemicals to break up the polymer molecule chains that form a network structure', they said.

'However, in this case, we used green LED light to stabilise the network. The trigger to break up the network, make it collapse and flow away is actually the mildest one of all: darkness. Switch the light back on and the material re-hardens and retains its strength and stability.'

'This is what you call an out-of-equilibrium chemical system. The constant energy of the green light keeps the chemical system in this bonded form, pushing it out of its equilibrium. Take away the light, and the system goes back to its relaxed, lowest energy state.'

Queensland University of Technology

## Cyanide-free gold goes into production

Australia is leading the charge towards greener and safer gold production with a gold recovery process technology that dispenses with toxic cyanide and mercury currently used in most gold production processes worldwide.

On the back of successful industry trials and the first gold pour last year, CSIRO will transfer its 'Going for Gold' process technology to Australian company, Clean Mining Limited.

CSIRO Research Program Leader, Dr Chris Vernon, believes the technology not only overcomes a significant environmental hazard, it also opens the door for Australian and international gold miners and end users to capitalise on demand for sustainable processes and products.

'Developing an alternative process, which eliminates hazardous chemicals while maximising gold recovery, meets industry and consumer demands for more sustainably produced gold.'

The process replaces cyanide with thiosulfate, creating a relatively cost-effective, non-toxic and safe alternative to

conventional cyanide-based gold recovery process.

Clean Mining will deliver the new technology solution to a global market of gold producers, offering technology products and licences as well as turnkey processing plant options, plus equipment and product support throughout the mine life.

Clean Mining Managing Director, Jeff McCulloch, says the technology is suitable for new greenfields mines, locations where cyanide cannot be used or is banned, as well as existing mines looking to upgrade and transition to the new technology.

'The technology is scalable and cost-effective, and the process has been tested and proven at an industrial scale to deliver commercially viable results.'

Clean Mining is currently in negotiations with ICA Mining Services Pty Ltd in the Northern Territory to commission the first commercial plant to process gold using this technology, and with Nu-Fortune Gold to commission a plant in Western Australia.

CSIRO

# Synthesis of potent anticancer agent

Researchers led by Yoshito Kishi at Harvard University in the US have synthesised sufficient quantities of E7130, a drug candidate from the halichondrin class, to enable for the first time rigorous studies of its biological activity, pharmacological properties and efficacy, all conducted in collaboration with researchers at Japanese pharmaceutical company Eisai.

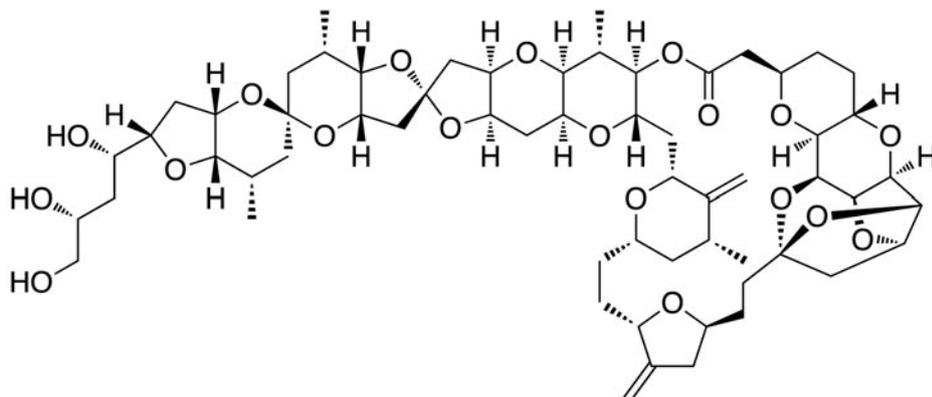
The molecule has undergone unusually rapid development and is already being tested in a phase I clinical trial in Japan. The company hopes to begin a second clinical trial in the US in due course.

The results are published in *Scientific Reports* (<http://dx.doi/10.1038/s41598-019-45001-9>). The paper reports the total synthesis of the highly potent halichondrin molecule E7130 (11.5 grams in 99.81% purity) and characterises its mode of action. In preclinical studies, the research team has identified it not only as a microtubule dynamics inhibitor, as was previously recognised, but also as a novel agent to target the tumour microenvironment.

The structure of the complete E7130 molecule derived by total synthesis is particularly challenging to replicate because it has 31 chiral centres. In other words, there are roughly 4 billion ways to get it wrong.

When the natural product was first identified 33 years ago by Japanese researchers, it sparked immediate interest. 'At that time, they realised the halichondrins looked exceedingly potent', recalled co-author Takashi Owa, Chief Medicine Creation Officer and Chief Discovery Officer for Eisai's oncology business group. Over time, investigators at the US National Cancer Institute of the National Institutes of Health testing tiny amounts of it recognised that it was affecting the formation of microtubules, which are essential to cell division.

'Due to the very unique structure of



Another molecule in the halichondrin class, halichondrin B, was synthesised in 1992 by Yoshito Kishi and colleagues at Harvard University. This led to the development of eribuline, used to treat some patients with metastatic breast cancer. Wikimedia/charlesy

the natural product, many people were interested in the mode of action, and the investigators wanted to do a clinical study', Owa explained, 'but a lack of drug supply prevented them from doing it. So 30 years have passed, very unfortunately, but Professor Kishi is a pioneer in this field.'

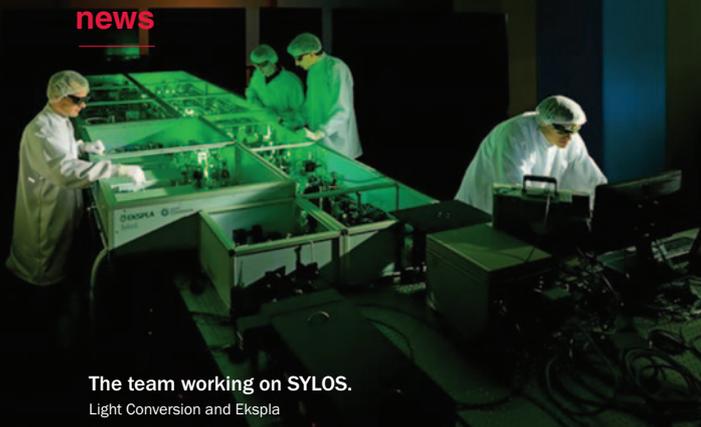
Over the years, the Kishi laboratory advanced methods of convergent synthesis, which enables complex molecules to be assembled from subunits, rather than constructed linearly. Another innovation, now known as the Nozaki-Hiyama-Kishi reaction, protected the highly reactive functional groups while they were being assembled. And in 1992, Kishi and colleagues achieved the first total synthesis of a halichondrin molecule (halichondrin B). The process required a sequence of more than 100 chemical reactions and produced a less than 1% overall yield. It was a major achievement, however, and a simplified version of that molecule, eribulin, became a drug to treat metastatic breast cancer and liposarcoma, now marketed by Eisai. Since then, Kishi's laboratory has been engaged in basic research on organic synthesis, including discovery and development of new reactions usable at a late stage of synthesis.

'In 1992, it was unthinkable to synthesise a gram-quantity of a halichondrin', Kishi said, 'but three years ago we proposed it to Eisai. Organic synthesis has advanced to that level, even with molecular complexity that was untouchable several years ago. We are very delighted to see our basic chemistry discoveries have now made it possible to synthesise this compound at large scale.'

'It's a really unprecedented achievement of total synthesis, a special one', said Owa. 'No one has been able to produce halichondrins on a 10-gram scale – one milligram, that's it. They have completed a remarkable total synthesis, enabling us to initiate a clinical trial of E7130.'

The team's *Scientific Reports* paper describes the results of studies conducted in vitro and in vivo, in animal models, that shed light on the molecule's complex mode of action. The team showed that E7130 can increase intratumoural CD31-positive endothelial cells and reduce alpha-SMA-positive cancer-associated fibroblasts, components of the tumour microenvironment that may be involved in the transformation to malignancy.

Harvard University



The team working on SYLOS.  
Light Conversion and Ekspla

## Laser with potential to tackle nuclear waste disposal

Two Lithuanian-based laser technology companies – Light Conversion and Ekspla – have developed a laser that could solve the nuclear waste management problem.

The jointly produced SYLOS is a high-intensity ultra-short pulse laser. The peak power of SYLOS exceeds the power of a nuclear plant by thousands of times, and impulses of this kind can be applied both to research and to nullify the impact of nuclear waste.

If the process of nuclear waste decomposition is accelerated by such a laser, the decay period can be cut to seconds, hours or months, depending on the material. However, several challenges are yet to be met before laser systems such as SYLOS can be applied on an industrial scale, according to Darius Gadonas, Head of the Scientific Laser Systems Division at Light Conversion, a Vilnius-based co-developer of the laser.

'We do believe that lasers like SYLOS can be adapted to solve the nuclear waste issue globally without leaving it for future generations to deal with. How soon this could be achieved will depend on the political will of governments, since lasers and infrastructure of this kind could cost up to billions of euros per unit', said Gadonas.

Vilnius is home to numerous laser developers and has an educational system geared towards providing the companies with a highly qualified workforce. Currently, more than 100 students enter studies of physics every year, and about a half of them continue on studying light technologies. Most of these students start working for one of the laser companies during their studies. In general, Lithuania holds the third place in the European Union for STEM bachelor graduates per capita.

The Lithuanian tradition of laser development dates back to 1970 when the School of Laser Physics was launched at Vilnius University. At the moment, the global laser technology market is dominated by two types of technologies: the chirped pulse amplification technology, invented by Gérard Mourou, and the optical parametric chirped pulse amplification technology. The latter technology was co-developed by Algis Petras Piskarskas, one of the key figures behind the School of Laser Physics in Vilnius.

Go Vilnius

## Comet inspires chemistry for making breathable oxygen on Mars

When we explore space, we need to bring our own oxygen supply. That is not ideal because a lot of energy is needed to hoist things into space atop a rocket, and once the supply runs out, it is gone.

One place molecular oxygen does appear outside of Earth is in the wisps of gas streaming off comets. The source of that oxygen remained a mystery until two years ago when Konstantinos P. Giapis, a professor of chemical engineering at Caltech, and his postdoctoral fellow Yunxi Yao, proposed the existence of a new chemical process that could account for its production. Giapis, along with Tom Miller, professor of chemistry, have now demonstrated a new reaction for generating oxygen that Giapis says could help humans explore the universe and perhaps even fight climate change at home. More fundamentally though, he says the reaction represents a new kind of chemistry discovered by studying comets.

Most chemical reactions require energy, which is typically provided as heat. Giapis's research shows that some unusual reactions can occur by providing kinetic energy. When water molecules are shot like extremely tiny bullets onto surfaces containing oxygen, such as sand or rust, the water molecule can rip off that oxygen to produce molecular oxygen. This reaction occurs on comets when water molecules vaporise from the surface and are then accelerated by the solar wind until they crash back into the comet at high speed.

Comets, however, also emit CO<sub>2</sub>. Giapis and Yao wanted to test if CO<sub>2</sub> could also produce molecular oxygen in collisions with the comet surface. When they found O<sub>2</sub> in the stream of gases coming off the comet, they wanted to confirm that the reaction was similar to water's reaction. They designed an experiment to crash CO<sub>2</sub> onto the inert surface of gold foil,



Comet C/2014 Q2, also known as Lovejoy.  
NASA/Damian Peach

which cannot be oxidised and should not produce molecular oxygen. Nonetheless,  $O_2$  continued to be emitted from the gold surface. This meant that the two atoms of oxygen come from the same  $CO_2$  molecule, effectively splitting it in an extraordinary manner.

'At the time we thought it would be impossible to combine the two oxygen atoms of a  $CO_2$  molecule together because  $CO_2$  is a linear molecule, and you would have to bend the molecule severely for it to work', Giapis said. 'You're doing something really drastic to the molecule.'

To understand the mechanism of how  $CO_2$  breaks down to molecular oxygen, Giapis approached Miller and his postdoctoral fellow Philip Shushkov, who designed computer simulations of the entire process. Understanding the reaction posed a significant challenge because of the possible formation of excited molecules. These molecules have so much energy that their constituent atoms vibrate and rotate around to an enormous degree. All that motion makes simulating the reaction in a computer more difficult because the atoms within the molecules move in complex ways.

'In general, excited molecules can lead to unusual chemistry, so we started with that', Miller said. 'But, to our surprise, the excited state did not create molecular oxygen. Instead, the molecule decomposed into other products. Ultimately, we found that a severely bent  $CO_2$  can also form without exciting the molecule, and that could produce  $O_2$ .'

The apparatus Giapis designed to perform the reaction works like a particle accelerator, turning the  $CO_2$  molecules into ions by giving them a charge and then accelerating them using an electric field, albeit at much lower energies than are found in a particle accelerator. However, he adds that such a device is not necessary for the reaction to occur.

'You could throw a stone with enough velocity at some  $CO_2$  and achieve the same thing', he said. 'It would need to be travelling about as fast as a comet or asteroid travels through space.'

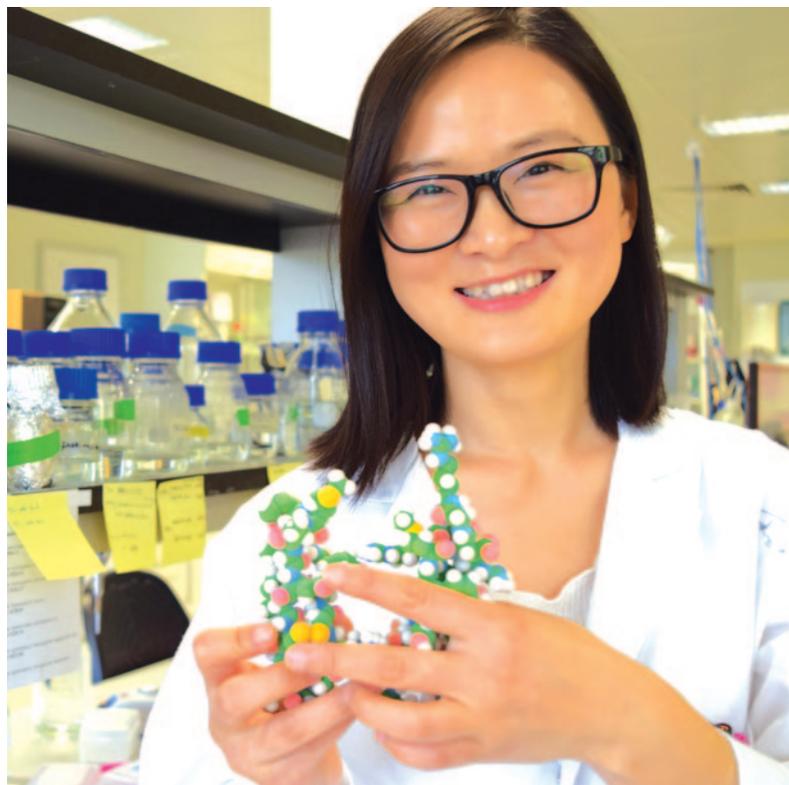
That could explain the presence of small amounts of oxygen that have been observed high in the Martian atmosphere. There has been speculation that the oxygen is being generated by ultraviolet light from the sun striking  $CO_2$ , but Giapis believes the oxygen is also generated by high-speed dust particles colliding with  $CO_2$  molecules.

He hopes that a variation of his reactor could be used to do the same thing at more useful scales – perhaps one day serving as a source of breathable air for astronauts on Mars or being used to combat climate change by pulling  $CO_2$ , a greenhouse gas, out of Earth's atmosphere and turning it into oxygen. He acknowledges, however, that both of those applications are a long way off because the current version of the reactor has a low yield, creating only one to two oxygen molecules for every 100  $CO_2$  molecules shot through the accelerator.

The paper describing the team's findings appears in *Nature Communications* (<http://dx.doi/10.1038/s41467-019-10342-6>).

California Institute of Technology

## Ancient family of tiny protein passengers revealed



PhD student Jingjing Zhang from the University of Western Australia team.

University of Western Australia researchers have discovered a new family of tiny proteins in plants that hide inside other, much larger and unrelated proteins.

Vicilin is one of several very abundant seed proteins. The researchers showed how several hundred million years ago, some vicilins acquired a small, extra protein passenger – a family they call the vicilin-buried proteins. The first vicilin-buried protein was shown to block enzymes and another was said to have anti-HIV activity. The researchers characterised half a dozen and have evidence that there are hundreds more of them in diverse types of seeds including those of tomato, date palm, sesame seeds and cucumbers.

Vicilin-buried proteins fold into a hairpin with two bridges connecting each arm of the hairpin, making them quite stable, and this can be useful for making protein bioactives.

The age and evolutionary retention of this family of small proteins suggests its members play important roles in plant biology.

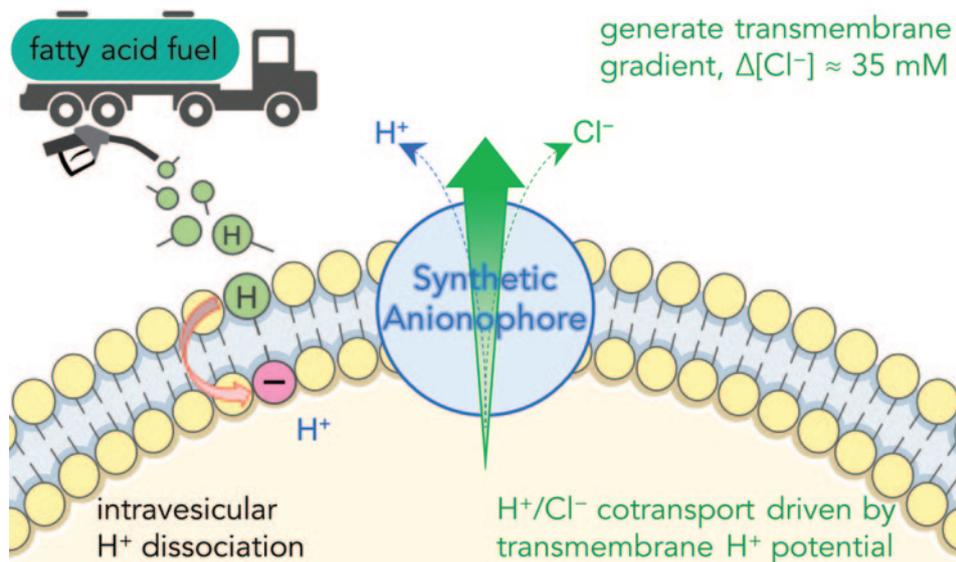
This family of buried proteins is the second one studied, suggesting a mechanism whereby small proteins can evolve inside a 'host' protein might be more common. The research has been published in *ACS Chemical Biology* (<https://doi.org/10.1021/acscchembio.9b00167>).

University of Western Australia



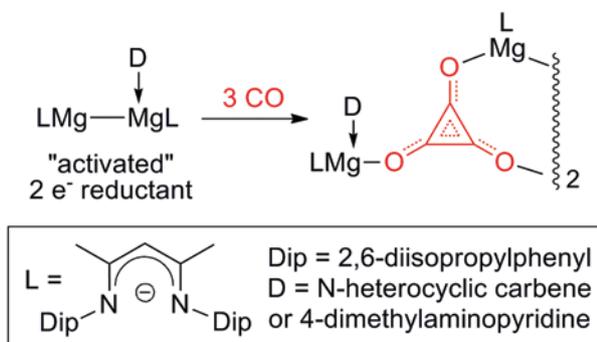
## Pumping ions with fatty acid fuel

Compartmentalisation by biological membranes plays a critical role in regulating asymmetric ion concentrations and electrochemical gradients in all living systems. The development of synthetic systems that can generate ion gradients across lipid bilayers has been a cornerstone for applications in biosignalling and bioenergetics and for advances in understanding of biochemical processes and evolution. With the biological importance and abundance of the chloride anion, it is surprising that until recently there were no examples of synthetic transmembrane  $\text{Cl}^-$  pumps in the literature. Now, researchers at the University of Sydney have developed a proof-of-concept transmembrane  $\text{Cl}^-$  pumping system fuelled by fatty acids to generate a transmembrane  $\text{Cl}^-$  gradient (Howe E.N.W., Gale P.A. *J. Am. Chem. Soc.* 2019, **141**, 10 654–60). Addition of long-chain fatty acids such as oleic acid and palmitic acids to phospholipid vesicles generates a transmembrane pH gradient ( $\text{pH}_{\text{in}} < \text{pH}_{\text{out}}$ ), and this electrochemical  $\text{H}^+$  potential is harnessed by an anionophore to drive chloride efflux via  $\text{H}^+/\text{Cl}^-$  cotransport. Fatty acids can be



added repeatedly to fuel this pumping system to continuously drive  $\text{Cl}^-$  flux against the concentration gradient, up to  $[\text{Cl}^-]_{\text{in}} 65 \text{ mM} \mid [\text{Cl}^-]_{\text{out}} 100 \text{ mM}$  upon addition of  $25 \mu\text{M}$  oleic acid (1400× efficiency). It is expected that most reported synthetic anionophores can be used in this system. Hence, this work could set in motion future developments in creating new artificial ion pumping systems.

## Magnesium(I) reductively trimerises CO



Carbon monoxide is a cheap and abundant feedstock that is used as a  $\text{C}_1$  building block in numerous industrial processes. An example is the Fischer–Tropsch process, which generates megatonnes of liquid hydrocarbons and oxygenates per annum from synthesis gas ( $\text{CO}/\text{H}_2$ ). Despite the importance of the Fischer–Tropsch process, little is definitively known about the fundamental steps that lead to reductive C–C bond formations that occur in this process, though soluble organometallic models are starting to shed light on this mystery. Now, the group of Cameron Jones at Monash University and his theoretician collaborator Laurent Maron at the University of Toulouse, France, have shown that the Mg–Mg bond of their magnesium(I) dimers can be activated, simply by the addition

of sub-stoichiometric Lewis bases (Yuvaraj K., Douair I., Paparo A., Maron L., Jones C. *J. Am. Chem. Soc.*, 2019, **141**, 8764–8). The resultant highly reactive adduct complexes readily reductively trimerise CO to give the first fully structurally characterised examples of s-block metal complexes of the deltate dianion,  $[\text{C}_3\text{O}_3]^{2-}$ . Such chemistry has only previously been achieved with uranium(III) species, highlighting the utility that magnesium(I) adduct complexes hold as cheap, non-toxic, diamagnetic, non-radioactive alternatives to f-block (and d-block) organometallic models in the study of reductive C–C bond-forming events.

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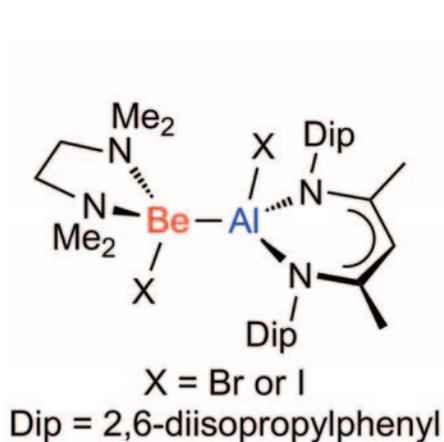
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## Beryllium bonds to aluminium

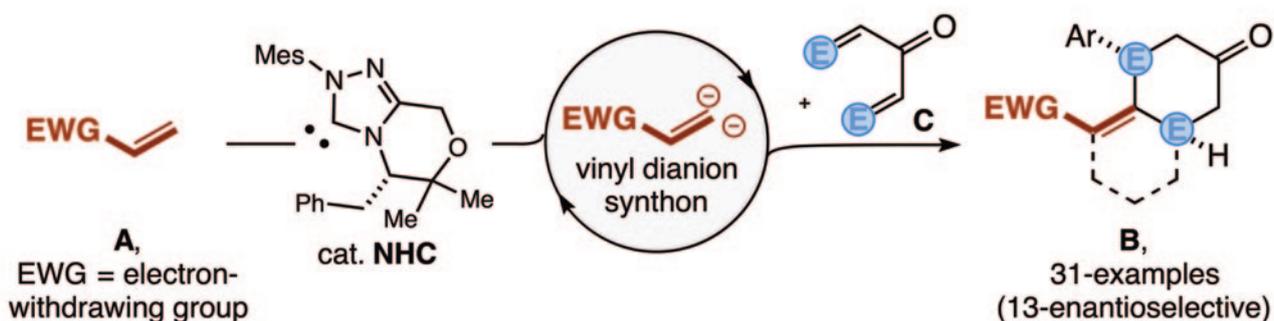


Beryllium is the least investigated of the non-radioactive elements, in large part due to its extreme, but often exaggerated, toxicity. Despite this, the last decade has seen a resurgence in the chemistry of molecular beryllium compounds around the globe. Given the rapidly emerging importance of magnesium(I) compounds that contain Mg–Mg covalent bonds, many efforts have been directed towards the preparation of



related low oxidation state and/or beryllium–metal bonded compounds, albeit with limited success. The group of Cameron Jones at Monash University has succeeded in preparing the first examples of compounds with beryllium–metal covalent bonds by the simple addition of beryllium–halide bonds across the metal centre of an aluminium(I) heterocycle (Paparo A., Smith C.D., Jones C. *Angew. Chem. Int. Ed.* 2019, **58**, 11459–63). DFT calculations reveal the Be–Al bonds to have a high degree of covalency, which is consistent with the similar electronegativities of the two metals, and their diagonal relationship in the periodic table. The compounds hold potential as precursors to Be/Al alloys, which are widely used in aerospace and satellite technologies due to their strength and lightness.

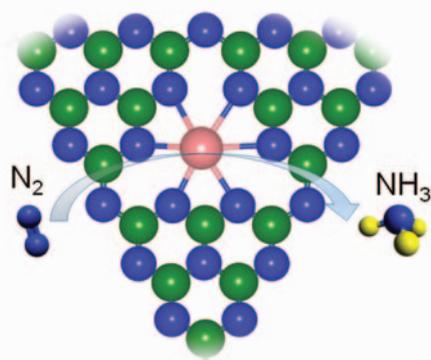
## A conjugate acceptor? No, it's two homoenolates



Functional groups have inherent polarity that must be considered when designing chemical reactions. If the polarity is inverted, new reaction designs are possible. While polarity inversion of the carbonyl group is ubiquitous (e.g. in acyl anion reactions) polarity inversion of the analogous  $\alpha,\beta$ -unsaturated carbonyl is far less developed. As part of a broader study into polarity inversion of conjugate acceptors (*Angew. Chem. Int. Ed.* 2016, **55**, 3135–9; 2018, **57**, 10 299–303), David Lupton and his team at Monash University recently postulated that simple conjugate acceptors (**A** in the figure) should undergo multiple

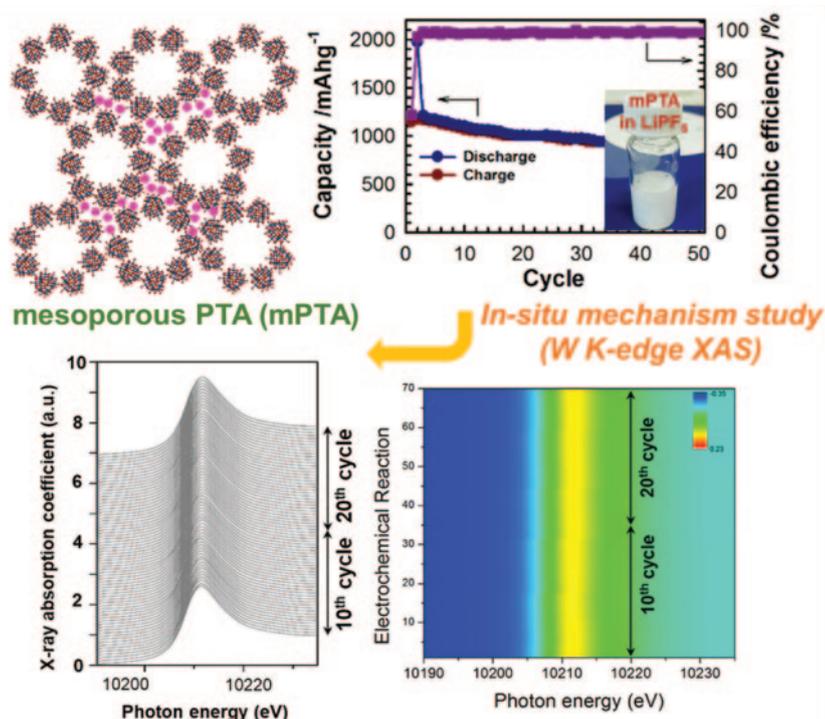
polarity-inversion events, allowing reactions of formal vinyl dianions (Nguyen X.B., Nakano Y., Duggan N.M., Scott L., Breugst M., Lupton D.W. *Angew. Chem. Int. Ed.* 2019, **58**, 11483–90). This strategy proved viable, with PhD scholar Xuan Nguyen and Dr Yuji Nakano discovering two reactions of this type, providing cyclohexanones (**B**) by coupling to bis-electrophilic partner **C**. The reaction was enantioselective in some instances using the catalyst shown (NHC). This chemistry expands the way conjugate acceptors can be considered in synthesis design.

## Designing single-atom catalysts for nitrogen reduction



Electrochemical reduction of  $N_2$  to  $NH_3$  provides an alternative to the energy-intensive Haber–Bosch process and enables distributed ammonia production. However, the inert nature of the nitrogen molecule and the competing hydrogen-evolution reaction impede the development of this technology. Thus, designing active, efficient and stable catalysts to boost this reaction is a major goal. Recently, Shi-Zhang Qiao's group at the University of Adelaide has used calculations to explore the potential of single-atom catalysts to convert  $N_2$  into ammonia (Liu X., Jiao Y., Zheng Y., Jaroniec M., Qiao S.Z. *J. Am. Chem. Soc.* 2019, **141**, 9664–72). The work establishes activity trends for single-atom catalysts and explains the origins of these trends based on thermodynamic and electronic structure analyses. Additionally, the extensive calculations indicate that the combination of Ru and a g- $C_3N_4$  substrate achieves the smallest limiting potential of the systems studied, while at the same time retaining high selectivity against hydrogen evolution and stability under relevant electrochemical conditions. This work provides guidelines for the rational design of single-atom catalysts supported by nitrogen-doped carbon materials for multi-electron redox reactions, such as electrochemical carbon dioxide or oxygen reduction.

## Mesoporous heteropoly acids for energy storage



Phosphotungstic acid (PTA) shows promise as a multifunctional material for applications in the energy sector. Although PTA possesses a high redox activity for use in high energy-density batteries, it suffers from poor stability in polar solvents and a low specific surface area, which limit its catalysis and energy applications. To tackle these issues, the Global Innovative Centre for Advanced Nanomaterials at the University of Newcastle has designed and developed a high-performance anode material based on mesoporous PTA (mPTA) (Ilbeygi H., Kim I.Y., Kim M.G., Cha W., Kumar P.S.M., Park D.-H., Vinu A. *Angew. Chem. Int. Ed.* 2019, **58**, 10849–54). The mPTA exhibits a high specific surface area, high thermal stability, non-solubility in  $LiPF_6$ , and low water content – beneficial properties for lithium-ion batteries. The mPTA has a high reversible capacity of  $872 \text{ mA h g}^{-1}$  even after 100 cycles. Critically, a novel lithiation mechanism of mPTA was unveiled through in-situ X-ray absorption spectroscopy, in which a Faradaic redox reaction occurs in the initial cycles, forming  $Li_{24}K_3[PW^{4+}_{12}O_{40}]$  and  $K_3[PW^{6+}_{12}O_{40}]$  upon lithiation and delithiation, respectively, whereas non-Faradaic  $Li^+$  adsorption in the mesochannels of mPTA is dominant as the cycle number increases. The researchers believe that this synthesis strategy can be extended to prepare a series of different heteropoly acids with porous structures that can be used for catalysis and energy applications.

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.



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# A cute & cuddly conundrum

BY **MERRAN GOVENDIR**

**Koalas are able to detoxify their diet of eucalypt leaves, but this ability means reduced efficacy of their medicines.**

**T**he koala is one of the most iconic Australian marsupials. It is immediately recognisable as an Australian symbol and greatly loved both in Australia and internationally. Additionally, koalas are estimated to add significant value to the Australian economy of \$1.1–2.5 billion annually by way of domestic and international tourism (NSW Government 2015, [www.environment.nsw.gov.au/animals/thekoala.htm](http://www.environment.nsw.gov.au/animals/thekoala.htm)). In this Anthropocene era, survival of wild koalas is threatened. Urban development, forestry and mining are fragmenting and destroying their habitat, especially

that near the hinterland of cities and towns along the east coast of mainland Australia. Increasing frequency of droughts and bushfires also threatens habitat and animal survival. Koalas being struck by cars while crossing freeways and roads, and attacks by feral and pet dogs, contribute to the alarming reduction in their numbers.

Wild koalas can be infected by many infectious diseases, including the bacterial disease chlamydiosis, which can result in painful inflammation of the membranes around the eye (conjunctivitis) and/or serious painful infections of the urinary–genital tract,

which invariably results in incontinence and infertility. Significant numbers of koalas are treated medically at wildlife hospitals annually for disease and trauma.

Until recently, koalas were administered medicines, such as antibiotics and analgesics, at the same dosages as for dogs and cats. Canine and feline medicine dosages were probably applied to koalas because a koala is comparable in body mass to a small-to-middle-size dog (the average mature koala weighs 5–8 kilograms and some of the larger males reach 10 kilograms). But, surprisingly, only in the last 15 years has it been

## The koala ... has an almost exclusive eucalypt leaf diet and has anatomical and physiological adaptations for detoxifying this diet.

recognised that treating koalas with these dosages is not appropriate, because of the significant differences in diet and digestive anatomy among these species.

The koala is classified as a specialised folivore, i.e. it has an almost exclusive eucalypt leaf diet and has anatomical and physiological adaptations for detoxifying this diet. This diet is low in minerals, proteins and carbohydrates (such as sugars and starches), but extremely high in oils.

Eucalyptus leaves contain high concentrations of plant secondary metabolites (PSMs). Most plants contain secondary metabolites as a defence against ingestion by herbivores or insects, or against attack by microbial disease. Eucalyptus leaves have many secondary metabolites, such as:

- lignin, which inhibits gastrointestinal microbial digestion of plant cell-wall constituents
- tannins, which bind to nutrient protein, inhibiting its absorption in the gut
- essential oils (or terpenoids), polyphenolic compounds and formylated phloroglucinol compounds (e.g. 1,3,5-benzenetriol), which are toxic to animal cells.

Consequently, the koala's diet has one of the highest concentrations of ingested PSMs, and is one of the most toxic diets of any terrestrial animal. Even a small proportion of the koala's daily dietary intake of PSMs, especially

the terpenoid concentration, would induce toxicity in humans (Pass et al. *Xenobiotica* 2001, vol. 31, pp. 205–21). Therefore, koalas have to expend significant amounts of energy to minimise PSM absorption and maximise PSM elimination. This constant and great energy demand to detoxify their diet contributes to their characteristic sleepy demeanour.

### Factors that affect nutrient absorption from the gastrointestinal tract

A couple of factors affect the rate of food absorption from the koala's gastrointestinal tract. The ingested mass of eucalypt leaf within the stomach and short small intestine is extremely fibrous, and although there is some PSM breakdown by normal gut microbes, it takes a long time to break down these substances at these locations. It is from the duodenum (the first section of the small intestine) that the dietary nutrients and PSMs are absorbed into the bloodstream. However, the small intestine of the koala is relatively short compared to that in carnivores and even other herbivores. Koalas have the largest hindgut (caecum) relative to the rest of their digestive tract of all marsupials and an expanded proximal colon. This large colon and hindgut acts as a fermentation chamber to facilitate decomposition and eventual elimination of residual gastrointestinal PSMs.

### Factors that accelerate absorbed PSMs and their elimination

Once the nutrients and PSMs from the eucalyptus leaves have been absorbed from the gastrointestinal tract into the bloodstream, the liver has an important role in further breaking down the toxic PSMs. The liver is the principal organ for metabolism of oily/fat-soluble substances in the blood. The word 'metabolism' can have many different meanings depending on context, but



*Eucalyptus amplifolia* Geekstreet/CC BY-SA 4.0

## An exclusive diet

Koalas are fussy eaters. Of the several hundred species of *Eucalyptus*, koalas have a preferred few (including those in the list below). They do seek secondary eucalypt sources when these aren't available, and will eat the leaves of plants such as paperbark and casuarina if they really have to. Koalas have several genes related to detection of bitter substances, which is useful for detecting potentially toxic chemicals such as terpenes (although they have a relatively high tolerance for them).

- *E. agglomerata* (blue-leaved stringybark)
- *E. amplifolia* (cabbage gum)
- *E. cytellocarpa* (mountain grey gum)
- *E. punctata* (grey gum)
- *E. tereticornis* (forest red gum)
- *E. viminalis* (ribbon gum)

List source: wariapendi.com.au



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## ... the koala's innate superior oxidative metabolism pathway means that current formulations of meloxicam don't last long enough in the koala to provide analgesia.

pharmacological metabolism, which is discussed here, means that the original parent molecule is catabolised in the liver and undergoes chemical conversion into one or more metabolites prior to elimination.

Pharmacological metabolism may occur by one or two 'phases' to catabolise the oily parent molecule

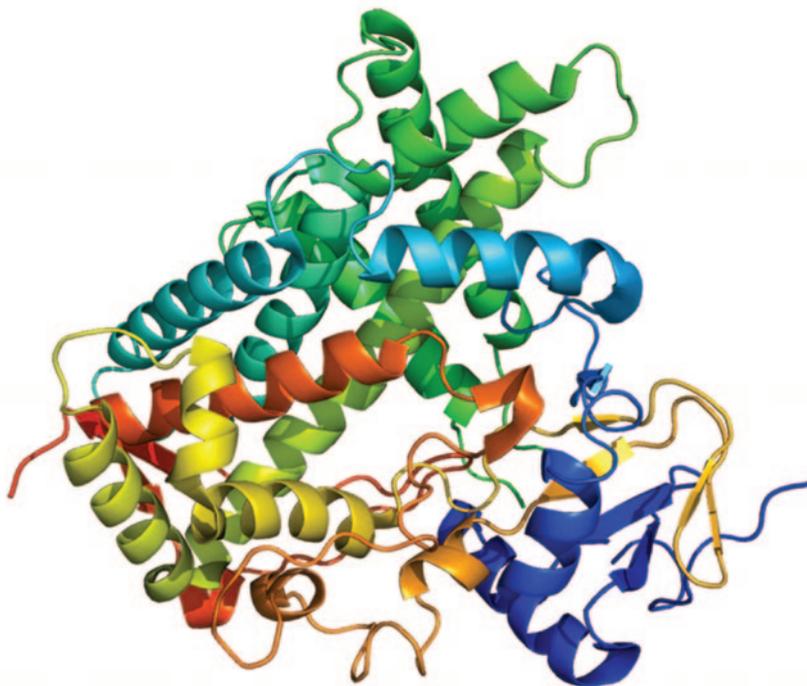
into one or more water-soluble metabolites that can be excreted in urine and/or via bile and into the faeces. Cytochrome P450 monooxygenases are a multigene family of enzymes that have a significant role as catalysts for many metabolic phase I reactions whereby the absorbed molecule undergoes hydroxylation, dealkylation or oxidation; ring-opening and reduction can also occur. Although the gene sequence and function of cytochromes are not greatly dissimilar among species, there are species differences of cytochrome activity with respect to substrate specificity and rate of metabolic activity.

The cytochrome enzyme superfamily is subdivided into various families; for example, CYP1, CYP2 and CYP3. This division into families is based on the similarity of gene sequences (for a cytochrome gene to be assigned to a family, there must be more than 40% amino acid sequence similarity with the other members of

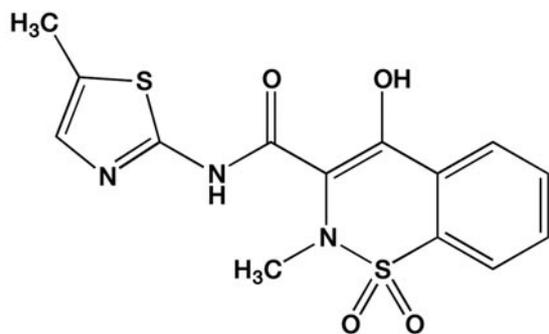
that family), and these families are further divided into subfamilies; for example, CYP2A, CYP2B and CYP2C (more than 55% amino acid sequence similarity). However, the difference between cytochrome families and subfamilies along divisions of amino acid sequence divergence results in the different cytochrome families catabolising different phase I chemical reactions, as well as differences in enzymic activity.

Investigations into the metabolism of various substrates by marsupial cytochromes over the last few decades have concluded that some, but not all, cytochrome metabolism pathways have superior activity in koalas (Liapis et al. *Comp. Biochem. Physiol. C* 2000, vol. 127, pp. 351–7; El-Merhibi et al. 2007 *Aus. J. Ecotox.* 2007, vol. 13, pp. 53–64). In humans, CYP2C is subdivided into four isoforms (CYP2C8, CYP2C9, CYP2C18 and CYP2C19) and is reportedly responsible for the clearance of approximately 15% of those medicines that undergo phase I reactions, including non-steroidal anti-inflammatory drugs (NSAIDs). Koala CYP2C activity is almost 17 times that of humans (Liapis et al. 2000). Recently, the koala genome has been sequenced and it was surprising that the greatest number of genes identified was those for the CYP2C enzymes (Johnson et al. *Nat. Gen.* 2018, vol. 50, pp. 1102–11). This high number of genes for CYP2C has not been observed in the genome of any other species to date. This probably reflects the great variety of genes necessary for the diverse range of enzymes required to detoxify a eucalypt leaf diet.

Phase II metabolism is characterised by conjugation of a glucuronyl, sulfate, methyl, acetyl or glyceryl moiety to either the parent molecule or the phase I metabolite, by transaminases such as uridine diphosphate–glucuronosyltransferases and sulfotransferases. Glucuronidation is an important pathway for the



This member of the CYP2C protein subfamily is an enzyme found in the liver and other tissues, and is involved in oxidative metabolism in many species, including humans and koalas. CYP2C activity in the koala liver is considered high. In humans, CYP2C has four isoforms (CYP2C8, CYP2C9, CYP2C18 and CYP2C19); in koalas, CYP2C47 and CYP2C48 have been identified and contain four extra amino acid residues at the NH<sub>2</sub>-terminal (Jones et al. *Comp Biochem Physiol C*, 2008, vol. 148, pp. 230–7). Emw/CC BY-SA 3.0



Meloxicam is widely prescribed to people as an NSAID, but it is poorly absorbed by koalas.

excretion of phenolic PSMs in koalas (McLean et al. *J. Chem. Ecol.* 2003, vol. 29, pp. 1465–77). Thus, the plant-eating marsupials that have been studied use both phase I (oxidative) and phase II (conjugative) metabolic reactions, which target different dietary PSMs (McLean et al. *J. Chem. Ecol.* 2003, vol. 29, pp. 1465–77), and these different biotransformation pathways can, likewise, target specific medicines.

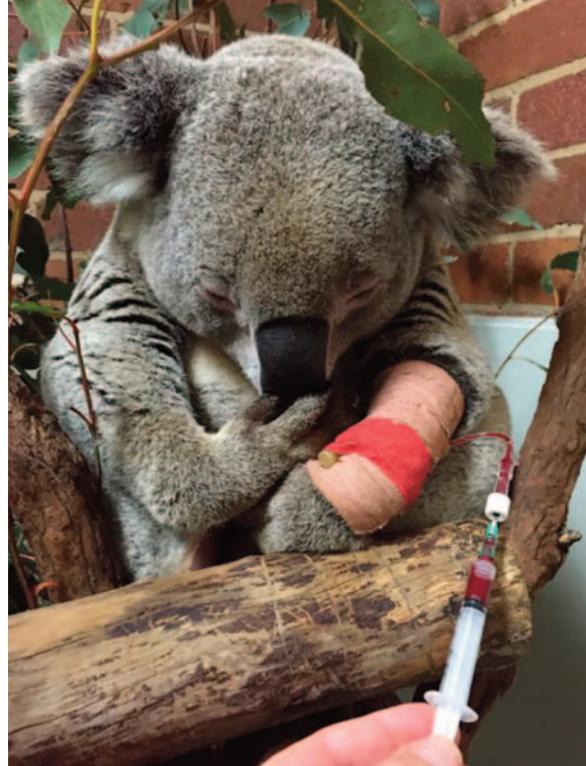
### What does this mean for giving koalas medicines?

Understanding the above information has resulted in recent changes in recommendations for treating koalas with medicines. One of the best examples is that NSAID meloxicam has been demonstrated to have little therapeutic effect when administered to koalas.

Meloxicam is one of the most frequently prescribed NSAIDs for humans and animals in Australia and globally. It is used for its anti-inflammatory and analgesic properties for animals. Trade names of meloxicam for humans and pets, respectively, include Mobic and Metacam. Meloxicam was the most popular analgesic administered orally to injured koalas for analgesia. Our group at the University of Sydney found that when it was administered by

mouth to koalas, meloxicam had very poor absorption in contrast to the excellent absorption in humans, dogs and cats. We think that the poor gastrointestinal tract absorption seen in the koala is due to the drug binding to the fibrous ingesta in the gut and not being free to be absorbed by the duodenal wall. In contrast, the relatively low fibrous diet of people and carnivorous pets does not inhibit meloxicam's oral absorption. So, the first lesson learnt was there is little point giving this drug (and many others) orally to koalas.

There was a further very important lesson to learn with administering meloxicam. We can also administer meloxicam to koalas by injection straight into their blood (i.e. an intravenous injection), muscles (intramuscular injection) or tissues (subcutaneous injection), where the local capillaries pick up medicine in the blood. The very efficient cytochrome oxidative pathways koalas use to detoxify terpenoids is the same pathway that they use to catabolise meloxicam. This active pathway means that koalas eliminate meloxicam in less than two hours (Kimble et al. *J. Vet. Pharmacol. Ther.* 2012, vol. 36, pp. 486–93), compared to dogs, which take more than 24 hours to eliminate a single dose of meloxicam, and humans, who take 15–20 hours. So, the second lesson is that the koala's innate superior oxidative metabolism pathway means that current formulations of meloxicam don't last long enough in the koala to provide analgesia. So, when possible, veterinarians who treat koalas should avoid oral administration and preferably administer the drug by injection. Additionally, the rate of elimination of the drug should be checked to ensure the drug is in the body long enough to be efficacious.



Max, a Taronga Zoo koala occasionally used in this research, sleeping in the fork of a tree while a blood sample is taken.

Courtesy Dr Larry Vogelneust and Taronga Zoo, Mosman, Sydney

### Current challenges

The koala/meloxicam story summarises a few of the issues we have observed when medications are administered to koalas. We are the only group researching this area. We have conducted many studies, and continue to conduct studies to improve the efficacy of many antibiotics and analgesics administered to koalas. Our biggest current challenges are to improve antibiotic treatment for chlamydiosis and to find analgesics that only need to be administered once a day, but which provide significant pain relief for koalas over that 24 hours.

**Merran Govendir** is Associate Professor in Veterinary Pharmacology, Sydney School of Veterinary Science, University of Sydney. To find out more about her research to improve medicine dosages for koalas visit <https://sydney.edu.au/science/people/merran.govendir.php> or email [merran.govendir@sydney.edu.au](mailto:merran.govendir@sydney.edu.au).

# Bitter pill

## Testing times for party drugs

BY **DAVE SAMMUT** AND  
**CHANTELLE CRAIG**

**Determined recklessness around party drugs, and the sometimes tragic outcomes, has fuelled the call for pill testing. So what's involved for chemists?**

Australia has an abundance of laws aiming to save people from themselves. Recreational drugs and narcotics are illegal in every state and territory. Billions of dollars are spent enforcing these laws. Our gaols are filling fast on the back of drug-related crime. And yet, says the Australian Bureau of Statistics, deaths caused by 'party drugs' have increased 300% in the last 20 years ([bit.ly/2Vd1s2t](http://bit.ly/2Vd1s2t)). Over the summer of 2018–19, pill testing at music festivals became a highly politicised issue in Australia. Arguments raged between two broad camps: 'just don't take drugs' and 'harm minimisation'. And while the two sides bickered, five young people died at music festivals in New South Wales alone.

'I know all the risks but I'm still going to take drugs at festivals', stated a 21-year-old student from Sydney, writing in *The Age*. 'Push legality aside and draw a comparison to drinking', says the student '... [drugs] simply offer something different on a night out, something that in moderation can help you have a better time.' ([bit.ly/2LaPntl](http://bit.ly/2LaPntl))

Across various festivals and pill-testing trials in Europe and the UK over recent years, published results show that about two-thirds of users decide not to take drugs found to contain harmful substances. Of course, this means that one-third still intend to do so.

Whichever side we might take individually, we can at least consider as chemists what pill testing involves – the methodology, the science (and its limitations) and what analyses can be realistically conducted, in the field, over short time periods.

Party drugs cover a very wide range of chemical compounds (see box p. 21), presenting a significant challenge even before considering the additional challenge of analysing unknown fillers and contaminants that could pose as much or greater risk than the intended drug itself.

Analytical methods vary widely, both in complexity and capability. This article focuses just on the methods that can be applied to drug samples that start as a powder or small-sample shaving from a pill, as is relevant to pill testing at festivals. Urine, saliva and blood

detection methods, for example in mobile drug detection in road policing (see April 2017 issue, p. 20), are a separate issue.

The simplest possible form of pill testing is the use of drug detection kits. These offer a basic, binary response to the presence or absence of a specific drug analyte. Drug detection kits typically involve a spot/colour test based on the presumed reaction between the target analyte and a chemical indicator.

Kits are relatively inexpensive, and can be used by an unskilled operator. However, they typically do not give a reliable indication of the drug purity, or of the presence of potentially lethal contaminants. And, of course, the test has to be selected on the basis of the anticipated drug or drug class. Multiple tests may be required to improve specificity, or for drug mixtures.

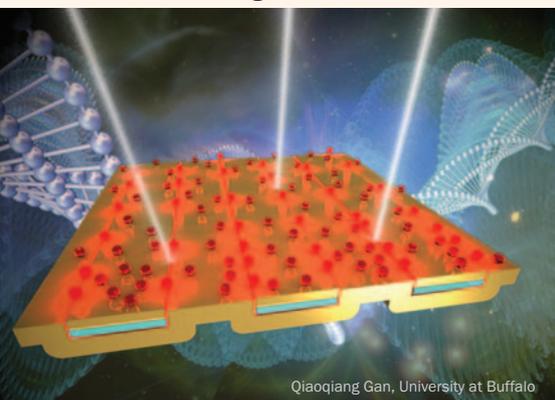
In a 2000 review of 12 kits, toxicologists O'Neal et al. concluded that, 'Although these tests are sensitive and can be relatively specific, the actual colour observed ... depends on many factors such as the concentration of the drug, whether the drug is a salt or free base, which salt form is present, the presence of contaminants in the sample, the colour discrimination for the analyst and the conditions under which the [test] is performed.'

([www.ncbi.nlm.nih.gov/pubmed/10725655](http://www.ncbi.nlm.nih.gov/pubmed/10725655))

Mass spectrometry-based methods – supported by gas or liquid



## Optical device could detect drugs, bomb-making chemicals



Qiaoqiang Gan, University at Buffalo

**Surface-enhanced infrared absorption spectroscopy.** Infrared light (the white beams) is trapped by tiny gaps in the metal surface, where it can be used to detect trace amounts of matter.

Infrared absorption is one of the most effective types of spectroscopy. Researchers are working to make the technology more sensitive, inexpensive and versatile, and now, a new light-trapping sensor, developed by a University at Buffalo-led team of engineers, is making progress in all three areas.

The new sensor, which works with light in the mid-infrared band of the electromagnetic spectrum consists of two layers of metal with an insulator sandwiched in between. The researchers used a fabrication technique called atomic layer deposition to create a device with gaps less than 5 nanometres between two metal layers. These gaps allow the sensor to absorb up to 81% of infrared light, a significant improvement from the 3% that similar devices absorb.

This process is known as surface-enhanced infrared absorption (SEIRA) spectroscopy. The sensor, which acts as a substrate for the materials being examined, boosts the sensitivity of SEIRA devices to detect molecules at 100–1000 times greater resolution than previously reported results. SEIRA could be used to find traces of molecules, including but not limited to drug detection in blood, bombmaking materials, fraudulent art and tracking diseases.

National Science Foundation

be relatively robust against the presence of small quantities of impurities, and as long as the test is performed quickly it should be relatively unaffected by moisture. A downside is the possibility of sampling error associated with shaving an inhomogeneous pill. It may also encounter difficulty if multiple drugs are present in the sample.

Infrared spectroscopy was the technique applied by Pill Testing Australia's Dr David Caldicott and his team of volunteers at the 'Groovin' the Moo' ACT festivals in 2018 and 2019, where Australia had its first opportunity to gather experience and data about the possibilities. The ACT sanctioned these trials, and Pill Testing Australia has offered free trials to all other Australian states and territories, where pill testing is currently banned.

The testing was conducted in an isolated tent with a private entrance, in an area in which police had agreed to avoid. As people came in, they were assessed for intoxication (and referred to the medical tent if considered not competent to accept advice), and given a questionnaire and a consent form to sign.

When a sample was submitted, it was photographed and weighed. The size of the sample varied from a few scrapings of a pill to half a tablet, at the user's discretion – the bigger the sample, the better the results. The service users were given a card with an identifier number. Tied to that number, information was retained for medical authorities about what was in the drugs, in case they have an adverse reaction at the festival or afterwards. In a couple of cases, samples were provided by the medical tent in the event of suspected overdose.

Medical volunteers and harm reduction counsellors were on hand to talk to revellers about their drug use, and amnesty bins were provided for people to dispose of unwanted drugs. The process reportedly took about 15 minutes to complete.

Two infrared spectrophotometers were staffed by professional chemists, including Associate Professor Malcolm McLeod FRACI CChem. At peak demand, samples were being analysed every 2–3 minutes – close to capacity. The query spectrum was matched to library spectra, ranked and scored to identify the major component. Further analysis was conducted by subtracting the major component and re-matching to the library.

Following the analysis, colour-coded results were posted to a board.

- Red was a warning, and meant the sample contained potentially lethal or dangerous compounds.
- Yellow was an alert, and indicated that there might be other elements in the sample (such as caffeine), or that the sample might be another drug altogether.
- White meant the drug was what they thought it was.

Some toxicologists continue to express concern. Dr John Lewis, quoted by the *RACGP News* in January, says, 'The Hippocratic Oath is *primum non nocere*, "First, do no harm", and I'm not sure pill testing complies with that'. Andrew Leibie expresses concern that FTIR says nothing about dose, and that 'The newer and the more exotic [new drug] compounds are, the less likely FTIR is to be able to detect them, because it relies on a library match – if it hasn't been told what some of these new drugs look like, it just won't see them.'

It is worth considering any liability that might accrue to the volunteer chemists conducting the pill testing. Marsdens Law Group has stated that the waivers signed by participants 'do not extinguish the duty of care which does exist. In circumstances where it is highly possible that a lot of patrons may be under eighteen, drunk, or under the influence of drugs, the legal effect of any waiver could be minimal'.

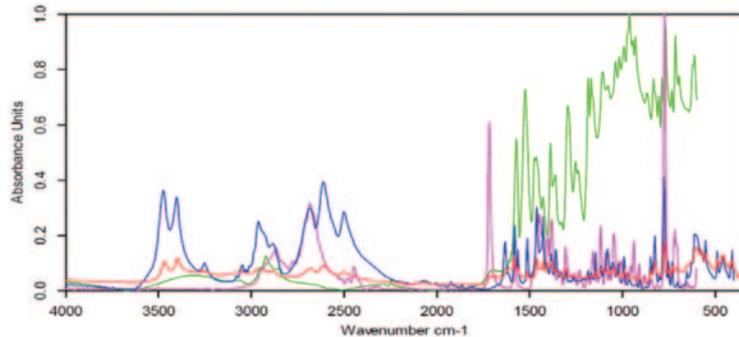
Pill Testing Australia disagrees: 'Our legal advice is very clear that prosecutions against such services would be very difficult to sustain given

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Hit No.	Hit qual.	Compound name	Entry no.	Lib. index	CAS number
1	745	TRIPROLIDINE HCL IN KBR	117	6	6138-79-0
2	206	KETAMINE HCL	910	2	1867-66-9
3	161	DORACRYL BRILLIANT RED X-4GS 300%	979	4	

Example of a single-component FTIR analysis of sample GTM001 presented as 'MDMA' that indicates MDMA as a component with low score with other ranked matches MDEA and safrole.



Example of a single-component FTIR analysis of sample GTM001 showing the IR spectrum of the sample (red) and overlaid IR spectra for MDMA (blue), MDEA (pink) and safrole (green).

Reproduced with permission from Makki T., MacLeod M., Vumbaca G., Hill P., Caldicott D., Noffs M., Tzanetis S., Hansen F., 2018, Report on Canberra GTM Harm Reduction Service, Harm Reduction Australia

our objectives and protocols'. It emphasises that at no point do the volunteers or health professionals ever say that a drug is 'safe'. In fact, they specify that the only way you can be sure that you won't have an adverse reaction is to not take the drug. 'We will give sound advice and information but in the end, it is the consumer that makes the final decision.'

The 2019 trial tested 170 samples, of which 113 returned a match score above instrument cut-offs. Matches were also achieved below instrument cut-offs, but with substantially lower confidence. MDMA was the prominent substance identified and to a lesser extent cocaine, ketamine and methamphetamines. Seven dangerous substances containing *N*-ethylpentylone were also identified, all of which were voluntarily discarded

to the amnesty bin provided.

Regardless of the pill testing itself, the opportunity to have a competent medical intervention between the purchase and ingestion of the drug must surely be a positive step in the harm minimisation approach. And international data has suggested that over time, pill testing results in a strong decrease in the presence of impurities in drugs sold illicitly, or of pills that don't contain what they are 'supposed to'.

According to Caldicott, there are two things that change young people's minds about drug taking: 'The idea that what they're taking could kill them and the idea that they've been ripped off ... We're able to provide both of those messages'. The Sydney student commented in *The Age* that, 'In the absence of a better system, most of us

just turn to past experiences and word of mouth as a safety net, which is exactly why we need pill-testing.'

The proponents would contend that the ACT trials argue strongly in favour of the pill-testing concept. A number of lives were potentially saved at the 2019 'Groovin the Moo' festival alone. Opponents would argue that pill testing condones and facilitates drug use. This article won't attempt to resolve the politics for either side.

What can be said is this: the Australian Medical Association has come out in favour of pill testing, as has the Royal Australian College of General Practitioners and the Royal Australasian College of Physicians. So it is worth considering whether the RACI should take a position on this as well, particularly as some of our members are already involved.

Perhaps the last word should go to Caldicott: 'As an emergency doctor ... there is not a parent I've ever spoken to who is prepared to turn around and say, "Do you know what? As long as [my child's] death serves as a lesson to others I'm OK with it"'

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

#### A note of thanks to RACI

As this is our 50th article for *Chemistry in Australia*, the authors (Dave Sammut and Chantelle Craig) would like to thank RACI for letting us contribute. We feel privileged to be able to pursue our hobby as writers, and we love the opportunity to learn about the topics as we research each article. Our particular thanks go to Sally Woollett, who has always offered a gentle and supportive editorial hand, and whose guidance makes us look better writers than we actually are; and to Catherine Greenwood, for all her hard work in making our simple words into attractive articles. And our thanks to all of the RACI members who have been so kind as to read our work, and occasionally to offer commentary or praise (no hate mail so far).



High-purity yttrium, sublimed-dendritic, and a 1 cm cube for comparison.

Alchemist-hp/CC BY-NC-ND 3.0

# Finite elements

BY **COLIN A. SCHOLES**

**Our dependence on certain chemical elements is becoming abundantly clear as they become scarce or run out.**

**T**he elements of the periodic table are universal and technically inexhaustible, but our ability to obtain many of them is not. Some elements can and should be considered finite resources because acquiring them in sufficient quantity and purity in the near future will become increasingly difficult, as we deplete natural reserves.

A critical element facing exhaustion is phosphorus, even though it is widespread in the environment, an integral part of every living organism and the 11th most common element on Earth. Phosphorus-rich ores are formed as part of Earth's phosphorus cycle, which, unlike the carbon and

oxygen cycles, is very limited. This is because phosphorus is not present within the atmosphere and the concentration of inorganic phosphorus is generally very low on land, due to orthophosphates being water soluble. This means phosphorus-rich ores form in very limited situations on the ocean floor from phosphorus precipitation. As such, millions of years of geological activity are required to transport the ore from the bottom of the ocean back to the land.

Hence, phosphorus-rich deposits are rare. They are mainly associated with the mineral fluoroapatite, predominantly found in Morocco and Russia. Phosphorus is extracted from

these minerals and converted into phosphoric acid, for use as fertiliser for agricultural crops. So prevalent is the need for phosphorus fertilisers that an estimated 90% of global food supplies will be affected by a phosphorus shortage.

In 2008, global fertiliser prices increased by 600%, affecting food prices throughout Europe, Africa, Asia and the Americas, in part because of the concern about phosphorus shortage. This was driven by the belief that the world would reach 'peak phosphorus' in 2010. Peak phosphorus is analogous to peak oil, the concept that production rate of a resource has passed the discovery rate, which is

considered an indication of terminal decline. This fear was alleviated when the United States Geological Survey increased their estimates of global phosphorus resources in the following year. However, current consumption rates are predicted to use up global phosphorus reserves in 80 years, and if agricultural output increases to meet expected world population growth, then depletion will be more rapid.



**Phosphorus is extracted from fluorapatite and converted to phosphoric acid, for use in fertiliser.** Rob Lavinsky, iRocks.com/CC BY-SA 3.0

The world has faced a phosphorus shortage in the past. Before the middle of the 20th century, almost all phosphorus was obtained by mining guano (accumulated excrement of seabirds). European demand for phosphorus fertilisers stripped islands in the South Atlantic and Pacific of their guano, leading to a critical shortage. Evidence of this demand for guano can be seen today in Nauru, where the interior of the island has been stripped to barren limestone, left over from phosphorus mining. The shortage of guano in the early 20th century impacted on food prices, and alternative phosphorus sources were sourced, leading to today's dependence on phosphorus mineral deposits.

Attempts continue to source alternative phosphorus resources. One approach has been to return to the phosphorus cycle and essentially

## Why researchers are mapping the world's manure

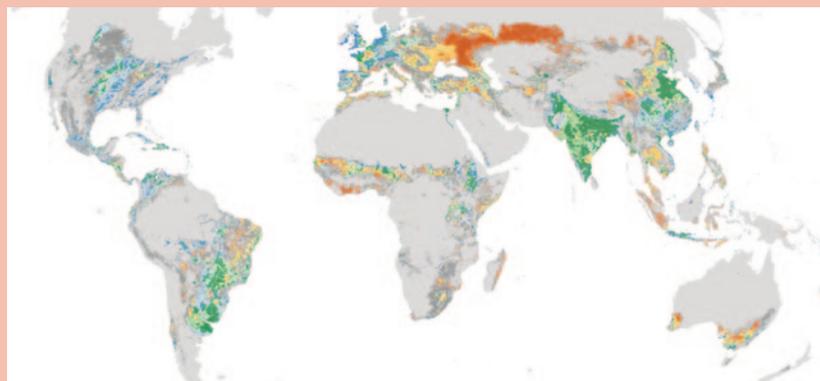
Farmers rely on phosphorus fertilisers to enrich the soil and ensure bountiful harvests, but the world's recoverable reserves of phosphate rocks, from which such fertilisers are produced, are finite and unevenly distributed. Stevens Institute of Technology in the US is spearheading an international effort to map the global flow of phosphorus – much of which will be absorbed by crops, then eaten and excreted as waste by animals and people – and jump-start efforts to recapture and recycle the vital nutrient.

In the April 2019 issue of *Earth's Future*, David Vaccari, director of the Stevens department of civil, environmental and ocean engineering, and his team map that process globally for the first time, and identify regional 'hot spots' where there's both significant demand for fertilisers and significant potential for recapturing phosphorus from animal and human waste.

The team shows there are significant untapped opportunities for recycling phosphorus, and in a field where lack of well-integrated data has often impeded both local and regional planning, the work is a breakthrough in bridging the global to the local, actionable level.

This year, the world's farmers will use over 45 million tonnes of phosphorus fertilisers, much of which will be absorbed by crops, then eaten and excreted as waste by animals and people. Vaccari's team, including researchers from China, Australia, Canada, Sweden, and Netherlands, combined recently developed datasets to map global crop production alongside human and livestock population levels. They then divided the planet into a grid of 10-kilometre-wide blocks, allowing detailed local insights with an unprecedented overview of global phosphorus flows.

Some 72% of croplands with significant manure production nearby, and 68% of croplands with significant human populations nearby, are in regions that are heavily dependent on imported phosphorus, including large swathes of major emerging economies such as India and Brazil. The study also identifies significant surpluses of phosphorus-rich waste in much of Asia, Europe and the US, suggesting that both developing and developed economies could benefit from increased recycling.



**Global distribution of manure-rich cultivated areas. Green shades represent manure-rich areas with the most potential for recycling phosphorus. Manure-rich cultivated grid cells were most abundant in India, China, Southeast Asia, Europe and Brazil. Smaller patches are seen in central and east Africa, central US and Central America.**

The results also show that at least five times as much phosphorus is contained in animal manure as human waste, suggesting that livestock operations are an abundant target for recycling efforts. Almost half of the world's farmlands – about 12% of the planet's landmass – are co-located with manure-rich livestock operations, suggesting that in many regions manure could be applied to fields directly, or processed by bio-digesters to extract phosphorus for efficient and economical transport to farms.

The scientists are now trying to work out exactly how much phosphorus can be recaptured from animal and human waste, and identify other opportunities for more efficient phosphorus use.

Stevens Institute of Technology

mine the element from manure and excrement. Animals excrete almost 100% of the phosphorus they consume and hence manure can be a continual rich source of phosphorus. This is not a new concept, but what is new is the potential scale of the process and its industrialisation, with global livestock and municipal sewage having potential as new phosphorus reserves. Already, small-scale plants are undertaking phosphorus manure recovery in Canada.

Another finite element is selenium, which is an essential element for humans and is added to commercial fertilisers in small quantities to be taken up by plants to enter our diet. Selenium is considered a finite element because it is not mined exclusively – no major deposits of the element exist. Selenium is a by-product of copper mining, associated with electrolytic refining of copper ore. Hence, global supplies of selenium are dependent on copper mining outputs, with a reduction in copper demand leading to reduced amounts of selenium being supplied to the market, irrespective of selenium

demand. Selenium is also used in the electronic industry for its semiconductor properties, and this application now competes with the fertiliser industry, so that selenium demand is beginning to outstrip supply.

This dependence on major metal mining is why indium, gallium and antimony are also facing scarcity. Indium and gallium are used for their low-melting-point alloys, which are critical in a range of industries, such as electronics and photovoltaics. Antimony is mainly used in the form of  $Sb_2O_3$  as a flame retardant, which is found in aircraft, automobiles and clothing. All three elements are produced exclusively as by-products of the processing of other metals. As with selenium, no minerals exist that have these elements in sufficient quantity and concentration to be mined solely for them. Indium is the by-product of zinc and lead smelting. Gallium is the by-product of bauxite processing to alumina for aluminium, and antimony is recovered from copper, lead, silver and gold ore processing, where it is present at around 0.5 ppm.

The dependence of selenium, indium, gallium and antimony on the production of other ores means that supply can be significantly curtailed during downturns in demand for the source ores. Indium is a good example of this, with zinc and lead smelting expected to remain relatively constant into the near future, in part because manufacturing industries are moving away from steels to composite materials. This has meant global indium supply has not changed and it is anticipated that 'peak indium' will be reached within 10 years. Similar timeframes have also been suggested for selenium and gallium, while antimony demand will overshoot supply in 15 years. When these events occur, the resulting shortage will significantly drive up prices for these metals. This is anticipated to make mining and processing these elements

exclusively attractive; however, the scarcity of mineral ores with these elements in sufficient concentration to be mined, will mean the price will be astronomical.

Rare earth elements, which are the lanthanide series with yttrium and scandium, are often considered to be finite, because of their name. However, the majority of these elements are actually common. The issue is that they are not found in sufficient quantity to be extracted economically, and until 20 years ago there was very little demand for them. This has changed with the development of the electronics industry; rare earths are now indispensable in modern technology. Yttrium is used in colour televisions, fuel cells and LEDs; similarly for europium. Dysprosium, neodymium and terbium are essential for micro-magnets and electronics used in computers and mobile phones, while cerium and lanthanum are required for catalysts.

Rare earths are currently in a 'structural scarcity', where production has been restricted by a lack of investment. This is because China currently produces more than 90% of rare earths and, in the case of dysprosium and terbium supply, 100% of global demand. The growing need for these elements and Chinese export restrictions have led to critical shortages, but new mining operations in Australia, USA and elsewhere will address these shortages in the coming decades. There have been creative ventures to address this shortage on shorter timeframes, such as the mining of e-waste to recover these elements from mobile phones. This recycling effort is cost-effective in part because the rare earth elements are in a more concentrated and refined form within e-waste materials than in the original ore body. This recycling of e-waste will become a significant industry, because neodymium demand is expected to grow by 700% over the next 20 years and dysprosium by 2600%. The only



Crystals of gallium. en:userfoobar/CC BY-SA 3.0



Indium is a by-product of zinc and lead smelting. Schtone/Public Domain





## Making molecular switches

Late last year, Dr Suzanne Neville – a lecturer and researcher in the University of New South Wales's School of Chemistry – received the prestigious Sandy Mathieson Medal, an award for distinguished contributions to science involving X-ray, neutron or electron diffraction/imaging by a researcher under 40 years of age. **Lachlan Gilbert** talks to her about the work that led to this recognition.

### Your work sounds very specialised – what exactly is it that you study?

My work is focused on making new materials called molecular switches. A molecular switch is a molecule that can exist in two (or more) different states that can interchange in response to environment stimuli, such as temperature, pH, light and pressure. In molecular switches, the distinct states show distinct properties and for this reason they are of interest in the field of nanotechnology for molecular computers in which the components are small (i.e. built up from individual atoms and molecules), rather than being manufactured as small devices.

### What is the state of this technology today?

In some cases, the molecular switches can be used to produce controlled molecular motion – this is a simple example of a

molecular machine. In fact, a Nobel Prize for such work was awarded in 2016. In the majority of work on molecular machines (and molecular switches), the switching between different states occurs with the molecules in solution.

My work looks at making molecular switches that function as solid crystalline materials. This is a particularly challenging task because initiating and controlling the motion of solids is less favourable than in solution. But if successful, it will allow controlling the properties of materials at the molecular level to be achieved in a more orderly fashion and bring us a step closer to molecule-based memory devices.

### What was it in particular about your work that led to you being awarded the Sandy Mathieson Medal?

My research on molecular switching materials intrinsically relies

on knowing and understanding the structure of the different states and this is obtained by using a range of X-ray diffraction techniques. Such structural information helps us understand the properties of each material and collectively build up a broader understanding of what structural features we can manipulate to make our properties even better in the future.

We typically use temperature change to induce the switching between states, but have also successfully used pressure changes, light irradiation and change of solvent molecules to trigger the molecular switching. One of the biggest reasons I was awarded this medal is that these types of experiments are non-standard and have involved extensive equipment and method development over the last 15 years, including novel techniques using synchrotron radiation. I also received this award because my work uses a non-typical combination of crystallographic techniques that I apply to every new material to develop a more comprehensive view of the structure dynamics that occur before, during and after the molecular switching event. Both of these aspects are now used as a standard around the world.

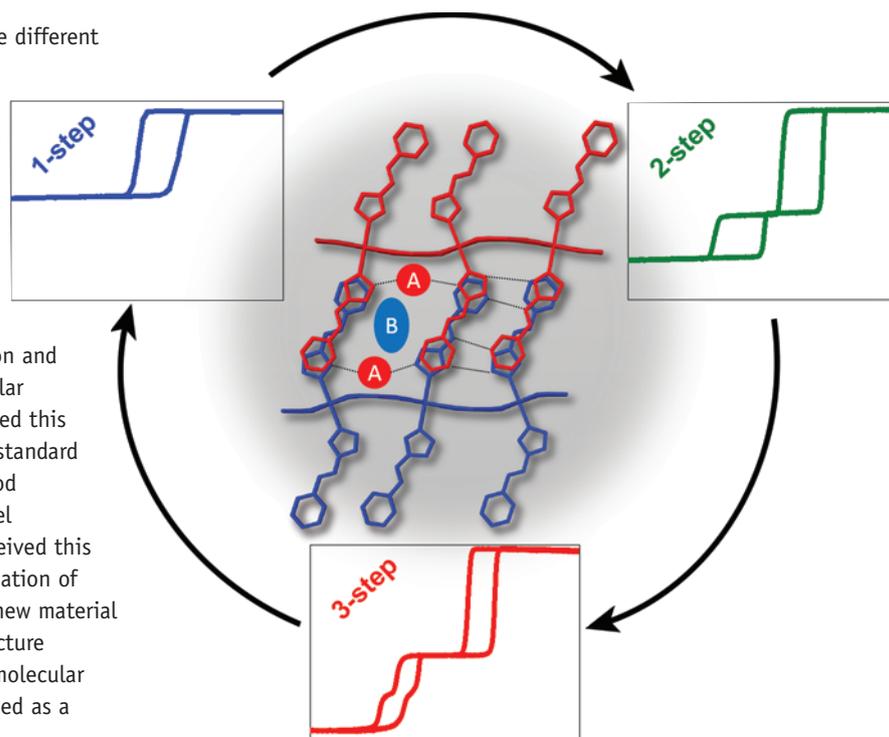
In recognition of Sandy Mathieson's contributions to crystallography, the Sandy Mathieson Medal is awarded to a researcher under the age of 40 for distinguished contributions to science involving crystallography. This medal is awarded by the Society of Crystallographers of Australia and New Zealand (SCANZ). I am very grateful and humbled to receive the award, in particular given that the award is interdisciplinary because crystallography is used across chemical, biological and materials sciences.

**The award is given to someone who's under 40, so you've achieved quite a bit at a young age, haven't you?**

I'm glad to hear that 40 is a young age! But in all honesty, I think rather than being an age-related achievement, I am prouder of doing so while being the primary carer of two young children (4 and 8 years old) – it has been a substantial challenge to maintain momentum with two maternity leave breaks. In fact, one of my long-term goals is to use my experience to inspire more females to continue on an academic career path.

**Can you tell me about any upcoming projects?**

In the past we have travelled overseas to the Advanced Photon Source synchrotron facility in Illinois, USA, to conduct in situ crystallography experiments. Recently, we have been working closely with the Australian Synchrotron and ANSTO to develop the same types of experimental set-ups in Australia. This will be a big time and cost advantage for us, and what we develop will be useful for many other Australian researchers. We have some promising results so far. We also have plans in the near future



The pores in this material can be used to expand the molecular switching to have two (1-step), three (2-step) or four (3-step) stable states that are accessible by temperature change.

Reprinted (adapted) with permission from Murphy J.M. et al. Guest programmable multistep spin crossover in a porous 2-D Hofmann-type material, *J. Am. Chem. Soc.* 2017, vol. 139(3), pp. 1330–5. Copyright 2017 American Chemical Society.

to develop some new methods so that we can make movies of the dynamic structure changes that occur over the molecular switching process – this will be both a great teaching tool and an excellent visualisation tool to understand the properties better.

**What about on the research side of things?**

We have been working on a new exciting avenue of molecular switches that are embedded in porous materials. These materials can be used as molecular sensors as the switching can be turned 'on' or 'off' depending on what molecules are in the pores, or the particular characteristics of the pore contents can be used to tune the molecular switching properties. This is a powerful tool. This is not novel in itself, but what we are doing within the pores is. We have been looking at using the breathing motion within the pores, which occurs over the molecular switching process to manipulate position and chemistry of the encapsulated molecules – this is a big challenge and we have made some good progress. Why would we want to do this? We want to mimic what nature does, for example, in ribosomes, by precisely positioning simple molecules and then doing chemistry on them to make more complex molecules.

Lachlan Gilbert is media adviser, UNSW Sydney's Media & Content team for the STEM faculties.

## Top stories from the periodic table

Storytelling brings people closer together. Conceived by the RACI in recognition of the International Year of the Periodic Table, *Stories from the Periodic Table* collects, publishes and celebrates the personal connections we have to the periodic table and its elements.

### Hydrogen

BY **JOSHUA MARLOW**

Sometimes, when I struggle with a problem, I think of hydrogen. I do work with hydrogen atoms in my work, but considering its ubiquity, I think most people can say they do. Regardless, that's not why I think of hydrogen. No, I think of hydrogen for the same reason I eat vanilla ice cream and drink water for nearly every meal: because, sometimes, plain is the way to go.

Perhaps that's unfair to hydrogen, much as it is to vanilla, an incredibly complex – and expensive – flavour. I mean no offence, however, to the element that makes up nearly 75% of all baryonic mass and 10% of my own body. In fact, the deceiving simplicity of the hydrogen atom is what gives it its charm. There's a reason, after all, that it's one of the first elements we teach students about.

One proton, one electron. The electron, a tiny negative particle, orbits the proton, a much larger positive particle. That's a description of most hydrogen atoms, but also a brilliant starting point for all discussion about the physical sciences, especially chemistry. It raises the questions: 'What if there were more protons or electrons?', 'Why are they both charged?', 'Why is one larger than the other?' and 'Wait, did you say "most" hydrogen atoms?'

By starting with a simple doodle of a small dot on a circle around the large dot, we can learn what an atom is, what a proton is, and what an electron is. If we add another large dot, we can learn about neutrons and isotopes. If we add an additional two large dots and a second small dot, we discover helium, which leads us to understand other elements, noble gases and nuclear fusion. Beginning only with a quick representation of hydrogen allows us to learn or teach almost anything about chemistry; it is the seed from which so much knowledge is drawn.

So then, why do I think of hydrogen when I struggle with any problem? How does it help me write when I'm unmotivated, or decide on what to have for dinner? Ultimately, it's about what hydrogen represents: a starting point. Every essay begins with a letter, which becomes a word, which becomes a sentence. Every mountain climb begins with a single step, and each two-metre-long sandwich sub with a single bite.



Steph Parflyn

And everything we know about chemistry begins with two dots and a circle, so you might as well start somewhere.

As a PhD student at Monash University, **Joshua Marlow** looks at how nanoparticles affect the properties of liquid crystals. Just like liquid crystals, which behave as both solids and liquids, Josh dreams of being both a scientist and a communicator. He hopes to help scientists convey their work to wider audiences, and to help non-scientists experience the wonders of the scientific world.

### New Periodic Table on Show available

In celebration of the International Year of the Periodic Table in 2019, we are pleased to launch the latest Periodic Table on Show. With new artists' impression artwork completed for elements 112–118 by printmakers Linda Abblitt (113, 115, 117) and Tina Curtis (114, 116, 118), the Periodic Table on Show is now up to date.

RACI Periodic Table on Show posters are now available to purchase online for \$15 plus postage ([racichemedcentral.com.au](http://racichemedcentral.com.au)) or discover the science and artists' descriptions at [raci.org.au/IYPT](http://raci.org.au/IYPT).

## Margaret Brimble joins ACS Hall of Fame

Dame Professor Margaret Brimble FRACI CChem of the University of Auckland is the first New Zealand woman and one of only two New Zealanders to be inducted into the Division of Medicinal Chemistry of the American Chemical Society's Hall of Fame.

The Hall of Fame publicly recognises research pioneers who have made meaningful contributions in the field of medicinal chemistry and, in particular, drug discovery, excellence in teaching and outstanding service. Her induction took place at a meeting of the Division of Medicinal Chemistry (MEDI) in San Diego in August.

Brimble's career has been marked by outstanding achievements in science. The MEDI honour follows national and international awards, prizes and honours, including being named a Dame Companion in this year's New Year's Honours list and being elected a Fellow of the Royal Society of London last year.

The Royal Society is widely regarded as the world's most prestigious scientific body and she is the first New Zealand-based woman scientist to be elected to its ranks.

Her research sits at the interface of chemistry and medicine and focuses on developing bioactive compounds that can be synthesised for development as potential treatments for a wide range of diseases, including cancer and infectious disease.

Drug discovery can take years or even decades and Brimble's research is regarded as pioneering. Her work has led to the development of the drug Trofinetide, a new treatment for Rett syndrome, fragile X syndrome and autism disorders. The drug is

in the last stages of formal approval. Once approved, it will be the first drug to be developed successfully by a New Zealand company and one of only a few to be discovered in an academic laboratory.

Brimble's research group is also developing innovative chemical technology to generate cancer vaccines. This work is being translated for clinical use by the spin-out company SapVax, which is developing a pipeline of products for the treatment of different cancers.

She holds the Chair of Organic Chemistry and is Director of Medicinal Chemistry in the School of Chemical Sciences and the School of Biological Sciences. She is a principal investigator in the Maurice Wilkins Centre for Molecular Biodiscovery and past-Chair of the NZ Royal Society Te Apārangi Rutherford Foundation.

She is a Fellow of the Royal Society of Chemistry UK, the NZ Royal Society Te Apārangi, the RACI and the New Zealand Institute of Chemistry, and is a recipient of the 2016 Marsden Medal, the 2012 RSNZ Rutherford Medal (NZ's top science prize) and the MacDiarmid and Hector medals.

Brimble is a passionate advocate for women in science and regularly speaks to groups of young women to encourage them to consider science as a career. In 2007, she was named the 2007 L'Oréal-UNESCO Women in Science laureate in materials science for Asia Pacific and in 2014 received the Westpac Trust Women in Influence Award for Science and Technology.

University of Auckland

## RACI Fellows become Fellows of AAS

Two Queensland researchers and RACI Fellows have joined the ranks of the nation's top scientists after being elected to the Australian Academy of Science.

Professor Debra Bernhardt and Professor Christopher Barner-Kowollik are among 22 new Fellows elected earlier this year.

Bernhardt, from the University of Queensland's Australian Institute for Bioengineering and Nanotechnology and School of Chemistry and Molecular

Biosciences, said she was honoured to be named a new Fellow.

'My research group is using computational methods to model systems, particularly at the molecular level, to help design and select new materials for technologies such as fuel cells, batteries and supercapacitors, which can store energy', she said.

Barner-Kowollik, at QUT's Science and Engineering Faculty, is a macromolecular

polymer chemist with a number of important scientific achievements based on his deep understanding of the fundamental mechanisms governing radical polymerisation processes, probed by laser experiments. His fundamental knowledge of complex polymer reactions has allowed the generation of new classes of advanced materials.

With University of Queensland and Australian Academy of Science

## John Bryan Willis

### An appreciation

John Willis FRACI CChem, with whom I had carried on a friendly correspondence for many years, died in April this year at age 96. He was born in 1922 in Birkenhead, just across the River Mersey from Liverpool, and came to Australia with his parents in 1935. John's father had been chief engineer of the *Athol Crown*, a diesel-engine tanker that carried oil and molasses from the Dutch East Indies (now Indonesia) to Britain. They moved to Sydney when he got the job of chief engineer on the coastal steamer *Duntroon* that plied ports between Fremantle and Brisbane.

John studied at the Sydney Church of England Grammar School, Shore, and then the University of Sydney where in 1943 he was awarded his BSc with first class honours and the University Medal for inorganic and physical chemistry. Two years later, he completed his MSc before heading back to Britain with a CSIR Senior Studentship to study for the PhD at University College London. There he worked with Samuel Sugden (1892–1950) on the exchange of bromine in organobromine compounds with radioactive bromide ion. In early 1949, Sugden drafted a paper describing their work, but after he died in October 1950 it remained unfinished. John, after discussion with Christopher Ingold, also a professor at University College, completed it and saw it published in the *Journal of the Chemical Society* in 1951.

Returning to Australia in 1948, John took up an appointment with CSIRO's Division of Industrial Chemistry, where he joined Alan Walsh working on infrared spectroscopy. Their first paper was published in 1950 in the *Journal of Chemical Physics*, and John's first single-author paper (in 1951) was in the *Australian Journal of Scientific Research*, a CSIRO journal that a few years later gave birth to the *Australian Journal of Chemistry*. The subject was the influence of slit-width on the shape and intensity of infrared absorption bands. This attention to instrumental and chemical effects in spectroscopy eventually led Walsh to the development of atomic absorption spectroscopy, a project in which John Willis was also deeply involved, and in his last chemical contribution he spoke about it in the science history program presented by Jenny Davis on radio 3RRR Melbourne.

The CSIRO group had some of the first infrared spectrometers in Australia, and as well as using them in their research, they frequently provided a service for other chemists who just needed a spectrum. John collaborated with medical researcher John Falk on the spectra of porphyrins, with any number of the CSIRO organic chemists who were involved in natural products research, and with

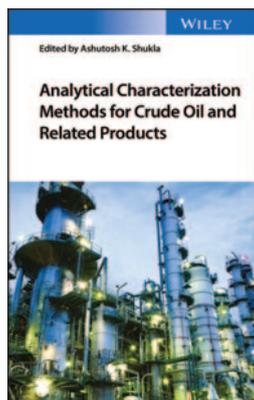
**Following his retirement ... John developed his interest in the history of chemistry. That became a meeting ground for us, although 'meeting' was more often by letter (and later by email) than face-to-face.**

university chemists. Especially in the latter cases, there were generous acknowledgments for spectra he provided.

Following his retirement from CSIRO in 1986, as Assistant Chief of the Division of Chemical Physics, John developed his interest in the history of chemistry. That became a meeting ground for us, although 'meeting' was more often by letter (and later by email) than face-to-face. He wrote about the Division and its spectroscopic work, and the way that its research was taken up by small companies in what he termed 'the birth of a major Australian scientific instrument industry'. His papers were published in the Australian Academy of Science journal *Historical Records of Australian Science*. He also helped me by providing information and contacts as I, too, worked on history of chemistry and chemists.

I knew that one of John's younger brothers, Don, who died in 2013, was also a chemist (DPhil, Oxford) employed by CSIRO. There were lots of things I didn't know, however, but you can learn a lot at a funeral. From the eulogy delivered by John's son, Tony, I got the details that in 1953 John married Amy Bettina (Betty) Fletcher, whom he had met while they were holidaying in the Blue Mountains. Their children Tony and Penny were born in 1954 and 1955, respectively. I also learned that, since 1978, John and his wife had been devoted members of the congregation of the Anglican parish of St James the Great, in East St Kilda. Betty died in 2000. Shortly before his death, John had completed a history of the first hundred years (it was founded in 1914) of this High Anglican Church. And in his spare (and I wonder if he ever had any) time, John was a book binder and member of that small fraternity in Melbourne.

Ian Rae FRACI CChem



## Analytical characterization methods for crude oil and related products

Shukla A.K. (Ed.), John Wiley & Sons Ltd, 2018, hard cover, ISBN 9781119286318, 296 pp., \$252.95

*Analytical characterization methods for crude oil and related products* ably covers the application of a variety of spectrometric techniques to the characterisation of crude oil and related substances, such as asphaltenes.

There are chapters covering optical interrogation, ESR, high-field pulsed and double resonance, NMR (both high and low field), NIR and Raman and IR spectroscopies. These chapters are stand-alone, well presented and extensively referenced. There is also a very brief and somewhat unsatisfying chapter devoted to rheology of crude oils. There are 24 contributing authors, representing a large part of the globe, which serves to confirm the importance of the study of crude oil and related materials.

I have no concerns with the actual contents of this book, rheology excepted. However, I do query the word 'analytical' in the title because it implies a comprehensive coverage that is simply not there. 'Spectroscopic' would better reflect the contents. If the book is to live up to its title, I would expect to see greatly enhanced treatment of rheology as well as, inter alia, healthy doses of chromatography, mass spectrometry and chemometric approaches to identifying the origins and sources of crude oil spillage.

In the preface, editor Ashutosh Shukla comments, 'Mathematical details have been kept to a minimum'. This is not a wise strategy. Assuredly, there are any number of 'math-phobic' chemists out there. (I spent 30-something years watching students' eyes glaze over whenever any faintly 'hard' mathematics cropped up in lectures.) However, throwing the baby out with the bath water always seems a tad defeatist. A preferable compromise would be to put the outcome in the main text and incorporate the detailed mathematics into text boxes. At least then the less informed would be able to appreciate the import of the mathematics and possibly even learn to love it, while the better informed could continue revelling in its beauty.

To summarise, if you are a scientist or engineer interested in the analysis of crude oil and want to explore applications and possibilities of current spectroscopic techniques, this is a useful book. The chapters start from the ground up and provide sufficient detail to allow scientists and managers to decide whether particular techniques, often implying significant financial investment, are useful and value for money in their situations. If, on the other hand, you have a broader interest in how crude oil behaves, what it contains and the broad battery of techniques that can be brought to its identification and characterisation, then you may find the book falls short.

R.J. Casey FRACI CChem

## Char and carbon materials derived from biomass: production, characterization and applications

Jeguirim M., Limousy L., Elsevier, 2019, paperback, 490 pp., ISBN 9780128148938, approx. \$260

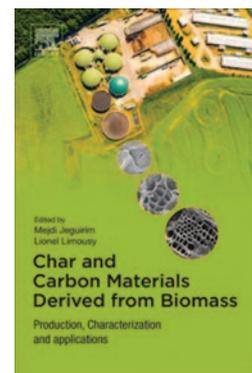
*Char and carbon materials derived from biomass: production, characterization and applications* is an excellent book. It provides an up-to-date, comprehensive and extensively referenced womb to tomb account of the production, characterisation and applications of chars derived from biomass.

If you are *not* interested in biochar (a material produced by heating biomass at moderate temperatures (<700°C) under low-oxygen conditions), then you jolly well ought to be! The material is not graphite (which is produced by high-temperature pyrolysis), nor is it charcoal (which is also produced at higher temperatures, contains fewer organics and more structure than biochar and is mainly used as a fuel/heating medium). Rather, biochar is an open-pored, carbon-rich material with variable properties, depending mainly on its feedstock. Its principal uses are in soil and water remediation and as a carbon sink.

Throughout the Amazon Basin, there are thousands of raised platforms of black and very fertile patches of soil. These are known as *terra preta de Indio* ('black earth of the Indian') and they have retained their fertility for centuries, well before their 'discovery' in 1879 by Herbert Smith. The Indians used to pile up grass and leaves and set fire to them on their land, producing biochar and leading to *terra preta*. As we come to better understand that Australia's First People were not just hunter-gatherers but farmers too, it is interesting to speculate that their use of fire could also be associated with soil enrichment by biochar. Certainly, the practice of burning the stubble (e.g. after harvesting wheat) can also be seen as adding biochar to the soil. Whether you like it or not and whether its users knew it or not, biochar has been around for a long time and it has a lot of potential.

We live in interesting times. In the last 50 years, estimates of the land free to feed the population have dropped from a bit less than one (0.8) hectare to about one-fifth of a hectare per person. Elevated carbon dioxide levels in the environment continue to be a major concern; unsustainable agriculture is a major cause of habitat loss; and the global vertebrate population has fallen by about 58% since 1970. Meanwhile, we continue to be deluged by the mountains of waste, putrescible and potentially recyclable, we create and bury in increasingly rare and expensive holes in the ground. In Australia, we live in an old, degraded and arid landscape, which we seek to prop up by often-injudicious use of fertilisers and over-exploitation of our limited supplies of water.

Biochars offer many potential solutions to our problems. First, they pull a lot of carbon out of the carbon cycle and lock

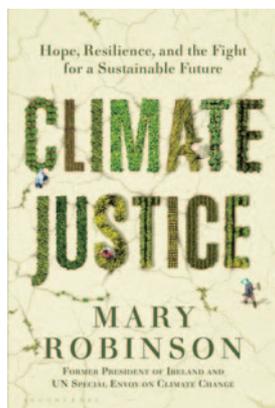


it up for centuries (biochar production is carbon negative). Second, when incorporated into the soil, biochars retain water, fertilisers and beneficial bacteria, assisting soil productivity and fertility and minimising fertiliser run-off and contamination of watercourses. Third, biochars would seem to have great potential as a means of beneficially disposing of municipal waste to produce a useful product.

The editors, Dr Mejdí Jeguirim (Associate Professor at the University of Haute Alsace, France, in the field of energy, process engineering and kinetics modelling) and Dr Lionel Limousy (Associate Professor at the Institute of Materials Science of Mulhouse, France), have assembled an impressive array of authors to contribute to the 12 chapters. Accordingly, the book covers the sources and properties of biomass feedstocks, their conversion to chars and the characterisation of these chars, the applications of biochar for soil remediation/amendment, the combustion and gasification of chars, as well as their uses as adsorbents for gas and water treatment, in catalytic processes, for gas storage, in supercapacitors and in the iron and steel industries. The sustainability of char production and application is also discussed. This is a very well-rounded treatment.

As I trust I have assured you, we all ought to be a bit interested in chars. Anything we can do to help clean up some of the mess we humans create ought to be worth thinking about, and chars seem to offer various interesting and, in some ways, 'left field' solutions. There are plenty of what I might term scientifically 'loose' books on biochars, but relatively few serious scientific works. This one, of the latter variety, is outstanding. In particular, it constitutes essential reading for materials scientists and environmental researchers and practitioners. It is not cheap, but it is very good.

R.J. Casey FRACI CChem



## Climate justice: hope, resilience and the fight for a sustainable future

Robinson M., Bloomsbury Publishing, 2018, hard cover, ISBN 9781408888469, approx. \$25

If your exhilaration at advances in medical science that will enhance your longevity is tempered by the gloomy realities of concurrent climate change, this little book will fill you with some hope for the future.

Author Mary Robinson is a most impressive person. Following her education at Trinity College and King's Inns, Dublin, and Harvard University, she became Reid Professor of Law at Trinity College where she made major contributions to both Irish and European law and was widely recognised as a notable supporter of human rights. She was a member of the International Commission of Jurists in Geneva for a period and sat in the Seanad (upper chamber of the

parliament of Eire) for 20 years. In 1990, she became the first female President of Eire and set about modernising the nation and continuing her strong advocacy for human rights. Subsequently, she was appointed a high commissioner by the UNHCHR, where, again, she ably pursued her promotion of human rights. More recently, she has been a UN Special Envoy on Climate Change. Mary Robinson is a most accomplished and very worthy person. Anything she has to say or write deserves your attention.

*Climate justice: hope, resilience and the fight for a sustainable future* offers a series of vignettes about people, farmers and activists, in Africa, Asia and the Americas, whose lives have already been diminished and devastated by the seemingly inexorable roll-out of climate change. Their experiences are quite moving, but what is even more moving is their resilience and efforts to adapt to their changing environment together with the willingness to seek and implement ameliorating strategies.

Robinson brings the whole issue of climate change down to the personal level as well as ranging across the globe. Examples include the case of Constance Okollet, a modest farmer in rural Uganda who led her local community to a better life; Sharon Hanshaw from Mississippi, who started a campaign from her hair salon that eventually led to her addressing the UN; and Christina Figueres from Costa Rica, a key architect of the Paris Agreement and whose country is now generating almost all its electricity renewably. Interestingly, Robinson's examples are largely initiatives of women, frequently the mothers and grandmothers of their communities. This is entirely in accord with observations of the Drawdown Project (see January/February, p. 37), which advocates investment in education of women and girls as an essential element for reducing global carbon emissions.

We are all familiar enough with the 'big picture', but seldom do we get the issues of climate change brought down to the individual, 'real person' level, as this book does. Everything becomes so much more cogent when climate issues become personal, about an (representative) individual.

The book is well written, easy reading on the train to work, as well as enlightening. At the risk of trying to teach my grandma to suck eggs, may I remind you, as the song goes, 'We are all in this together'. Climate change is a global problem and the solutions must benefit *all* of humanity, not just the affluent. Nations need to pull their weight, but so too do individuals if Mary Robinson's plea for climate justice is to achieve its aims.

R.J. Casey FRACI CChem

**John Wiley & Sons** books are now available to RACI members at a **20% discount**. Log in to the members area of the RACI website, register on the Wiley Landing Page, in the Members Benefits area, search and buy. Your 20% discount will be applied to your purchase at the end of the process.

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## Perhaps people, not plastics, are the problem

I want to say one word to you. Just one word. 'Plastics'. So goes the dialogue in a scene from *The Graduate*, filmed in 1967. Fast forward to 2019, and it's not hard to imagine that this might be the answer to an exam question, 'Name one of the planet's biggest environmental problems'. While plastics might have many desirable properties – they are durable, lightweight, cheap – the corollary to that set of properties could easily be: persistent, buoyant, abundant.

Hardly a week goes by without a story emerging about how or where plastics have turned up in an unexpected place. If it's not in the local creek or Sydney Harbour, it's at the bottom of the Mariana Trench, photographed by a remote-controlled deep-sea submersible. Any number of famous people are having their say, with even the Prince of Wales lamenting how he was ignored 40 years ago when he raised concerns about plastics.

The problem is well illustrated by the piles of recyclable waste that have been growing around Australia following the refusal of several countries in Asia to take any more of our contaminated 'recyclable' wastes. Disposable nappies contain plastic, so used ones must be recyclable, so the thinking seems to go. Never mind that the plastic tube of caulking compound is still a quarter full; it's made of plastic so it must be recyclable.

The sight of an ephemeral urban creek in western Melbourne, with the reed beds festooned with waste plastic items, got me thinking about the pathways by which plastic items and materials make their way into the environment. The empty soft-drink bottle doesn't go directly from the factory to the creek. Fishing line and plastic mesh don't leap off jetties and boats, fatally attracted to sea life. No. The common vector is the human hand. The disposable cup, the plastic bag, nearly every piece of plastic got into the environment by human action. Why should this be so?

I'd suggest that a major factor is that the positive attributes I listed for plastics all lend themselves to plastic items being used only once. It's the 'single-use' item that is discarded. If something is designed for repeated use, there is a strong chance that someone will take care of it and seek to use it again. The proliferation of single-use items has fostered the throw-away mentality.

Perhaps the exemplar is the story of cutlery and crockery on planes. Fifty years ago, the knives and forks were likely to be metal, but the tea/coffee cups were often lightweight melamine, and all were intended for multiple use. The spectre of hijacking put an end to metal cutlery, but the quest for light weight, and lower costs, has seen the disposable item come to the fore; plates, cups, trays, spoons, all used once and then thrown away. Qantas has recently sought to make a virtue of this, with a recent flight that produced no items for landfill. All the food and beverage containers were compostable, but still only single use. Maybe the environmental footprint of washing a planeload of reusable items is greater than that of using



compostable, single-use items, but it's all the same approach. Use once, throw away.

So, the answer is obvious. It consists of one word: people. It's people who are to blame for the piles of plastic clogging up the water and the land. The question is, which is easier – changing the human behaviours that cause littering and pollution, or going down the biodegradable and compostable path. However, to do the latter still requires the former. People need to recognise what is recyclable or compostable, and then take action to ensure this can happen. Unfortunately, collection systems for recyclable and compostable materials are almost identical to those for more intractable wastes. It's all a black box (well, a big green bin) that solves the problem for us. A truck empties your domestic wheelie bin once a week or fortnight. It seems that many householders lack the knowledge to make the right the decision. The ACT Government has recognised this, and is running an awareness campaign to improve the composition of the recyclable waste stream. We await the outcome with interest. The old manual systems of collection, usually employing a two-person team (a truck driver and a runner), with separate crews for paper and glass items, were effective at segregating the waste but were labour intensive. Now, one driver in a truck collects the comingled contents of the bin, and sorting becomes someone else's problem. Except, we can now see that it's a problem for all of us. With the recent financial collapse of a Victorian recycling company, things may get worse before they get better.



**Paul Moritz** FRACI CChem CEnvP (Paul.Moritz@douglaspartners.com.au) is a Principal Contaminated Land Consultant with Douglas Partners, and an EPA-appointed Environmental Auditor in Victoria, New South Wales and the Northern Territory.

## Lessons from ‘Spider-Man’: how video games could change college science education

Like many people do over their holidays, I spent some time – maybe too much – playing one of the most popular and best reviewed video games of 2018: ‘Spider-Man’.

While I thought I’d be taking a break from chemistry research, I found myself web-swinging through virtual research missions all over New York City. I collected samples of polycyclic aromatic hydrocarbons in Hell’s Kitchen, studied vehicle emissions in Chinatown and determined the chemical composition of atmospheric particulate matter in Midtown.

‘Spider-Man’ has many of these eco-friendly research missions. But what I found most encouraging is that the game also includes tools that can potentially teach advanced concepts in chemistry and physics. These tools include adjusting the wavelength and amplitude of radio waves, rewiring circuits to meet target voltages, and what will be examined here, using absorption spectroscopy to identify unknown chemicals.

Believe it or not, the millions of people playing ‘Spider-Man’ have been unwittingly introduced to principles of quantum mechanics. There is a lot of veiled science to this aspect of the video game. Perhaps more importantly – as a chemistry researcher and university lecturer – I believe the game represents an interesting opportunity to teach science in a fun and engaging way in higher education.

### Spectroscopy and ‘Spider-Man’

To better understand the scientific technique that players simulate in ‘Spider-Man’, it helps to have a short primer on what absorption spectroscopy is.

The interaction of light with matter is the most powerful means scientists have to understand what matter is made of. When matter does not interact with light, we are quite literally left in the dark. This problem is made obvious in the still

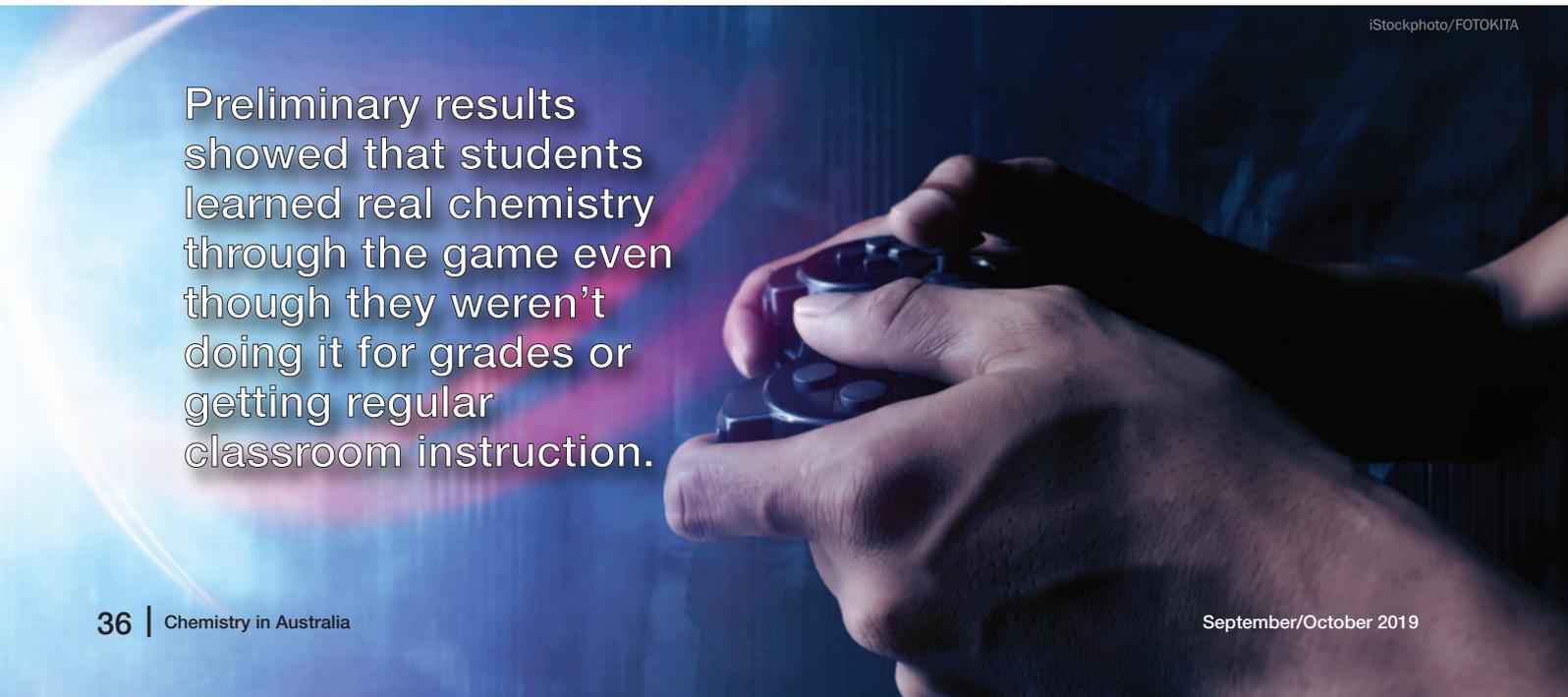
unknown composition of dark matter that constitutes the vast majority of matter in the universe.

Using light to study ordinary matter like atoms and molecules is a broad field of science known as spectroscopy. It is an important part of university courses in chemistry and physics. There are currently many different types of spectroscopy. However, the underlying concepts are almost entirely the same as the original version that began in the 17th century when Isaac Newton first dispersed sunlight with a prism.

As famously illustrated on Pink Floyd’s ‘Dark Side of the Moon’ album cover, dispersing the white light of the sun with a prism reveals its continuous colour spectrum extending from violet (higher energy, shorter wavelength) to red (lower energy, longer wavelength). However, if this is done carefully, you would find that this continuous spectrum is patterned with intermittent dark bands.

While the origin of these dark bands was not fully understood until the 20th century, scientists now know that they are due to absorption of specific wavelengths of light by atoms and molecules present in the sun. In fact, this kind of spectroscopy led to the discovery of helium in the solar spectrum before it was identified on Earth. This is why it derives its name from the Greek *helios*, meaning ‘sun’.

So, what causes this phenomenon? Atoms and molecules have a set of energy levels that depend on how their electrons are arranged. The absorption of light – which remember is energy – can cause the electrons to rearrange into these different levels. The catch is that the energy – or wavelength – of light must exactly match the energy difference between two electron arrangements in an atom or molecule for absorption to occur. This set of energies is unique for each chemical and leads to a distinct absorption spectrum much like a fingerprint from which it can be identified.



Preliminary results showed that students learned real chemistry through the game even though they weren’t doing it for grades or getting regular classroom instruction.

iStockphoto/FOTOKITA

In 'Spider-Man', the player identifies unknown substances using simplified versions of absorption spectra.

The goal is to match the pattern in the spectrum using the fragment inventory provided to give the absorption spectrum of the unknown substance. Unfortunately for chemists everywhere, determining the chemical structure of an unknown molecule is much more complicated.

Still, there is a significant amount of science conveyed in the video game version of what a spectroscopist would call assigning this spectrum. Only slight modifications and additional explanation could make these parts of the game an excellent way to teach these concepts to undergraduate science students. But are video games ever used in higher education?

### Video games in higher education

Video games for teaching more elementary skills like arithmetic or spelling are common. Similarly, colleges and universities are increasingly infusing video games into their coursework.

In a recent publication in the journal *Nature Chemistry*, researchers presented a modified version of the video game 'Minecraft' called 'PolyCraft World'. In this game, the player learns polymer chemistry by crafting materials in the game. Preliminary results showed that students learned real chemistry through the game even though they weren't doing it for grades or getting regular classroom instruction.

In the popular game 'Kerbal Space Program', the player builds their own space program by successfully launching

rockets into orbit. The game was not originally intended for educational purposes but implements rigorous orbital mechanics in its physics calculations. It is so accurate that NASA joined the game's developers to create new missions, and it now has a teaching-ready standalone game that could be used directly in university physics courses.

A unique approach has been taken with the biochemistry-based game 'FoldIt'. This game serves as both an educational as well as a citizen science platform. In the game, players manipulate the structures of real proteins to search for the 'best' or lowest energy structures. Results published in the journal *Nature* showed that the player's search methods can be successfully combined with computer-based algorithms to solve actual scientific problems.

The use of video games in higher education is a real possibility and could even have a promising future in higher education given the advantages of delivering educational content through a video game format. These advantages include things such as remote access, personalised student progress and immediate feedback. However, creating an engaging video game from scratch is challenging, costly and time-consuming. As indicated by the creators of 'PolyCraft World', finding existing games to modify for educational purposes – like the research missions in 'Spider-Man' – could be the best way forward.

**Aaron W. Harrison** is a Teaching and Research Fellow at Chapman University, California. This article first published at [www.conversation.com](http://www.conversation.com).

## How chemistry can be heard by policymakers

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## Crabby chemicals

The great claw of crabs lends its Greek name, via Latin, to a group of chemicals called chelates. Chelates hold a central metal in a claw-like embrace. The strength of the embrace is measured by a stability constant. The larger its value, the more tenacious the hold.

In the 1960s, Sydney University chemists, inorganic Frank Dwyer and organic Francis Lions, collaborated. Francis made the chelates 'in tank car lots' and Frank then wrapped them around metal ions.

Wrapping metal ions prevents them from grabbing a negative ion and precipitating as a solid out of a solution. It also prevents these ions from taking part in reactions involving catalysts. Bottom line – the chelate must have a stronger hold on the ion than undesirable competitors.

Chelates are useful in many everyday products in the laundry, in the kitchen, in the medicine cabinet, on the cosmetic counter, and out in the garden. Industrial use is huge and varied.

### Laundry and cleaning

For laundering, chelates include polyphosphates, citrates and EDTA (ethylenediamine tetraacetic acid) and modifications thereof. They hold the ions in hard water (calcium, magnesium and iron) to prevent precipitating soap and interfering with detergents.

Citric acid (naturally in lemon juice and also a food additive) can chelate iron. Hence, it is useful for removing bloodstains after their colour has changed from blood red to rusty, indicating that the natural, very stable chelate haem has degraded. It is good for ordinary rust stains as well.

### Kitchen

Kettle surfaces calcified by the boiling of hard water can be cleaned with citric acid to chelate away the calcium salts (watch at [bit.ly/2YzLpy2](http://bit.ly/2YzLpy2)).

Food Standards Australia and New Zealand (FSANZ) allows calcium disodium EDTA as an additive (385) in some foods

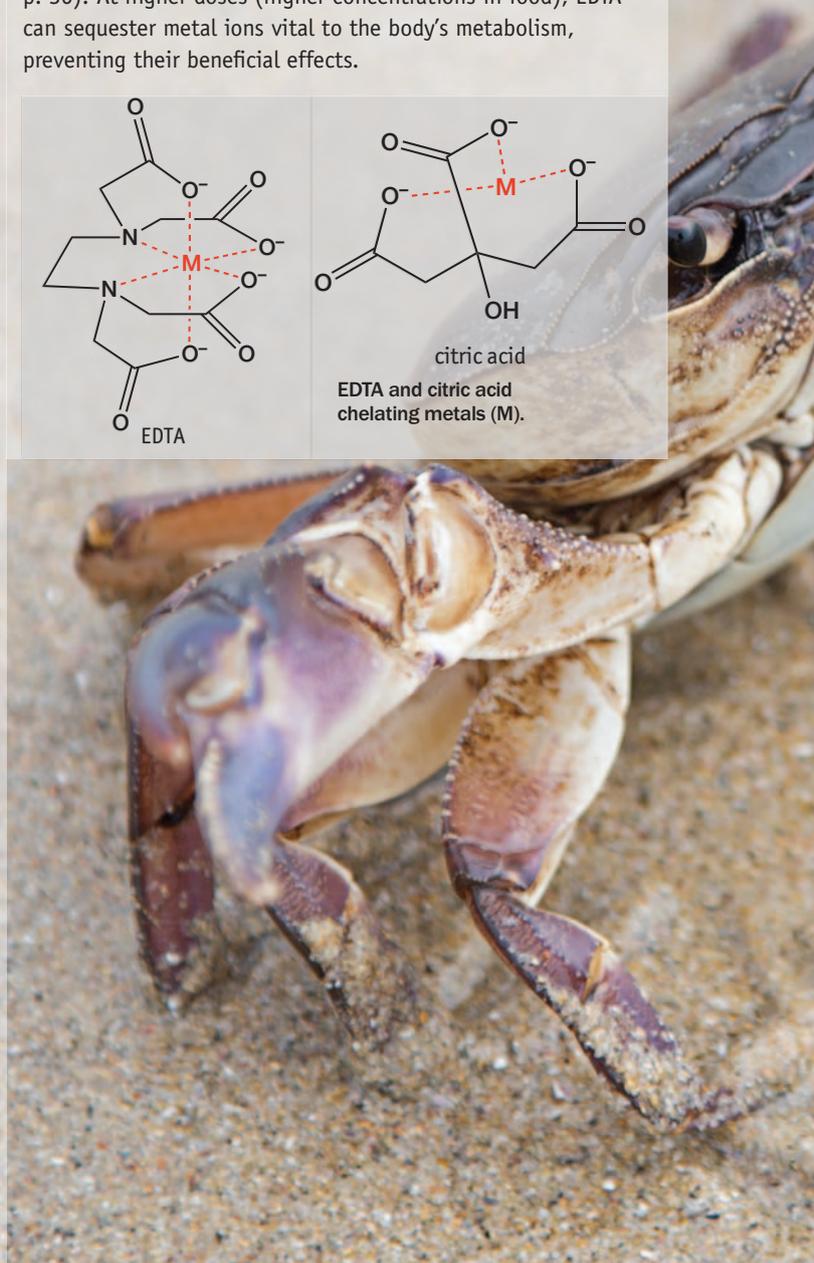
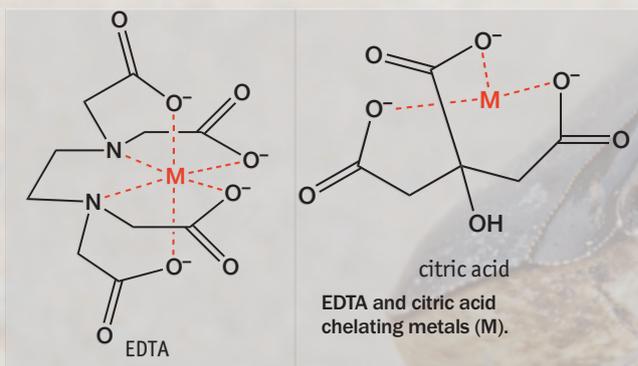


Crystals of citric acid, a common food preservative that can be used to chelate calcium. iStockphoto/hekakoskinen

where it can remove those metals with higher stability constants. It is added to mayonnaise and salad dressings where metals such as copper, iron and manganese catalyse the production of rancid tastes and odours. The large surface area of the dispersed oil-water interface makes it particularly vulnerable compared to bulk oil.

EDTA also prevents off-colours occurring when cooking kidney beans, black-eyed peas and chickpeas. The metal-catalysing ions can come from the cooking water or the legume itself. Unless, of course, you prefer mushy red-grey kidney beans.

But heed the warning from Paracelsus (see March/April issue, p. 36). At higher doses (higher concentrations in food), EDTA can sequester metal ions vital to the body's metabolism, preventing their beneficial effects.



## Medicine cabinet

The earliest deliberate medical search for a metal chelating agent was possibly for an antidote to the arsenical poison gas lewisite. British biochemist Sir Rudolph Peters developed BAL (British anti-Lewisite (dimercaprol)) in 1940–5. In the event, this gas was never used in World War II, but the research led to further medical developments in chelation control of metals in the body. EDTA chelation therapy is now widely administered for lead and other heavy metal poisoning ([bit.ly/2WYrzvM](http://bit.ly/2WYrzvM)).

EDTA is in eye drops and contact lens wetting and cleaning solutions. Its role here is subtle. It deals with certain types of bacteria, particularly *Pseudomonas* species. Some are more difficult to destroy because they have an added encapsulating cell wall that slows the entry of preservatives and reduces resistance to them. EDTA removes calcium and magnesium ions that maintain the structure of this capsule, which then disintegrates.

Chelated iron is a cheap way of treating malnutrition, particularly in the developing world. It is added to maize (corn) flour. In contrast, powdered iron alters the flour's colour, taste and shelf life. Non-chelated soluble iron compounds (such as iron citrate) precipitate in the small intestine (at a pH above 3.5) and consequently are not efficiently absorbed.

EDTA-chelated iron survives the stomach's low pH and is steadily released in the small intestine. FSANZ permits ferric sodium EDTA in some foods.



The maize plants in the foreground have a pronounced zinc deficiency. This is a common deficiency in crops and pastures globally.

Wikicommons/Alandmanson/CC BY-SA 4.0

## Cosmetics case

Shampoos and liquid soaps have the same problem with bacteria and thus the same approach is used to deal with them. There is also another reason. Traces of the usual suspect metals can catalyse the auto-oxidation of some perfume components.

EDTA also seems to stabilise colour, thickeners and proteins during storage. It is added to cosmetic creams for the same reason as it is put in salad dressing: to protect the large surface of oil-soluble components exposed in cosmetic emulsions.

## Garden shed

Without chelates, fertilisers have a problem. Plants require trace elements (iron, zinc, copper and manganese) as well as macro amounts of phosphorus, usually in the form of orthophosphate. Orthophosphates immediately precipitate iron, zinc, copper and manganese as insoluble phosphates and make these trace elements unavailable.

Chelated with EDTA, the trace elements are protected and can make their way to the plant roots. Adding trace elements without orthophosphates wouldn't help; these positively charged ions would immediately become 'stuck' on negatively charged clays.

## Industry

Chelation also has many applications in industries other than those that are directly consumer orientated. You might like to check out a useful commercial website ([chelates.nouryon.com/products/guide](http://chelates.nouryon.com/products/guide)) for examples.

Meanwhile, raise your glass to crabby chemicals and propose a toast with an EDTA-chelated wine ([bit.ly/2HwsyhB](http://bit.ly/2HwsyhB)).

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

## Astringency and tannin size

Some readers of this column have sought my thoughts on a paper recently published in the *Journal of Agricultural and Food Chemistry* (doi/10.1021/acs.jafc.9b01480) on the relationship between tannin size and dryness perception. The paper from the University of California, Davis is headed 'Red Wine Dryness Perception Related to Physicochemistry', a somewhat more rigorous title than in the online *Food & Wine* magazine of 'Dry Red Wines "Big Tannins" Are Literally Bigger, Study Says' (bit.ly/20faE8F). The researchers – Aude Watrelot, Hildegard Heymann and Andrew Waterhouse – examined the chemistry and sensory effects of condensed tannins in relation to the perception of mouthfeel dryness. Condensed tannins are found in grape skins, seeds and flesh and consist of repeating units of flavan-3-ol units; for example, (+)-catechin.

Two wines were used in the study: a Cabernet Sauvignon and a Pinot Noir. Using plots of intensity of sensory response versus time in mouth (commonly called time/intensity plots), the group of trained tasters found that the Cabernet Sauvignon showed a higher overall intensity and a longer time in mouth response than the Pinot Noir. The tannins were extracted from each wine, the mean degree of polymerisation (mDP; the number of repeating flavan-3-ol units) determined and the extent of their interaction with protein assessed through turbidity measurement. The same measurements were performed on the original wines and on wines to which the extracted tannins had been added.

The tannins in the Cabernet Sauvignon were 'bigger' with a mDP value of 6.3 compared with 2.4 for the Pinot Noir. This difference was even more pronounced with the tannin extracts: 9.4 versus 3.6. There were also structural differences between the two extracts, particularly with respect to substitution on the B-ring. Both wines came from very ripe grapes showing high alcohol concentration (15.4% and 14.5%) and a relatively high pH for red wine (3.97 and 3.77).

Dryness is a common mouthfeel descriptor for astringency. A major contributor to dryness is the consequence of salivary protein interaction with tannin. Proline-rich proteins are known to be significantly involved in generating the astringent response. So, the authors examined the interaction between the two tannin extracts as well as the two wines themselves with poly-L-proline, a commonly used model compound for proline-rich proteins. Mucin and human saliva were also used with turbidity as a measure of the interaction.

Limited turbidity was observed with mucin, perhaps not surprisingly because it is a glycoprotein, a class not generally known for its contribution to astringency. Significant turbidity was found when poly-L-proline was used, but the most extensive turbidity was found when saliva was used – the saliva was actually a pooled sample from 4 (two female and two male) participants in the study. In essence, the Cabernet Sauvignon

wine with added tannin extract from either wine showed the highest turbidity, with the somewhat quirky result that the Pinot Noir wine with added tannin from the same wine had a higher turbidity than when the Cabernet Sauvignon extract was used.

In these experiments, turbidity measurements are based on the formation of aggregates of sufficient size to cause particle formation. The turbidity results here agree with those for the sensory assessment of astringency, thereby reinforcing the idea that larger tannin molecules are the basis for 'big tannin' taste.

The actual mechanism of astringency is extremely complex and our understanding is still evolving. An extensive review published in 2014 summarises the state of knowledge at that time (*Trends Food Sci. Technol.* 2014, vol. 40, pp. 6–14). It is well known that there can be marked differences in individual saliva composition and this alone can result in differences in astringency assessment. To add to this complexity, it has been shown that salivary protein profile can change with food ingestion and with a tentative suggestion that the profile may be influenced by circadian rhythm (Brandão et al. *Food Res. Int.* 2014, vol. 64, pp. 508–13).

There is increasing evidence from research at the University of Porto, Portugal, that oral cells contribute to astringency by binding tannins to their surface. These tannins then interact with and bind salivary proteins, leading to the formation a network of oral cell–tannin–salivary protein complexes (Soares et al. *J. Agric. Food Chem.* 2016, vol. 64, pp. 7823–8). This opens up a new level of complexity in astringency assessment.

One of the frustrations in obtaining a molecular handle on astringency has been the inability to assess interactions in actual solutions. Rather, surrogates such as turbidity have been used. Here again the University of Porto group has taken the lead, using fluorescence quenching and saturation transfer difference-nuclear magnetic resonance (STD-NMR) (see *J. Agric. Food Chem.* 2017, vol. 65, pp. 6415–25). STD-NMR allowed the binding sites of various tannins (the 'epitopes' in the authors' terminology) to be mapped while discrimination of tannin–salivary protein binding efficiencies could be achieved with fluorescence quenching.

The role of polysaccharides in influencing the tannin–salivary protein interaction is another complicating factor and still the subject of extensive research, as is the difference in salivary protein structure (disordered versus structured) and its effect on astringency. Some rather exciting research still needs to be carried out. Something to contemplate when next consuming a red wine or two.



**Geoffrey R. Scollary** FRACI CChem (scollary@unimelb.edu.au) has been associated with the wine industry in production, teaching and research for the last 40 years. He now continues his wine research and writing at the University of Melbourne and the National Wine and Grape Industry Centre at Charles Sturt University.

## Ever heard of LEMCO?

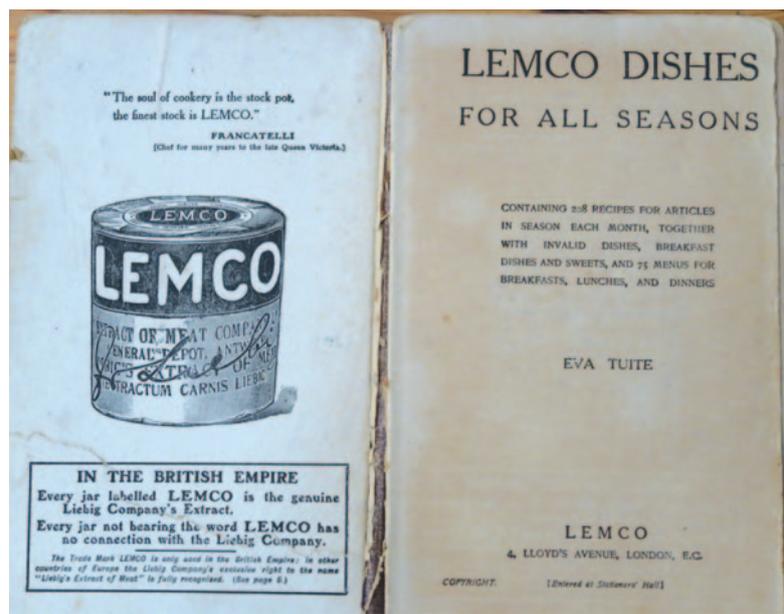
My resolve to stay away from the book tables at church fetes, garage sales and places where the detritus of people's libraries wash up, was undone when a friend went shopping on my behalf and brought me a small book entitled *Lemco dishes for all seasons*. The author is Eva Tuite and the book was published in the early years of the 20th century to promote the consumption of the meat extract invented by Justus Liebig. The title is, in fact, an acronym for Liebig's Extract of Meat Company. The book is available online and was republished in hard copy in 2007.

To quote from the book, 'the Liebig Company's Extract is the only meat extract ever prepared under the control of Baron Justus von Liebig. The Liebig Company was formed in 1865, and Justus von Liebig was in charge of its Scientific Department until his death' in 1873 at age 69. 'He allowed the Liebig Company to use his name, on the strict understanding that every parcel of extract produced by them was analysed, examined, and approved by him or his successors. This control is still in force.'

'Owing to a decision of the Courts prior to the passing of the Trade Marks Registration Act in 1875, inferior meat extracts, in no way connected with Justus von Liebig, or the Liebig Company, were allowed to be called Liebig's Extract, and are sometimes still so sold. In order fully to protect the public, and render confusion impossible, the Liebig Company now affix their

initials LEMCO to every jar. Every jar labelled LEMCO is the genuine Liebig Company's Extract. Every jar not bearing the word LEMCO has no connection with the Liebig Company. The trade mark LEMCO is only used in the British Empire: in other countries of Europe the Liebig Company's exclusive right to the name 'Liebig's Extract of Meat' is fully recognised.'

The Lemco Company was established in 1865, and seemed to have had the field for itself for a while with its



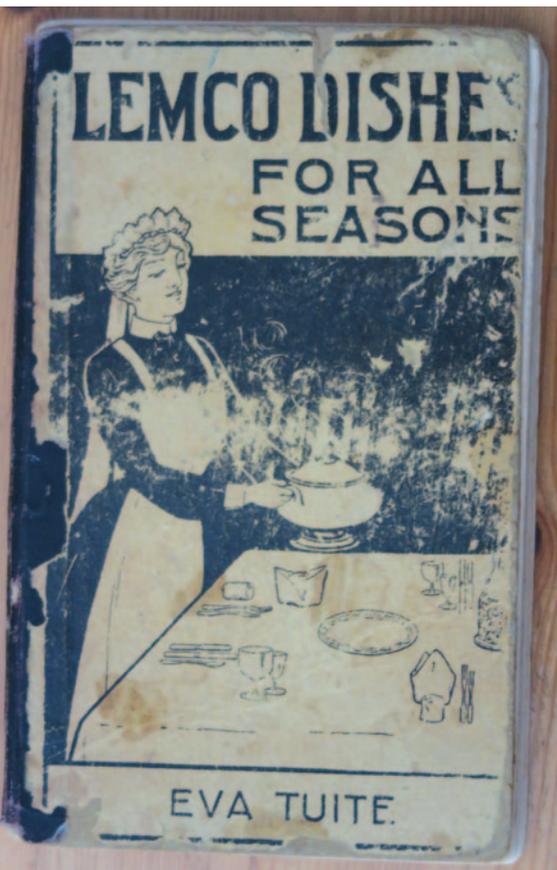
thick, brown extract. The beef came from Hereford cattle pastured in Uruguay, from which co-products such as hides and tallow were also marketed. The meat was cooked for 6–8 hours, fat was removed, and the aqueous mixture reduced in volume by evaporation at reduced pressure. A tonne of meat yielded 2.5 kilograms of extract. The works were located in the town of Fray Bentos, and the Fray Bentos name was used for canned products such as ox tongues, corned beef, ox-tail soup and beef marrow.

Advertisements for Tuite's book began to appear in Australian newspapers in early 1904. They stressed that 'besides being very nourishing, Lemco dishes are so delicious and tempting that the faddiest individual relishes them; they are so digestible that the weakest stomach can assimilate them'. The book contained 188 recipes for meat and fish dishes incorporating the extract, 20 for sweets (not containing Lemco product) to accompany them, and menus (25 in each case) for breakfasts, lunches and dinners.

Another meat extract that comes readily to mind these days is Bovril ('a bull to a bottle'), first known as Johnston's Fluid Beef that was developed by John Lawson Johnston for French troops serving in the Franco-Prussian War in 1870. On the other side, the Prussians were boosted by Liebig's Extract, so in some ways it was a battle of the beef (extract). Since the Prussians won a decisive victory, maybe their beef extract was better, although the reason usually given for their superiority was that the big guns that Krupp made for them were made of steel. They could take a bigger charge and send projectiles further than those from the brass guns used by the French forces. The shelling of Paris by Germans who remained beyond the range of the French artillery was a significant event.



**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.



**Asian Federation for Medicinal Chemistry International Medicinal Chemistry Symposium**

8–11 September 2019, Istanbul, Turkey  
aimecs2019.org

**13th International Symposium on Ionic Polymerization**

8–13 September 2019  
Beijing, China  
ip19.net

**21st Mendeleev Congress on General and Applied Chemistry**

9–13 September 2019  
Saint Petersburg, Russian Federation  
mendeleev2019.ru/index.php/en

**6th International Environmental Best Practices Conference**

22–26 September 2019  
Olsztyn, Poland  
ebp6.eu

**International Congress on Engineering and Food**

23–26 September 2019, Melbourne Convention Centre, Vic.  
icef13.com

**Chemeca 2019**

29 September – 2 October 2019, Sydney, NSW  
[chemeca2019.org](http://chemeca2019.org)

**Hazards Australasia 2019**

13–14 November 2019  
Brisbane, Qld  
[icheme.org/hazardsaus2019](http://icheme.org/hazardsaus2019)

**2019 New Zealand Institute of Chemistry Conference**

24–28 November 2019  
Christchurch, New Zealand  
nzcic.org.nz

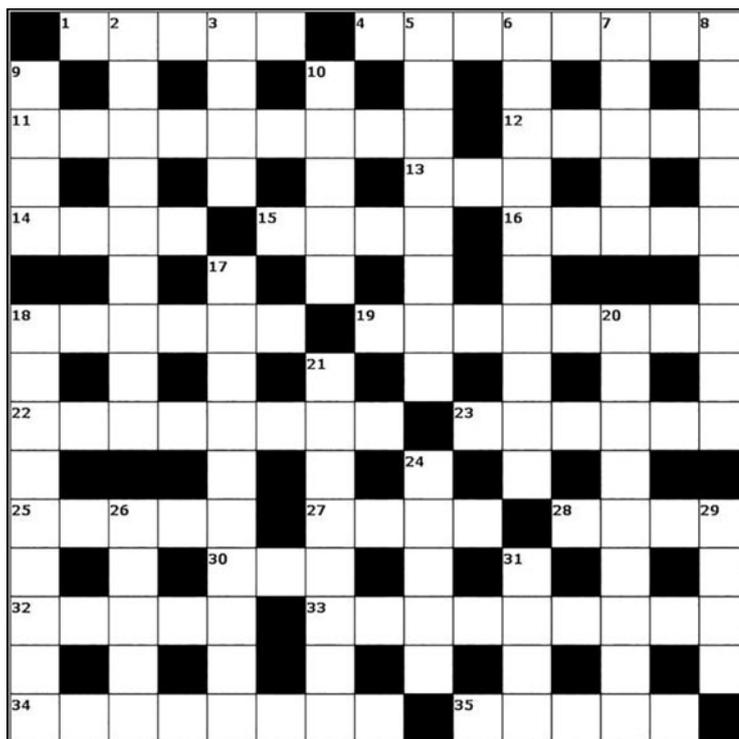
**27th R&D Topics Conference**

1–4 December 2019  
Flinders University, Adelaide, SA  
[www.rndtopics.com](http://www.rndtopics.com)

**Inorganic19 (IC19)**

15–19 December 2019  
Wollongong, NSW  
[www.ivvy.com.au/event/IND895/home.html](http://www.ivvy.com.au/event/IND895/home.html)

RACI events are shown in blue.



**Across**

- 1** States: mature custom. (5)  
**4** Strays use sedative. (8)  
**11** Everybody make room with pH of a distinct crystalline form of the same substance. (9)  
**12** Skids around the media. (5)  
**13** Three elements make the second person object. (3)  
**14** See 15 Across.  
**15 & 14 Across** Congratulations! It's not rare! (4,4)  
**16** Carbon and aluminium in selenium mount. (5)  
**18** Polyphenolic formed a tin reaction with N<sub>2</sub>. (6)  
**19** Spectroscopy makes rare find. (8)  
**22** Deep in thought: 6-pack or bunk?! (8)  
**23** The first and the last in 9 Down risk. (6)  
**25** Places pick up spectacles. (5)  
**27** The first and the last calorimeter utilised residue. (4)  
**28** Transfer protocol that stops regularly. (4)  
**30** Carve the chop. (3)  
**32** MnO + I<sub>2</sub> → HN= ?! (5)  
**33** Alter loop around graphite, as it is for carbon. (9)  
**34** Do away with TV! Less on. Thinner and thinner, perhaps. (8)  
**35** Count on iron oxide after time. (5)

**Down**

- 2** Lenses one makes from compounds having the structure R<sub>3</sub>Se(=O)<sub>2</sub>. (9)  
**3** Match hunted animals. (4)  
**5** Teen with lye and hydrogen makes dehydrated alcohol! (8)  
**6** Run a distil process which is massive in scale. (10)  
**7** Colonist Spooner is known for contributions to the design of the modern AC electricity supply system. (5)  
**8** Delayed hanging. (9)  
**9** Difficult and unyielding. (4)  
**10** European beats me. (5)  
**17** Magnifies cosmic rope tricks. (10)  
**18** Passes on smart tin sulfide process. (9)  
**20** Responses to new cater charges. (9)  
**21** Trace around a territory which participates in 20 Down. (8)  
**24** Well-stocked with yttrium, in all respects. (5)  
**26** Use hot lithium to make RSH. (5)  
**29** Inside Apple accessory claim. (4)  
**31** Distinguished sulfur salt. (4)

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



## IUPAC 2019: 47th World Chemistry Congress

'Being present everywhere, [chemistry] can often go unnoticed', said Nobel Laureate and Honorary Chair of the 47th World Chemistry Congress Professor Jean-Marie Lehn at the conference opening. Eliciting furious nods from the audience, this sentiment also set the stage for the scientific program. The conference set out to explore the 'frontiers in chemistry' to find where modern chemistry fits in the global and historical context.

As the meeting coincided with the centenary of the International Union of Pure and Applied Chemistry, it would have been remiss not to reminisce. Delegates heard about the evolution of the periodic table (and argued about the appropriate year to celebrate its 150th anniversary) as well as the role of IUPAC in defining standards and terminology for a 'universal language of chemistry' in the last 100 years. The involvement of Australia in IUPAC was covered by Emeritus Professor John Webb, based on a report compiled for *Chemistry International* in 2018 ([doi.org/10.1515/ci-2018-0103](https://doi.org/10.1515/ci-2018-0103)).

The bulk of the meeting was focused on the present. Delegates could hear about advances in fundamental chemistry and chemistry education. Unique to this meeting, however, was the focus on the global context of chemistry, especially where relevant to the United Nations Sustainable Development Goals. The CEOs of major chemical companies Solvay, BASF, PhosAgro and Arkema publicly affirmed their commitment to tackling major world issues through chemistry. The role of chemistry to protect the environment was discussed, from carbon capture to mitigate climate change to the socially responsible management of waste such as plastics and electronics. Unusual but fascinating topics of discussion included the nature of

knowledge and ignorance presented by philosopher Dr Mathias Girel, and whether chemistry is free to innovate from a legislative point of view courtesy of Dr Christopher Séné. Preliminary results from the Global Survey on the Gender Gap in Sciences ([gender-gap-in-science.org](http://gender-gap-in-science.org)) were presented and comparisons between chemistry, biology and physics – perhaps surprisingly – showed similar results across the board.

The plenary program featured no less than four Nobel Laureates, although one was (apologetically) a physicist and three shared the responsibility. Highlights included Professor Angela Belcher's astonishingly versatile genetically engineered viruses, Sir Fraser Stoddart summarising 35 years of work to the tune of 'Non, je ne regrette rien' and Professor Zhenan Bao's snapshot of her work to bring about the electronics of the future.

The future of chemistry was also represented. Delegates heard about the emerging uses of augmented and virtual reality, augmented and artificial intelligence, and emerging data management practices by FAIR (Findable, Accessible, Interoperable and Reusable) principles. 'We're nowhere near where we want to be when it comes to the lab of the future', said Dr Beeta Balali-Mood, Lab of the Future Lead for Pistoia Alliance. 'We need a cultural shift.'

In closing, Professor Lehn grinned at the audience and said: 'See you all in 100 years'. Having seen the enormous scientific strides made in the last century and inspired by the possibilities beyond the chemistry we do today, I really do wish I could be back in Paris in 2119 to see how it plays out.

Anna Ahveninen



## Reasons to join

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