Chemistry March/April 2019 March/April 2019

The periodic system: more than the sum of its parts

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- Where does the periodic table end?
- Molecules that power the majestic glowworm
- From seeds to anticancer compounds







































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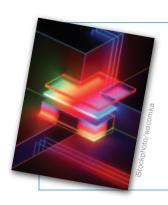
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chemistry in Australia

March/April 2019





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From the President

Welcome to the RACI 2019. It is with great pleasure that I am writing this to you as the President and only the second female President in the association's 100-year lifetime.

As you all know, this year is the International Year of the Periodic Table (IYPT). This year commemorates the 150th anniversary of the establishment of the periodic table of chemical elements. UNESCO describes IYPT as an opportunity to reflect upon many aspects of the periodic table, the role of women in chemistry, global trends and perspectives on science for sustainable development, and the social and economic impacts of this field.

Already the RACI has been celebrating the IYPT through and taking the opportunities suggested by UNESCO. Many of our members and their research have been highlighted in social media posts with stories from the periodic table. Many states also participated in the Empowering Women in Chemistry: a Global Networking Event in early February. This event connected women in chemistry around the world. On top of these initiatives, Branches are planning a number of activities that will also celebrate the IYPT at a local level.

All these initiatives support the strategic plan of the RACI. At its November meeting, the Board reviewed the progress against the plan, which is now into its third year. While there has been significant progress, there is still much to be done.

For those who do not know me, I am not a practising chemist. I have taken the leadership and management route for my career and recently started working as the Director of Policy for an industry association that advocates for the importance of a vibrant pharmaceutical industry in Australia for the benefits of Australian patients and their right to choice in health care and medicines.

I can already hear some people saying that there is no pharmaceutical industry in Australia. But what I have learned is that Australia is a destination of choice for clinical trials and research for companies. Australia has extraordinary talent in the pharmaceutical sector, and many of them are chemists.

But, like me, many of our chemists chose a non-technical career pathway. The RACI has a diverse membership, not only in their discipline and sectors, being either technical or management experts, but for being also at various career points. This brings an amazing depth to our membership from which we can all learn, but also a challenge in how we offer value to all our members.

And my chosen career pathway is an example of this. How do I get the best value for my membership when I do not align with any Divisions or technical areas of the association?

My focus for the next two years as President is to build on the work on the Strategic Plan that Peter Junk has led, in order to increase membership value while improving and maintaining a stable financial position for the organisation.

To managing expectations, these two objectives are going to be challenging. As an organisation, we cannot keep doing things the way we have been for the last 100 years. While there is no intention of throwing out the baby with the bath water, the Board and the Assembly do need to think differently to identify new opportunities.

These two groups of membership leaders need to work together and with the broader membership to build member value. And the IYPT is a vehicle through which we can progress the strategic plan.

The strategic plan has five pillars – membership attraction and retention, relevance, internal structure, strategic partners, and marketing and communications. All of these pillars are critical in building a RACI for the next 100 years – to build an institution that Australian chemical science professionals want to be a part of because it exists to improve the quality of life through leadership in the field of chemical sciences.



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Some recollections of Emeritus Professor Lloyd Smythe

I was sad to learn from Paul Hassad's article (January/February, p. 5) that Professor Lloyd Smythe has died. I was born just six weeks after Lloyd, and we first met as first-year science students at Sydney University in 1940, took our honours degrees in chemistry at the end of 1943, and began MSc work the following year.

We MSc students were required to spend several hours each week supervising the practical work of the large numbers of first-year chemistry students, many of whom would never do any further study of chemistry. We received a small payment for this, which of course was very welcome, but most of us felt it represented time taken from our own research. I remember that Lloyd seemed to be the exception – in particular, he put a lot of effort into organising the work on qualitative analysis, in which students were handed 'unknown' samples and had to identify them. A portent perhaps of his later career in analytical chemistry?

Our ways parted when I left to spend two years (1946–8) at University College London, after which I joined the CSIRO Division of Chemical Physics in Melbourne, where for some 10 years I was engaged in infrared spectroscopy. From 1958, I was busy exploring the analytical applications of the atomic absorption spectrometer, an instrument recently invented by my section leader, Alan (later Sir Alan) Walsh. Lloyd, by now leader of the Analytical Chemistry Group at the Australian Atomic Energy Commission, was an early user of this technique, and so we came into contact again.

In later years, I was particularly interested in Lloyd's work on the lead burden of Sydney schoolchildren, as I was doing similar work on the measurement of lead and other heavy metals in body tissues, principally in connection with the mining and metallurgical industries. Dr Haddad's account of Lloyd's work on the precision and accuracy of the newly introduced 'Breathalyser' when operated by those with limited training also struck a chord, as we had a somewhat similar experience here in Victoria.

I retired from CSIRO in 1986, but was in contact again with Lloyd when I accepted an invitation from him and the late Hugh McKenzie (another contemporary of ours at Sydney University) to contribute a chapter to a book that they were editing, *Quantitative trace analysis of biological materials* (Elsevier, 1988).

When Lloyd and I began our careers in chemistry, there was little recognition of analytical chemistry as an important branch of the subject, in Australia or in the academic world. Like so many others, I was delighted when in 2001 Lloyd was made a Member of the Order of Australia '... particularly [for] the development of the discipline of analytical chemistry'.

The excellent photograph of Lloyd in Dr Haddad's article brought back vivid memories. Dr Haddad commented that Lloyd was very much an 'old school professor' and was always formally dressed. Yes, our generation belonged to the collar-and-tie brigade – in fact, it wasn't until after I retired that I began to wear open-necked shirts on a weekday!

Farewell, Lloyd!

John Willis FRACI CChem

Defining 'natural' and 'organic'

In the November/December 2018 issue (p. 40), Geoffrey Scollary explores the use of the terms 'natural' and 'organic' as part of the nomenclature of Australian wines. The term 'natural' in relation to foods has not been officially defined in any food regulation jurisdiction in the world, including the USA, the UK, the EU, Canada, Japan and, of course, Australia and New Zealand. Many people have tried to create a definition, but so far there has been no acceptance, so the term gets used whenever and wherever the marketers see a commercial advantage, without any enforcement agency being brave enough to tackle this issue in a court.

The Australia Competition and Consumer Commission attempted a definition but included a restriction that a natural food should not 'be interfered by man', which on reflection, in the case of wine, would prohibit the picking of grapes off the vines by man or machine. Obviously, a nonsense, but this non-enforceable definition has not been challenged.

'Organic' is used for certain prescribed practices in food production and manufacture and is found to be acceptable by a large section of the public and advantageous by food growers/suppliers. I assume, as it is for me, this term is completely anathema to most chemists, who understand the real meaning of 'organic' and the misuse and lack of understanding of this term in food. In reality, some other expression should have been originally derived, but too late, we chemists all over the world, protested too little.

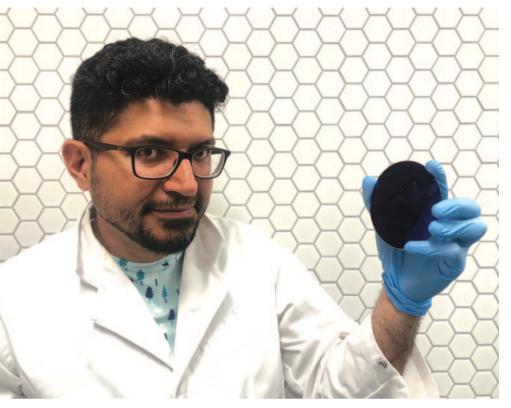
Strangely, I would have thought that at least 'organic' foods would have used only food additives that are 'natural' or have some close relationship to a natural equivalent. However, once again I have been misled because many food additives and processing aids permitted by the Organic Standard AS6000:2015, which is not legally enforceable, and permitted within the strictly enforceable *Australia New Zealand Food Standards Code* (ANZFSC), are synthetically derived. Some, at best, might be called 'nature identical' – a term no longer acceptable in Australian food standards.

For instance, organic wine is permitted to use potassium metabisulfite (INS224 or E224), which has no natural equivalent and is an entirely synthetic chemical. Incidentally, Australian wine, but not New Zealand wine, is permitted by ANZFSC to contain a very, very long list of food additives and processing aids (about 70 substances). Most of them are not permitted in the Organic Standard, but some of these substances have a basis or equivalent in nature, while many do not – a very confusing situation.

Overall, as chemists, learn from Geoff's wisdom and knowledge in his regular column, forget the argy bargy above, definitely ignore the pretentious wine writers/reviewers and then partake in a glass of the wine that you select and enjoy!

Anthony Zipper FRACI CChem

Harnessing light for a solar-powered chemical industry



ARC Future Fellow Associate Professor Daniel Gomez holding a disc covered in the nanoenhanced palladium.

New technology that harnesses sunlight to drive chemical reactions is paving the way for a more sustainable chemical manufacturing industry, one of the globe's biggest energy users.

RMIT University researchers have developed a nano-enhanced material that can capture an incredible 99% of light and convert it to power chemical reactions. As well as reducing the environmental impact of chemical manufacturing, the innovation could one day be used to deliver technologies such as better infrared cameras and solar-powered water desalination.

The research addresses the challenge of finding alternative energy sources for chemical manufacturing, which accounts for about 10% of global energy consumption and 7% of industrial greenhouse gas emissions. In the US, chemical manufacturing uses more energy than any other industry. In 2017, it

accounted for 28% of industrial energy consumption.

While photo catalysis – the use of light to drive chemical reactions – is growing in the industry, efficiency and cost continue to be significant obstacles to wider take-up.

Lead investigator Associate Professor Daniel Gomez said the new technology maximised light absorption to efficiently convert light energy into chemical energy.

'Chemical manufacturing is a powerhungry industry because traditional catalytic processes require intensive heating and pressure to drive reactions', Gomez, an ARC Future Fellow in RMIT's School of Science, said.

'But one of the big challenges in moving to a more sustainable future is that many of the materials that are best for sparking chemical reactions are not responsive enough to light. 'The photo catalyst we've developed can catch 99% of light across the spectrum, and 100% of specific colours. It's scalable and efficient technology that opens new opportunities for the use of solar power – moving from electricity generation to directly converting solar energy into valuable chemicals.'

The research focused on palladium, an element that's excellent at producing chemical reactions but usually not very light responsive. By manipulating the optical properties of palladium nanoparticles, the researchers were able to make the material more sensitive to light.

While palladium is rare and expensive, the technique requires just four nanometres of nano-enhanced palladium to absorb 99% of light and achieve a chemical reaction. An average human hair, for comparison, is 100 000 nanometres thick.

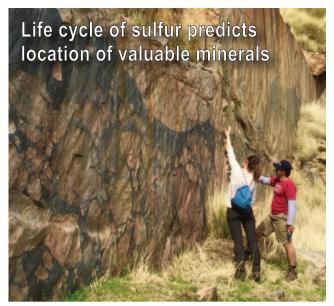
Beyond chemical manufacturing, the innovation could be further developed for a range of other potential applications, including better night vision technology by producing more light-sensitive and clearer images.

Another potential use is for desalination. The nano-enhanced material could be put in salty water and then exposed to sunlight, producing enough energy to boil and evaporate the water, separating it from the salt.

Gomez, who leads the Polaritonics Lab at RMIT, said the new technology could significantly increase the yield in the emerging photo-catalysis sector, with leading firms currently producing about 30 kilograms of product each day using light as the driving force.

The research, with collaborators from CSIRO, the Melbourne Centre for Nanofabrication and University of Melbourne, is published in ACS Applied Energy Materials (doi: 10.1021/acsaem.8b01704).

RMIT University



Dr Crystal LaFlamme (Laval, University of WA) and Associate Professor Marco Fiorentini (UWA) collaborate to unravel the cryptic link between the global sulfur cycle and the genesis of world-class mineral deposits.

Researchers from the University of Western Australia and two Canadian universities have applied a first-of-its-kind technique that measures the long-term life cycle of sulfur, helping to explain the preferential location of high-value mineral deposits at the edges of ancient continents.

The study, in *Nature Communications* (https://doi.org/10.1038/s41467-018-06691-3), charts the life cycle of sulfur over hundreds of millions of years, from its origins as a volcanic gas emitted into the primordial atmosphere and oceans, and all the way throughout its journey across Earth's deep crust.

Sulfur plays a critical role in a variety of fundamental earth processes because it regulates the global climate, is essential to the living cell, and is the primary molecule necessary to transport and concentrate precious metals such as gold and platinum.

The team, which included researchers from Canada's Université Laval and McGill University, initially set out to better understand the behaviour of sulfur in the ancient Earth. During the process, the researchers were able to create a technique using sophisticated technology based at UWA that could help explorers identify new mineral-rich provinces in Australia and around the world.

Co-author Associate Professor Marco Fiorentini, from UWA's School of Earth Sciences, said that the largest and richest deposits of precious metals in Australia and on Earth were generally associated with large concentrations of sulfur-rich minerals.

The technique presents a new way to engage with the minerals industry, helping them to explore vast areas of the planet that may host valuable resources.

University of Western Australia

Mapping elements at nanometre scale

Researchers at the University of Manchester, the University of Oxford and Macquarie University have translated a biological technique to reveal atomic-scale chemistry in metal nanoparticles. These materials are one of the most effective catalysts for energy-converting systems such as fuel cells. This technique will potentially reduce the cost of fuel cells used in electric cars and reduce harmful emissions from conventional vehicles.

The particles have a complex star-shaped geometry and this work shows that the edges and corners can have different chemistries, which can be tuned to reduce the cost of batteries and catalytic convertors.

The 2017 Nobel Prize in Chemistry was awarded to Joachim Frank, Richard Henderson and Jacques Dubochet for their role in pioneering the technique of 'single particle reconstruction'. This electron microscopy technique has revealed the structures of a huge number of viruses and proteins but is not usually used for metals.

This Nobel Prize-winning technique has been built on to produce three-dimensional elemental maps of metallic nanoparticles consisting of just a few thousand atoms.

Published in *Nano Letters* (doi: 10.1021/ acs.nanolett.8b03768), the research demonstrates that it is possible to map different elements at the nanometre scale in three dimensions, circumventing damage to the particles being studied. The new 3D chemical imaging method has been used to investigate platinum–nickel metal nanoparticles.

'Like "single particle reconstruction", the technique works by imaging many particles and assuming that they are all identical in structure, but arranged at different orientations relative to the electron beam. The images are then fed into a computer algorithm, which outputs a 3D reconstruction', said Professor Sarah Haigh, from the University of Manchester.

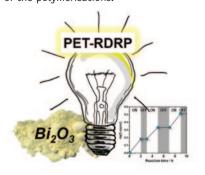
Author Dr Thomas Slater added, 'We are aiming to automate our 3D chemical reconstruction workflow in the future'.

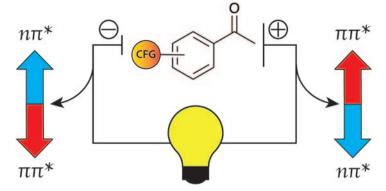
University of Manchester



Low-cost catalyst for light-activated radical polymerisation

Radical chemistry has greatly affected polymer science, allowing an increasingly large diversity of polymers to be made robustly and reliably. More recently, with the development of reversible deactivation radical polymerisation (RDRP), polymers can be synthesised with controlled and near uniform molecular weights, allowing precision at the atomic scale. The continual introduction of novel photocatalytic radical chemistry into existing RDRP processes has led to a rapidly propagating area of polymer research in recent years. The Polymer Nanostructures Group at the University of Sydney, led by Markus Müllner, has recently introduced bismuth oxide (a visible band gap semiconductor) as a heterogeneous photocatalyst for polymerisation by photo-induced electron transfer (PET) that operates at room temperature and with visible light (Hakobyan K., Gegenhuber T., McErlean C.S.P., Müllner M. Angew. Chem. Int. Ed. 2019, 58, 1828-32). Bismuth oxide introduces favourable properties to PET-RDRP, such as low toxicity, reusability, low cost, and ease of removal from the reaction mixture. Formidable control normally associated with degenerative chain-transfer polymerisations, such as macromolecular design by interchange of xanthate (MADIX) and reversible additionfragmentation chain-transfer (RAFT) polymerisation, was observed. Homopolymers and diblock copolymers with differently activated monomers were successfully synthesised, while the PET process allowed excellent temporal control of the polymerisations.





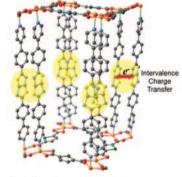
Altering photochemistry with static electric fields

It has recently been shown that static electric fields can be used to catalyse non-electrochemical reactions, opening up a new approach to chemical catalysis. Now, researchers at the Australian National University have expanded electrostatic catalysis into the realm of molecular excited states. Using state-ofthe-art computational methods, they have shown that static electric fields can be used as an approach to modifying the relative energies of different types of excited state in a predictable and significant manner (Hill N.S., Coote M.L. J. Am. Chem. Soc. 2018, 140, 17800-4). They showed that the energies of two

types of excited state with different wavefunction symmetries can be altered in opposite directions, providing the ability to invert their ordering, in order to enhance certain desirable photochemical properties. These field effects can be harnessed using carefully placed charged functional groups (CFGs) in the form of acids or bases, which can be turned on or off by simple changes in pH. These oriented electric fields could allow the design and synthesis of a new generation of highly efficient photoactive molecules that may find application in a wide range of industrial, synthetic, and biochemical applications.

Relating structure and charge transfer in electroactive MOFs

A key structural feature of photosynthetic organisms such as purple bacteria is a cofacially arranged photoreaction trap, often described as the 'special pair'. This cofacial system plays a vital role in facilitating the conversion of light to chemical energy, by stabilising the photo-excited mixedvalence radical state through a process called intervalence charge transfer (IVCT). This intriguing phenomenon has been the focus of a number of qualitative biomimicry studies using discrete organic molecules, mostly based on porphyrin derivatives. However, quantitative experimental and theoretical studies on model inorganic systems have been limited. Recent research led by Deanna D'Alessandro from the University of Sydney with colleagues Bowen Ding, Carol Hua and Cameron Kepert has now demonstrated subtle structure-function relationships that govern through-space IVCT in metalorganic frameworks (MOFs) with

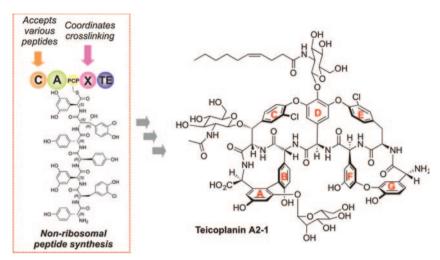


cofacially aligned ligands (Ding B., Hua C., Kepert C.J., D'Alessandro D.M. Chem. Sci. 2019, 10, 1392–400). This work follows a previous report from the same group that revealed a new mechanism for charge transfer interactions in MOFs (J. Am. Chem. Soc. 2018, 140, 6622–30). Uncovering structure–activity relationships in MOF materials that emulate processes in natural systems, and establishing methods for quantifying their charge transfer properties, represents an important advance in fine tuning solid-state materials for device applications.

Revealing the selectivity and mechanism of glycopeptide antibiotic

biosynthesis

The glycopeptide antibiotics (GPAs, including vancomycin and teicoplanin) are highly cross-linked heptapeptide antibiotics that are assembled in a modular fashion through non-ribosomal peptide synthesis. The production of a linear peptide precursor is followed by a cyclisation cascade of three or four cytochrome P450 enzymes that occurs late in biosynthesis, with the exact timing and peptide structure when crosslinking occurs previously unclear. Recently, Max Cryle and his group at Monash University, working with German collaborators, have shown that differences in results from in vitro and in vivo studies on these systems can be explained by the surprising tolerance of the final peptide-bond-forming domain for altered peptide substrates (Schoppet M., Peschke M., Kirchberg A., Weibach V., Süssmuth R.D., Stegmann E.,



Cryle M.J. *Chem. Sci.* 2019, **10**, 118–33). The substrate tolerance displayed by this domain during peptide biosynthesis has important implications for the ability to undertake biosynthetic redesign of such systems via the incorporation of different amino acid monomers. Furthermore, it

explains why the alteration of nonribosomal peptide synthetase assembly lines in vivo can lead to the accumulation of off-pathway intermediates that are not normally seen during wildtype biosynthesis.

New dual-gold catalysis mode for enediyne cycloaromatisation

Dual-gold catalysis involving σ,π -activation has emerged as an important reactivity mode in homogenous catalysis. This activation mode requires the presence of a terminal alkyne in the substrate to form a gold acetylide. A new mode of σ_{τ} dual gold catalysis has now been discovered experimentally by Christopher Hyland, Stephen Pyne and PhD student Farzad Zamani at the University of Wollongong and supported by computational and structural studies at the University of Tasmania (Zamani F., Babaahmadi R., Yates B.F., Gardiner M.G., Ariafard A., Pyne S.G. Hyland C.J.T. Angew. Chem. Int. Ed. 2019, 58, 2114-19). This new method involves electronic differentiation of two alkynes in a non-conjugated enediyne, which enables selective formation of a gold acetylide at a propiolic position. This leads to the formation a highly reactive intermediate that contains both a vinylidene gold and allenyl gold moiety in a single structure. This strategy allowed the preparation of a range of biologically relevant and enantioenriched isoindolinones. It is anticipated that this new catalytic mode can be applied to a range of other cyclic molecules.

Making difficult peptide bonds like a Pro-Pro

Proline (Pro), the most conformationally rigid amino acid, is an essential component of protein secondary structure. Clusters of this unique cyclic amino acid, known as polyproline motifs, are common features of protein sequences across all taxa and are

predominantly responsible for the secondary structure of collagen. Despite such prevalence and importance in nature, Pro-Pro junctions have eluded construction by traditional chemical ligation methods, owing to steric congestion and electronic deactivation.

Now, a team led by Rich Payne has developed the first method to efficiently access the challenging Pro-Pro motif (Sayers J., Karpati P.M.T., Mitchell N.J., Goldys A.M., Kwong S.M., Firth N., Chan B., Payne R.J. J. Am. Chem. Soc. 2018, 140, 13 327-34). A diselenideselenoester ligation reaction between a trans-y-selenoproline dimer and a prolyl selenoester was shown to successfully forge the Pro-Pro peptide bond cleanly and in high yield. Importantly, following the ligation reaction, in situ deselenisation of the v-selenoproline moiety could be performed to provide native Pro-containing peptides. To showcase the utility of the technology, two biologically relevant polypeptides (submaxillary gland androgen regulated protein 3B and the antimicrobial peptide lumbricin-1) were synthesised in one pot and with excellent overall yield. As an invaluable addition to the toolbox of chemical ligation methods, this technology will provide unique access to an abundance of previously intractable, proline-rich polypeptide and protein targets in the future.

New sulfur hosts for better sodium-sulfur batteries

Limited resources of lithium mean that lithium-based batteries will not be able to meet increasing energy-storage demands. Consequently, the price of Li is expected to skyrocket. Room-temperature sodium-sulfur (RT-Na/S) batteries are a promising alternative due to resource abundance (of both sodium and sulfur), non-toxicity, low cost and the high theoretical capacity of sulfur (1672 mAh g⁻¹). But, the dissolution of polysulfides into the electrolyte during cycling causes a low reversible capacity and fast capacity fade. Now, researchers led by Shi-Zhang Qiao at the University of Adelaide have designed a new class of sulfur hosts for RT-Na/S batteries:

nanometre-sized transition metal clusters decorated on hollow carbon nanospheres. These clusters are able to assist the immobilisation of sulfur and enhance the conductivity and activity of sulfur (Zhang B.-W., Sheng T., Wang Y.-X., Chou S., Davey K., Dou S.-X., Qiao S.Z. Angew. Chem. Int. Ed. 2019, 58, 1484-8). They serve as electrocatalysts to quickly reduce polysulfides into short-chain sulfides, thus improving the electrochemical performance of RT-Na/S batteries. Among these sulfur hosts, iron-based clusters exhibited excellent cycling and rate performance for RT-Na/S batteries.

res.

Sulfur hosts

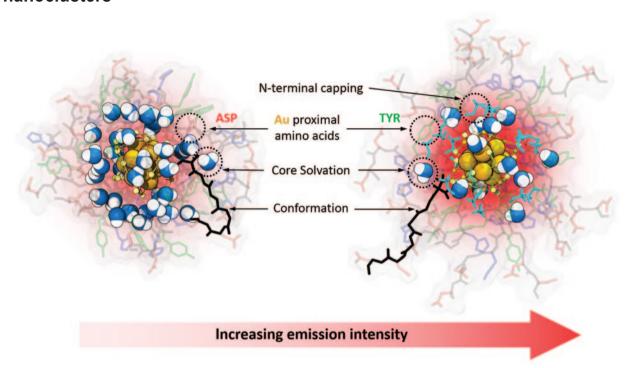
Fe nanoclusters

the

polysulfides

Na₂S

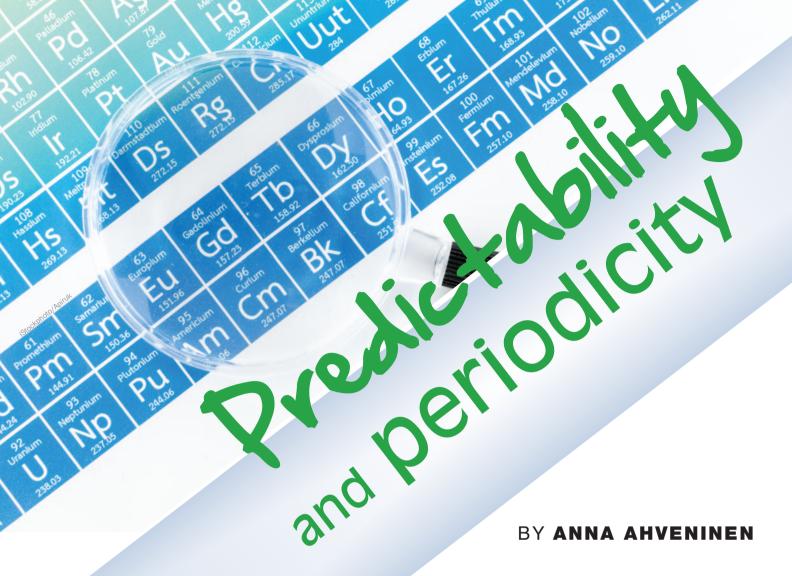
Ligand design enhances photoluminescence of biocompatible metal nanoclusters



Water-soluble metallic nanoclusters coated with biological ligands such as peptides exhibit precise physical, chemical and luminescent properties with a variety of biomedical and industrial applications. But optimising these ultrasmall materials remains a challenge due to limited understanding of their atomistic and electronic structure and the origin of photoluminescence. Researchers from the Materials Modelling and Simulation group at RMIT University and the Stevens Group at Imperial College London, UK, have combined molecular simulations with experimental characterisation to reveal how peptide ligands can be designed to modulate gold nanocluster fluorescence (Lin Y., Charchar P., Christofferson A.J., Thomas M.R., Todorova N., Mazo M.M., Chen Q., Doutch J., Richardson R., Yarovsky I., Stevens M.M. J. Am. Chem. Soc.

2018, 140, 18 217–26). Through systematic synthesis and simulation of hexapeptide-protected gold nanoclusters, they discovered that the photoluminescent emission intensity can be tailored by controlling peptide-ligand composition (e.g. N-terminal acetylation, electronegativity or aromaticity/hydrophobicity) or by adjusting the environmental pH. Classical molecular dynamics simulations accompanied by electronic-structure calculations identified the peptide conformation, interfacial water and ligand-core interactions as major contributing factors to the enhancement of nanocluster emission. The findings of this work provide key design principles for understanding and maximising the photoluminescence of metallic clusters through the exploitation of biologically compatible ligands.

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.



A century and a half ago, a set of symbols, carefully arranged in rows and columns, was published. The 'collection' was incomplete and the gaps hinted at undiscovered relatives.

he periodic table of the chemical elements has become perhaps the most recognisable symbol of chemistry. Printed on various merchandise hoarded by chemists and enthusiasts, the periodic table proclaims passion for chemistry or the sciences as a defining character trait or, depending on who you ask, as membership of the nebulous 'nerd club'. As pop culture has turned to embrace science and other aspects of this club, the symbolism of the periodic table is no longer limited to

the sciences, elevated instead into a general sign of shared interests. Google images is awash with collections of boxes arranged in a vaguely familiar shape, claiming to be the periodic table of dragons, meat, musical instruments, wrestling, magic, dumbbells, epic reads, swearing, cryptocurrencies, alcoholic drinks, languages and more.

Most of these 'periodic tables' misunderstand or misrepresent the nature of the original. Presenting the periodic table as an inventory, most of the imitations boil down to a collection

of all the things someone could think of that belong to a certain category, presented in boxes. The periodic table of chemical elements is, however, part of a much bigger and more complex picture.

It's true that the periodic table does act as a list of every known element. Even this simple fact contains some useful knowledge, because the need to list or tabulate the elements follows from an understanding that they are somehow fundamentally distinct. The question of how they can be distinguished opens the gates to

discussions of chemical and physical properties, and their relations to various configurations of subatomic particles. The atomic number, atomic mass and isotopes are fundamental concepts to explore when determining elemental identity, while the more adventurous guides to the periodic table may also wish to discuss the role of radioactive decay in transforming one element into another.

The shift to the next layer is subtle – from 'How are the elements different from each other?' to 'How do the elements relate to one another?' However, it's a significant distinction: this is where we begin to lose the creators of the periodic tables of magic, meat and more. It is not because Dmitri Mendeleev arranged all the known elements in an aesthetically pleasing manner that he is remembered 150 years later.

That comprehensive list of the elements described earlier is only fit to be called a 'table of the chemical elements'. The periodic system, for which the periodic table is named, looks beyond the distinctions between individual elements and considers them instead as a continuous whole. Looking at elements 1–118, this does not appear so difficult, but to account for continuity by ascending atomic number, a list would be sufficient. What is the function of the table? The periodic system, as reflected in the structure of the periodic table, reveals elemental relationships: groups (columns) of elements that perform similar chemistry thanks to their valency, and trends within periods (rows) of elements in electronegativity, ionisation energy, atomic radius and more. The realisation that elements belong precisely at their given location on the periodic table because of their relationships to the elements around them is what unlocks an understanding of the periodic table as an indispensable tool. Because of this property of the periodic table, much can be inferred about the chemistry of an element just by its position on the

... Mendeleev recognised that there were gaps in his knowledge and accounted for them.

table – patently untrue of almost all of its imitations.

Although this United Nations International Year of the Periodic Table of Chemical Elements celebrates Dmitri Mendeleev's contributions to the periodic table, the periodic system was not a sole invention of his. The concept of periodicity was first contemplated by French chemist Alexandre Béguyer de Chancourtois, who noted that the atomic masses of elements with similar properties varied systematically. Yet, a plaque from the Royal Society of Chemistry at his place of birth attributes instead the 'discovery of the Periodic Law for the chemical elements' to English chemist John Newlands, a contemporary of Mendeleev's, and another of the many early chemists who sunk their teeth into the problem of rationally organising the elements. Newlands, Mendeleev and German chemist Julius Lothar Meyer all made attempts at tabling the elements around 150 years ago. This is a fact often forgotten in the celebration of any historical scientist the romantic notion of an earthshattering Eureka moment by a single genius, I would venture, has never actually been true.

Given his contemporaries – of which surely only some are remembered – working on the problem, why is only Mendeleev celebrated as the 'father of the periodic table'? Perhaps what captures public imagination even today was his role as elemental Nostradamus. Where earlier attempts to table the elements by John Newlands kept to a periodic pattern only by occasionally cramming two elements into a box, Mendeleev recognised that there were gaps in his knowledge and accounted for them. Not only did his periodic table contain spaces for as-yet-undiscovered elements, he also confidently made predictions on their properties, including atomic mass, melting point, valency and even the probable method of discovery. As these spaces began to be filled in the proceeding years, these predictions proved startlingly accurate, and Mendeleev's position in the canon of modern chemistry was secured.

Of course, there have been many refinements to this early work over the years. Mendeleev's original periodic table is not the one we find on Google images today. Noble gases didn't appear on the table until 1904, when William Ramsay received the Nobel Prize in Chemistry (and Lord Rayleigh the corresponding prize in physics) for the discovery of this new class of elements. Having had no way to quantify the atomic number until Henry Moseley's work to measure nuclear charge by X-rays in 1914, Mendeleev and his contemporaries also arranged the table by atomic mass - although Mendeleev allowed some exceptions in his table due to the properties of the elements. Much later, work on the Manhattan Project prompted Glenn Seaborg to propose the inclusion of the actinide series, while proceeding research in radiochemistry eventually led to the filling of the seventh period with the unstable, mostly laboratory-made transuranium elements.

History shows us that the development of the periodic table has been intrinsically linked with fundamental advances in chemistry since the 19th century. As Mendeleev's predictions show, the periodic table has been a map for the elemental

World's oldest periodic table chart at University of St Andrews



A periodic table chart discovered at the University of St Andrews is thought to be the oldest in the world.

The chart of elements, dating from 1885, was discovered in the University's School of Chemistry by Dr Alan Aitken during a clear-out. The storage area was full of chemicals, equipment and laboratory paraphernalia that had accumulated since the opening of the chemistry department at its current location in 1968. Following months of clearing and sorting the various materials, a stash of rolled-up teaching charts was discovered. Within the collection was a large, extremely fragile periodic table that flaked upon handling. Suggestions that the discovery may be the earliest surviving example of a classroom periodic table in the world meant the document required urgent attention to be authenticated, repaired and restored.

Mendeleev made his famous disclosure on periodicity in 1869; the newly unearthed table was rather similar, but not identical to Mendeleev's second table of 1871. However, the St Andrews table was clearly an early specimen. The table is annotated in German, and an inscription at the bottom left -'Verlag v. Lenoir & Forster, Wien' - identifies a scientific printer who operated in Vienna between 1875 and 1888. Another inscription - 'Lith. von Ant. Hartinger & Sohn, Wien' - identifies the chart's lithographer, who died in 1890. Working with the University's Special Collections team, the University sought advice from a series of international experts. Following further investigations, no earlier lecture chart of the table appears to exist. Professor Eric Scerri, an expert on the history of the periodic table based at the University of California, Los Angeles, dated the table to between 1879 and 1886 based on the represented elements. For example, both gallium and scandium, discovered in 1875 and 1879 respectively, are present, while germanium, discovered in 1886, is not.

In view of the table's age and emerging uniqueness, it was important for the teaching chart to be preserved for future generations. The paper support of the chart was fragile and brittle, its rolled format and heavy linen backing contributed to its poor mechanical condition. To make the chart safe for access and use, it received a full conservation treatment. The University's Special Collections was awarded a funding grant from the National Manuscripts Conservation Trust for the conservation of the chart in collaboration with private conservator Richard Hawkes (Artworks Conservation). Treatment to the chart included brushing to remove loose surface dirt and debris, separating the chart from its heavy linen backing, washing the chart in de-ionised water adjusted to a neutral pH with calcium hydroxide to remove the

soluble discoloration and some of the acidity, a 'deacidification' treatment by immersion in a bath of magnesium hydrogen carbonate to deposit an alkaline reserve in the paper, and finally repairing tears and losses using a Japanese kozo paper and wheat starch paste. A full-size facsimile is now on display in the School of Chemistry. The original periodic table has been rehoused in conservation-grade material and is stored in Special Collections' climate-controlled stores in the University.

A researcher at the University, M. Pilar Gil from Special Collections, found an entry in the financial transaction records in the St Andrews archives recording the purchase of an 1885 table by Thomas Purdie from the German catalogue of C Gerhardt (Bonn) for the sum of 3 Marks in October 1888. This was paid from the Class Account and included in the Chemistry Class Expenses for the session 1888-9. This entry and evidence of purchase by mail order appears to define the provenance of the St Andrews periodic table. It was produced in Vienna in 1885 and was purchased by Purdie in 1888. Purdie was Professor of Chemistry from 1884 until his retirement in 1909. This in itself is not so remarkable, a new professor setting up in a new position would want the latest research and teaching materials. Purdie's appointment was a step-change in experimental research at St Andrews. The previous incumbents had been mineralogists, whereas Purdie had been influenced by the substantial growth that was taking place in organic chemistry at that time. What is remarkable, however, is that this table appears to be the only surviving one from this period across Europe. The University is keen to know if there are others out there that are close in age or even predate the St Andrews table.

University of St Andrews

explorers of the world, telling them where and how to look. Even now, with the seventh period completed by oganesson, theoretical chemists are considering how far the (debatable) stability of superheavy elements can stretch, and how these hypothetical additions would fit into the periodic system.

What is perhaps most frustrating about the imitation periodic tables is that basic information about the periodic system and its significance is quite easy to find and understand. Chemists much more knowledgeable than me will have noticed that I have been terribly non-specific in describing the construction and uses of the periodic table. Even all this information reaches only the second layer of complexity, after all.

... there is still an appreciable elegance to being able to put fences around particular sections of the periodic table for particular kinds of chemistry ...

Peeling away the groups and the periods, we enter a layer that may be inaccessible to the non-chemically inclined. Underneath the relationships between elements with their neighbours, we find a term by which

inorganic chemists in particular sometimes identify their area of interest: the block. Although even the most ardent defender of chemical knowledge may concede that there is no real benefit to a non-chemist being able to name the blocks, there is still an appreciable elegance to being able to put fences around particular sections of the periodic table for particular kinds of chemistry – thanks to chemical properties bestowed by electronic orbitals.

It isn't my intention to detail what the periodic table is and how it can be used - only why it matters. The periodic table quietly and succinctly encompasses many of the principles that make chemistry work. But wait, there's more, for it also represents some of the core tenets of science: a marriage of theory and experiment, the periodic table embodies a rich history of scientists probing the edges of current knowledge. I wonder if, 150 years ago, Mendeleev could imagine his periodic table growing quite so far – and I wonder whether we can envision the ways it could still transform, 150 years hence?

The periodic table has become a symbol of chemistry because in so many ways, it is chemistry. In this International Year of the Periodic Table, we chemistry professionals have an opportunity to spark the imaginations of those previously dismissive of our discipline. In 2019, let us not be the silent central science, but instead proudly proclaim our profession, and that most of the modern world's technological advances, food security and medicines exist because of us.

Anna Ahveninen (anna.ahveninen@raci.org.au, @Lady_Beaker) is communications officer at the RACI.



Linda Abblit

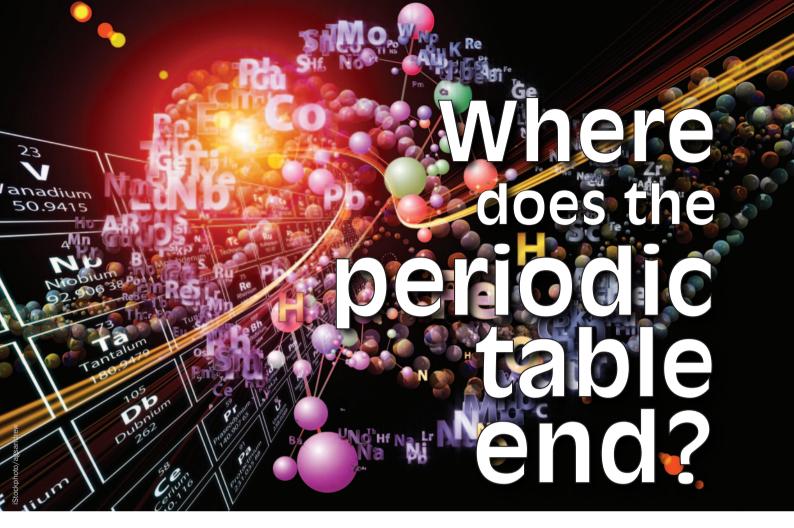
New elements on show

In celebration of the International Year of the Periodic Table in 2019, the RACI has completed the Periodic Table on Show with new artwork for elements 112–118. For enquiries on the updated poster, contact Jane O'Keefe at jane.okeefe@raci.org.au.

The Periodic Table on Show was first created to celebrate the International Year of Chemistry in 2011 by collaborations between 79 chemists and 38 printmakers with generous sponsorship by Questacon and the Australian Government Department of Innovation, Industry, Science and Research. Find out more at raci.org.au/periodic-table-on-show.



Linda Abb



Where does the periodic table of elements end? Is there a final element, or are ever-increasing atomic numbers possible?

BY COLIN A. SCHOLES

he periodic table could be considered to end at the largest stable element, lead (atomic number 82). All elements with higher atomic numbers have unstable nuclei, because the assembled protons become too large for the strong nuclear force to hold together. Hence, all those elements with atomic numbers greater than that of lead will eventually undergo radioactive decay to reduce their atomic number to 82 or less: as such. these elements can be considered transients. However, many of these higher elements have half-lives comparable to the age of the universe. For instance, bismuth (atomic number 83) was considered stable, until in 2003 it was found to be very slightly unstable with a half-life of 1.9 × 1019 years. This half-life is more than a billion times longer than the current age of the universe, and so bismuth as an element may outlast the universe. Similarly, the longest-lived isotope of thorium (atomic number 90) has a half-life of 1.4×10^{10} years and will remain with us for billions of years to come. The longest-lived isotope of uranium (atomic number 92) has a half-life of 4.5×10^9 years, followed by plutonium (94, with a half-life of 7.9×10^7 years) and curium (96), whose most stable isotope has a halflife of 1.6×10^7 years. As atomic number increases after curium, the half-lives of elements rapidly reduce to days and then minutes. Einsteinium (99) at its most stable has a half-life of 1.3 years, while nobelium (102) has a half-life of 2.8 hours and copernicium (112) a half-life of 20 minutes. The highest element currently recognised is oganesson (118) with the isotope produced having a half-life of 5 milliseconds. These elements are so short-lived that they are not found outside of high-energy particle research institutes, and so are considered only as curiosities.

However, the behaviour of the larger elements points to the possibility of an 'island of stability' in

heavier elements on the outer reaches of the periodic table. This island corresponds to longer-lived elements and was first postulated to exist in the 1960s, based on nuclear shell models. The concept is that superheavy elements with nuclei of 108, 114, 120 and 126 protons, with around 184 neutrons, will have unique properties that increase stability. This is because these numbers of protons and neutrons complete shells within nuclei, which lead to very strong binding energies.

Furthermore, the superheavy nature of these nuclei is expected to deform the nucleus, with interesting shapes such as a bubble with a hole in the middle being adopted, which will confer additional stability. This stability is anticipated to provide those superheavy elements with half-lives long enough for them to exist outside of a laboratory. Such shapes have yet to be observed but the increase in half-life in these large atomic number elements as the neutron count approaches 184 has been confirmed.

The hypothetical element unbihexium-310 (126) is considered one of the best candidates in the island of stability because it will have both 126 protons and 184 neutrons - double the magic number in terms of nuclei shell theory - and will likely be longlived enough to have practical uses. Theorists have suggested that these superheavy elements should have half-lives of minutes to days, with some suggesting millions of years. If this island of stability is confirmed, then it will extend the periodic table into a new row of elements and open the further possibility of a second island of stability existing when the atomic number reaches 164.

Current superheavy elements are synthesised by bombarding smaller elements together in the hope that the nuclei will 'stick' and create a higher atomic number. For example, tennessine (117) is created by combining calcium (20) with berkelium (97). These atom smashers utilise magnetic fields to confine and

speed up beams of atoms together. Most collisions result in the atoms ricocheting off each other, but every now and then two nuclei combine to form the bigger element. This research takes a very long time – Japanese researchers spent 553 days over a nine-year period smashing atoms to produce enough copernicium to confirm its existence (bit.ly/2MgZpYm).

Part of the problem in trying to reach the island of stability is that current technology is reaching its limits and facing the problem of neutron shortage. For the superheavy elements to be long-lived, they require more neutrons than can currently be provided by smashing together

There is some anecdotal evidence that superheavy elements exist in space, associated with the Przybylski's star ...

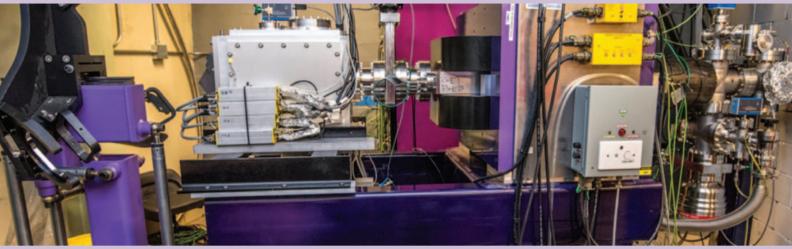
elements with smaller atomic numbers. This means that all synthesised elements can be considered neutron deficient, which is contributing to their instability. Researchers are struggling to develop methods to add additional neutrons to these processes, and until this problem is overcome, all future superheavy elements will fall short of the island of stability.

There is some anecdotal evidence that superheavy elements exist in space, associated with the Przybylski's star (HD101065), 370 light-years away in the constellation of Centaurus. This star has evidence of actinium. americium and einsteinium within its solar spectrum, while also being low in iron and nickel. These elements are of the actinides series and have half-lives that are far too short compared to the life of the star, so these elements should have disappeared millions of years ago. Hence, there must be a mechanism within the star that is constantly producing and replenishing these actinide elements. One possibility is the presence of superheavy elements, given that their decay sequence is expected to produce actinides. However, probing the star's light for these superheavy elements is extremely difficult because



Przybylski's star, in the Centaurus constellation (image shows Alpha Centauri (left) and Beta Centauri), may contain superheavy elements. Skatebiker/CC BY-SA 3.0

FIONA measures mass numbers of moscovium and nihonium



FIONA is a new system at Berkeley Lab's 88-Inch-Cyclotron that enables direct mass number measurements of superheavy elements.

A team led by nuclear physicists at the US Department of Energy's Lawrence Berkeley National Laboratory (Berkeley Lab) has reported the first direct measurements of the mass numbers for the nuclei of two superheavy elements: moscovium (element 115) and nihonium (element 113).

They obtained the results (https://doi.org/10.1103/ PhysRevLett.121.222501) using FIONA, a new tool at Berkeley Lab that is designed to resolve the nuclear and atomic properties of the heaviest elements.

FIONA stands for For the Identification Of Nuclide A, with 'A' representing an element's mass number – the total number of protons and neutrons in an atom's nucleus.

The mass number and atomic number of superheavy elements have relied on the accuracy of nuclear mass models. So it's important to have a reliable way to measure these numbers with experiments in case there is a problem with models, noted Ken Gregorich, a recently retired senior scientist in Berkeley Lab's Nuclear Science Division who worked closely with Jackie Gates, who leads FIONA's mass-number-determination efforts, to build and commission FIONA. For example, superheavy elements could possibly exhibit unexpected nuclear shapes or densities of protons and neutrons that are not accounted for in the models, he said.

FIONA is an add-on to the Berkeley Gas-filled Separator (BGS). For decades, the BGS has separated heavy elements from other types of charged particles that can act as unwanted 'noise' in experiments. FIONA is designed to trap and cool individual atoms, separate them on the basis of their mass and charge, and deliver them to a low-noise detector station on a timescale of 20 milliseconds.

In its early operation, FIONA was specifically tasked with trapping individual moscovium atoms. 'We have about a 14% chance of trapping each atom', Gregorich noted. So researchers had hoped to capture a single measurement of moscovium's mass number per week.

To produce moscovium, scientists at the 88-Inch Cyclotron bombarded an americium target with a particle beam produced from the rare isotope calcium-48.

There is a distinct looping signature for each atom trapped and measured by FIONA. The trajectory of this looping behaviour is related to the atomic mass-to-charge ratio – the timing and position of the energy signal measured in the detector tells scientists the mass number.

Ideally, the measurement includes several steps in the particle's decay chain: moscovium has a half-life of about 160 milliseconds. Capturing its energy signature at several steps in this decay chain can confirm which parent atom began this cascade.

In FIONA's first scientific run, researchers identified one moscovium atom and its related decay daughters, and one nihonium atom and its decay daughters. The measurements of the atoms and the decay chains confirm the predicted mass numbers for both elements.

While researchers had been seeking only to create and measure the properties of a moscovium atom, they were also able to confirm a measurement for nihonium after a moscovium atom decayed into nihonium before reaching FIONA.

Fallon said that another scientific run is planned for FIONA within the next six months, during which nuclear physics researchers may pursue a new round of measurements for moscovium and nihonium, or for other superheavy elements.

There are also plans to install and test a new tool, dubbed 'SHEDevil' (for Super Heavy Element Detector for Extreme Ventures In Low statistics) that will help scientists learn the shape of superheavy atoms' nuclei by detecting gamma rays produced in their decay. These gamma rays will provide clues to the arrangement of neutrons and protons in the nuclei.

Berkeley Lab

their atomic spectrum is unknown, as they have yet to be synthesised on Earth.

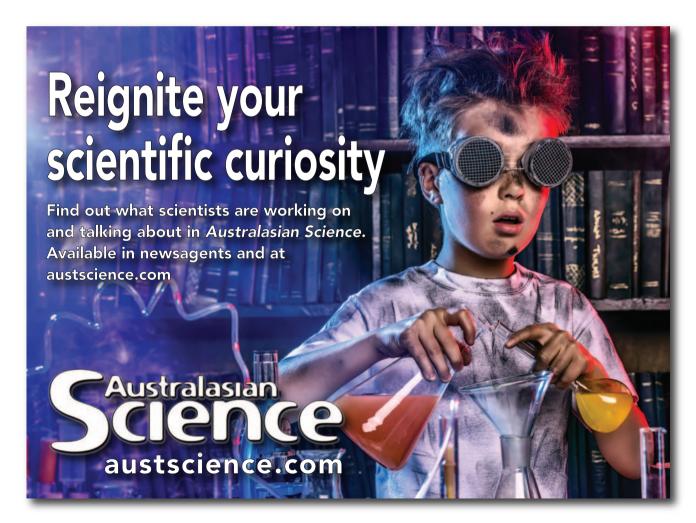
If these superheavy elements could exist outside of the laboratory, their potential applications are questionable. They would be expected to have very small critical masses, possibility of the order of a few grams. This would make them ideal for small compact nuclear weapons, either directly or as primaries to ignite secondary fusion explosives. Hence, nuclear weapons could become the size of a grain of salt. Their superheavy dense state would also make them ideal for armour-piercing ammunition, similar to how depleted uranium is used today.

The potential of these islands of stability and the existence of superheavy elements suggest that the periodic table could extend indefinitely. However, as atomic number increases, another limitation arises: the electrons.

Along a row of the periodic table. the atomic radius shrinks with increasing atomic number as the electron binding energy of the nucleus increases and the electron's orbitals contract. This confinement of the electrons within a smaller and smaller radius closer to the nucleus corresponds with an increase in the electron's momentum, because of the uncertainty principle - it is impossible to know both the position and momentum of a particle below a certain limit. An increasing atomic number restricts the electron to an ever-decreasing radius, and therefore the electrons adopt velocities approaching the speed of light to remain stable within their orbitals. An additional consequence of this velocity increase is that the mass of the electron

increases as well, in line with special relativity. Gold (79) is a good example of this phenomenon: with the strong binding energy of the gold nucleus forcing the electrons to move at half the speed of light to remain stable in their orbitals. This increases the mass of the electron slightly, resulting in a contraction of the orbitals because of the additional mass, and a shift in the outer electrons' energy levels. Consequently, the absorption spectrum of gold shifts towards the blue end of the spectrum, which results in gold taking on its attractive colour hue. Silver (47), in the row above gold on the periodic table, does not exhibit this phenomenon and so its absorption spectrum remains unshifted, resulting in its metallic hue.

US physicist Richard Feynman calculated that when an element had an atomic number of 137, the electron



binding energy would become so strong and the contraction in the orbitals so great that the electrons would need a velocity faster than that of light to be stable within their orbitals. This scenario would mean the electrons break special relativity, and hence electrons in elements larger than this atomic number would be unstable and collapse into the nucleus. Subsequently, analysis has extended the periodic table further, with this scenario occurring for elements with atomic numbers of 173 and above. The discrepancy is because Feynman considered the nucleus as a point source, which is not a valid assumption for these superheavy elements.

If elements with atomic numbers greater than 173 were to be synthesised, then no electrons would be associated with these elements and they would remain a naked nucleus that has unique properties. The electron binding energy of these elements would be so great that it would surpass the rest mass of an electron. This means that the superheavy nucleus could rip electrons directly from the surrounding

subatomic vacuum. This corresponds to the quantum mechanics view of a vacuum being a bubbling foam of virtual particles and their antiparticles, being constantly created and annihilated. The superheavy element would be strong enough to hold onto the virtual electron and make it real, at which point the electron would rapidly become unstable because the velocity needed to stay in the corresponding orbital would be greater than the speed of light, and hence the electron would collapse into the nucleus. This would lead to electron capture, where the electron combines with a proton to create a neutron and neutrino, and reducing the atomic number of the element. This superheavy nucleus would continue to capture electrons from the vacuum until enough protonelectron annihilations have occurred to reduce the atomic number to 173. The only evidence of this would be a burst of positrons (electron antiparticles) and neutrinos at the time of synthesis and the lingering presence of an element with atomic number 173.

Approaching the atomic number 173 will give rise to interesting

phenomena, because the velocity of the electrons would approach the speed of light and hence their mass will increase accordingly. This would result in the bizarre scenario where the mass of the electrons is comparable to the nucleus. This could deform or completely alter the welldefined atomic orbitals of the electrons. Elements would have unique and exotic chemical properties, given chemical reactions are the province of the electrons and their orbital configurations. The exact nature of these chemical properties for now remains a mystery. Importantly, the merger of quantum mechanics and special relativity at the subatomic level has placed an upper bound on the periodic of table of elements. Research endeavours into reaching this upper limit will create some exotic elements that will change our understanding of the elements and their behaviour, although any useful applications of these elements remain to be seen.

Colin A. Scholes FRACI CChem is a senior lecturer in the Department of Chemical Engineering at the University of Melbourne. He is a world recognised researcher in the clean energy field and a passionate science communicator.

UN lauds special chemistry of the periodic table, kicking off 150th anniversary celebrations

The United Nations Educational, Scientific and Cultural Organization (UNESCO) has launched the International Year of the Periodic Table of Chemical Elements at its headquarters in Paris, kicking off a series of events and activities to be held throughout the year, as the world celebrates the 150th anniversary of the creation of the periodic table by Russian scientist Dmitri Mendeleev.

The decision two years ago by the UN General Assembly to hold this year-long celebration aims to recognise the importance of the periodic table as 'one of the most important and influential achievements in modern science, reflecting the essence not only of chemistry, but also of physics, biology and other basic science disciplines'.

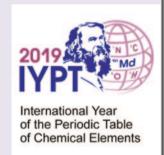
The launch event held in Paris brought together scientists and representatives of the private sector, and was opened by UNESCO's Director-General, Audrey Azoulay. The launch featured such notable quests as Mikhail Kotyukov, Russia's

Minister of Science and Higher Education, Pierre Corvol, the President of the French Académie des Sciences, and Professor Ben Feringa, 2016 Nobel Laureate in Chemistry.

UNESCO will present its educational initiative, 1001 Inventions: Journeys from Alchemy to Chemistry, designed to help young people in schools all over the world improve their understanding of chemistry and its numerous uses.

Other notable activities organised throughout the year include symposiums in Paris, France, and Murcia, Spain, and an online competition to test the knowledge and stimulate the curiosity of secondary education students on the subject.

United Nations



South Eff The unique bioluminescent chemistry of New Zealand's glowworms Markrosenrosen/CC BYSA 4.0

BY NIGEL PERRY, OLIVER WATKINS, MIRIAM SHARPE AND KURT KRAUSE

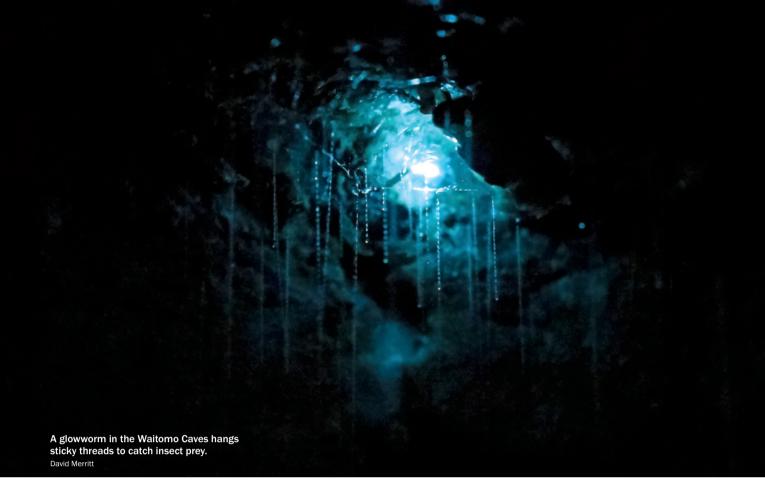
Researchers have extracted the molecules that power the majestic glowworm displays in New Zealand's Waitomo Caves.

he creatures that produce the beautiful light shows at Waitomo are actually glowing maggots: the larvae of a type of fly called a fungus gnat. Always found close to water - they are called titiwai by Māori, a name that refers to lights reflecting in water - glowworms use their blue-green light to attract prey: tiny flying insects that become entangled in sticky threads that the larvae hang beneath them. There is only one species of glowworm found throughout New Zealand, Arachnocampa luminosa, but their cousins can also be found in Australia; eight different Arachnocampa species have been found across the east coast and in Tasmania. Many different organisms produce their own light, a phenomenon called bioluminescence. Perhaps the best-known are the glowing fireflies of the northern hemisphere and the jellyfish and dinoflagellates (plankton) in the sea. There are also glowing millipedes, bacteria, squid, fish, fungi and others.

Bioluminescence is always the result of a chemical reaction: a small molecule called a luciferin reacts with oxygen to produce light, and the reaction is always helped along by an enzyme called a luciferase. Most creatures have independently evolved their own systems, using luciferin and luciferase combinations that are chemically unique.

These various bioluminescent organisms have given us valuable tools for biomedical research. Osamu Shimomura shared the 2008 Nobel Prize for Chemistry for his discovery of green fluorescent protein (GFP) while investigating the bioluminescence of the glowing jellyfish Aequorea. With the aid of both GFP and luciferases, researchers have developed ways to watch processes that were previously invisible, such as the development of nerve cells in the brain or how cancer cells spread.

The chemistry and biochemistry of fireflies, which signal to each other with red or green flashes to attract



mates, are very well understood. The luciferin and luciferase components have not only been studied in great detail, but are now produced commercially and used in a range of applications, including tracking where and when genes are turned on in cells, sequencing DNA, and detecting bacteria on hospital wards, all facilitated by producing a tell-tale glow.

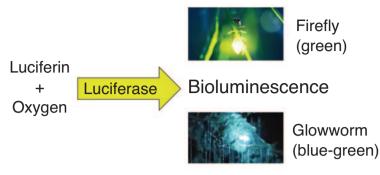
Shimomura and other researchers started to study the biochemistry of glowworm bioluminescence in the 1960s and 1970s. They showed that this bioluminescence is also a luciferin-luciferase system requiring oxygen and adenosine triphosphate (ATP), one of the main energy molecules in all living organisms, and demonstrated that the glowworm luciferin was different from the firefly luciferin. However, the chemical composition of the luciferin and the identity of the luciferase remained unknown. We have cracked this longstanding challenge and published the results in Scientific Reports (https://goo.gl/uRkBKZ).

Our first task was to collect enough glowworms to enable us to purify the glowworm's small luciferin molecule and solve its structure. Fortunately, there is a large population of glowworms only 2 kilometres from the University of Otago. These were picked individually from cold, wet, forested gorges at night, and from inside caves.

The tiny glowworm lanterns, measuring just 1–2 millimetres long, then had to be dissected from the larvae to get the best yield of crude luciferin. All of the extraction and purification work had to be done quickly while excluding oxygen as much as possible.

We then isolated the luciferase enzyme and carried out genetic

Firefly luciferin is biosynthesised from two cysteines with *p*-benzoquinone; glowworm luciferin is biosynthesised from tyrosine and xanthurenic acid.

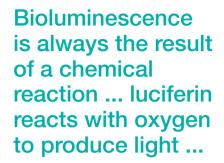


The general mechanism of bioluminescence, which can be separated into functional components in the laboratory. The colour depends on the particular luciferin (small molecule) and luciferase (large molecule enzyme) reaction of the glowing organism.

analyses. These revealed that the firefly and glowworm luciferases belong to the same family of enzymes. This means that although fireflies and glowworms evolved their abilities to make light entirely independently of each other, they both co-opted enzymes from the same family to do the job. This is an example of convergent evolution at the molecular level that had not been previously seen with any other bioluminescent enzymes.

At first our team was unable to purify the luciferin itself, but a breakthrough came when liquid

chromatography-mass spectrometry analyses showed that the common amino acid tyrosine and the insect metabolite xanthurenic acid were both major components in semi-purified glowworm extracts. Putting pure samples of these together with a glowworm extract containing luciferase, along with other glowworm proteins, gave the brightest light we had measured in this project. Tyrosine is a part of some of the luciferins in other organisms, but xanthurenic acid had never been found to be part of any other luciferin.



By combining pure tyrosine and xanthurenic acid (from other sources) with crude extract containing glowworm luciferase, we were able to purify about ten-millionths of a gram of a luciferin-related compound. This glowed brightly in a luciferase test assay. Mass spectroscopy and nuclear magnetic resonance spectroscopy on this tiny unstable sample yielded enough information to propose a possible structure that is unlike any of the other known luciferins.

The next task is to work with synthetic chemists to make this luciferin-related compound in the laboratory and definitively prove if it, or a related chemical, is the glowworm luciferin. Doing this will uncover another of nature's mechanisms for converting chemical energy into light. Further work on producing functional glowworm luciferase in cell cultures would then be needed to provide a distinct bioluminescence toolkit for laboratory use. These efforts will be boosted by collaborating on the related Australian Arachnocampa glowworms with Associate Professor David Merritt of the University of Oueensland.

Miriam Sharpe and Kurt Krause are based in the Department of Biochemistry, and Nigel Perry is in the Department of Chemistry, at the University of Otago. Oliver Watkins is based at the Agency for Science, Technology and Research, Singapore. This article first published in Australasian Science (www.australasianscience.com.au).





Seeds offer anticancer promise

BY GISELLE ROBERTS

Professor John Moses, chemist at the La Trobe Institute for Molecular Science at La Trobe University, walks to the corner of his lab and opens the lid on a large bucket of brown seeds. 'We paid \$10 a kilo for this lot of *Voacanga africana*', he tells me. 'We first bought them on eBay and now we source them from a farm in Ghana.'

At first glance, they look fairly nondescript, but Moses has a knack for taking low-value natural products and transforming them into something remarkable – in this case, an anticancer compound in just nine synthetic steps.

Moses is a chemist who specialises in identifying alternative routes to molecules that optimise pharmaceutical yield and effectiveness. This kind of work is critical to the drug pipeline and, most importantly, to the patients dependent on life-saving medications that may otherwise be difficult and expensive to make.

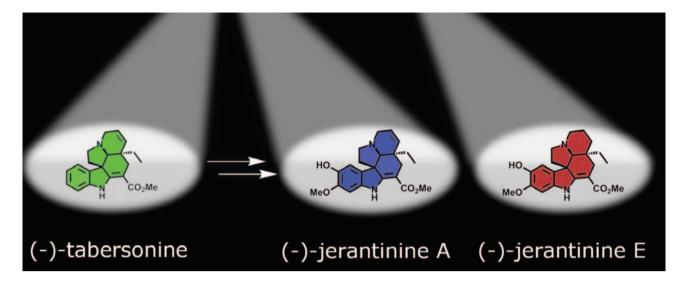
'Chemists play a key role in the pharmaceutical process', he says. 'We design molecules, synthesise them, screen them, find lead hits, and refine processes to cut down production costs. We create a recipe of sorts, where simplicity and function are critical to success. The less steps involved and the simpler the chemistry, the more cost-effective the product will be.'

Moses has recently used an extract from *Voacanga africana* seeds, an alkaloid that is inexpensive and with no significant biological properties, to synthesise a powerful anticancer compound. Using a biomimetic

strategy inspired by nature, the synthesis all happens efficiently and inexpensively in nine steps.

'Often, total syntheses of complex compounds can take multiple steps, often more than 15, and this can reduce the overall synthetic yield', he says.

'We have taken a compound from inexpensive, benign seeds with no known or significant biological activity, and performed a series of robust chemical transformations to create a potent anticancer compound that will pave the way for new biological investigations. Not only is our compound active, but it has a 30% overall yield, which is significant.'



If it ticks all the boxes in terms of pharmacokinetics, there's the possibility it could one day be taken forward to advanced trials.

Future work will involve tweaking the compound to modify and improve its function.

'Function is what I really care about', says Moses, 'but part of that focus is also about up-value. We take a handful of seeds, or some other natural source and turn them into something of considerable value. Combine that

with the principles of click chemistry, and we can perhaps help to optimise the drug pipeline to get pharmaceutical outcomes that are quick, simple and cost effective.'

Dr Giselle Roberts is Communications Coordinator at the La Trobe Institute for Molecular Science.

Stories from the Periodic Table

Do you have a story connected to a certain element?

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Rb	Sr	39 Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	53 	Xe
Cs	₅ Ba	57-71	72 Hf	73 Ta	74 W	Re	76 Os	77 r 1922	78 Pt	Au 197.0	Hg	81 TI	Pb	Bi	Po	Åt	ển
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Round	Submissions Close	Best Story Winner Announced	Audience Poll	Audience Poll Winner Announced
1	15 December 2018	8 March 2019	April 2019	19 April 2019
2	31 March 2019	7 June 2019	July 2019	19 July 2019
3	30 June 2019	6 September 2019	October 2019	18 October 2019
4	30 September 2019	15 November 2019	-	

Whether it's from your work, studies or everyday life, the RACI wants to hear your personal connection to this element.

Over the course of the International Year of the Periodic Table in 2019, the RACI will publish these stories on the RACI website and social media to highlight the personal connections that people have to science, and to chemistry.

Story submissions will be accepted in four rounds. Each round will feature a best story, as well as an audience favourite story (excepting round four (4)).

Submissions from residents in Australia or New Zealand will be entered into a competition for the chance to meet and mingle with the leadership in Australian chemistry at the RACI National Awards Dinner in November 2019. The winners will also have their stories and/or biographies published in Chemistry in Australia and will each receive a copy of A Century of Bonds.

Submissions in text (up to 500 words) or video (up to four minutes) will be accepted and are to be sent to communications@raci.org.au.

For full competition details visit raci.org.au



RACI's new leadership team

The RACI proudly introduces the RACI's Leadership Team for 2019.



Vicki Gardiner, President

Dr Vicki Gardiner is a chartered chemist who has substantial experience in leadership, organisational strategic planning, operations (including risk management), stakeholder relationship and project management experience in research and development and commercialisation.

She has held senior management

positions in academia, government, small and medium-sized enterprises and industry not-for-profits, and has been a member of the National and Tasmanian advisory group.

In 2012, Vicki was awarded the RK Murphy Medal for her contribution to the promotion and commercialisation of science. She is currently the Director of Policy & Research at Medicines Australia and a Board member of ARRB Group.



Steven Bottle, President Elect

Professor Steven Bottle is a keen educator and an active researcher, playing key roles in ARC and CRC research centres. He is a Fellow of the RACI and has previously served as the Queensland Branch President and on the RACI Board.

He has published more than 160 papers in his specialist area of free radical

chemistry and is a current member of the ARC College of Experts.

Steven envisions the RACI brokering internships, offering new awards and building stronger links with government and industry groups.



Matt Sykes, Hon. Gen. Treasurer

Dr Matt Sykes is currently the Program Director for Pharmaceutical Science at the University of South Australia, and has a PhD in computational chemistry from Flinders University, where he joined the RACI as a third-year student in 1995.

After completing his PhD, Matt worked as a postdoc at the University of

Sheffield/AstraZeneca in the UK, looking at the development of computational tools to expedite the drug discovery process. Matt then worked in the Department of Clinical Pharmacology at Flinders University for two years as a research fellow.

Matt joined UniSA in 2008, and is a passionate chemistry educator who has won several awards for his teaching, including the UniSA Citation for Outstanding Contribution to Student Learning for 'For sustained excellence in the teaching of chemistry to large first year student cohorts from a diverse range of programs and backgrounds'. Matt has also recently been awarded New Colombo plan funding to enable his undergraduate students to undertake study tours in the Philippines, where they will be able to gain an international perspective on the pharmaceutical industry.

Dave Winkler, Hon. Gen. Secretary

Professor Dave Winkler joined the RACI in 1975 and has been heavily involved in RACI activities over many years. Dave was an RACI Board member from 2003 to 2007 and was Chairman of the Board for two years. He was Chair of the Biomolecular Chemistry Division from



2002 to 2005 and was the RACI's representative on the Board of Science and Technology Australia from 2011 to 2013 and the Australian Academy of Science National Committee for Chemistry between 2012 and 2015. He currently serves as Board representative on the External Relations and Structure Committees, and is the RACI representative on the international organising committee of Pacifichem 2010. He is also the President of the Federation of Asian Chemical Societies and a past President of the Asian Federation for Medicinal Chemistry, international umbrella organisations of which RACI is a member society.

Dave is a computational chemist with deep expertise in the use of machine learning and evolutionary methods to design bespoke bioactive molecules and materials. He has a particular interest in translational research and has several drug candidates in clinical trials. Dave has received several awards for his research, including the CSIRO Medal for Business Excellence, the 2013 Adrien Albert award for Medicinal chemistry (RACI), a 2015 Royal Academy of Engineering (UK) Distinguished Fellowship, and the 2017 ACS Skolnik award for excellence in cheminformatics.

Renate Griffith, Board Member

After a PhD in polymer science in Germany, in 1986, Dr Renate Griffith emigrated to Australia and undertook postdoctoral studies in synthetic organic chemistry with Professor Pyne (University of Wollongong).

After a break to raise children, Renate began research in computational chemistry and molecular modelling, and



now works mainly in the area of computer-aided drug design. In 2001, she started as a lecturer (later senior lecturer) at the University of Newcastle, and took up a position as an associate professor in pharmacology at the University of NSW in 2008.

Retiring from full time work in 2017, she is currently an adjunct associate professor in the School of Chemistry at UNSW. Renate was elected as a RACI Fellow in 2013 and as a Fellow of the Asian Federation of Medicinal Chemistry (AFMC) in 2017.

In 2017, Renate was the president of AFMC and chaired the organising committee of AIMECS17, held in conjunction with the RACI Centenary Congress. She is a past chair of the RACI Division of Medicinal Chemistry and Chemical Biology.



Amanda Ellis, Board Member
Professor Amanda Ellis graduated with a
PhD (Applied Chemistry) from the
University of Technology, Sydney in 2003.
Currently, she is a professor in Chemical
Engineering at the University of
Melbourne, having previously been an
Australian Research Council Future Fellow
(2014–2018). Her research focus is on

carbon and DNA nanotechnologies.

Amanda became a Fellow of the RACI in 2013. She is the past-Chair of the RACI Polymer Division (2013–2015). She has served on a number of RACI conference committees, including ICCC39 (IC'10, Adelaide), 34 APS (Darwin, 2013), 35 APS (Chair, 2015) and the RACI Polymer Division Solomon Lecture Series (2012). She was the Chair of the inaugural RACI Inclusion and Diversity Committee, founded in 2017. She currently serves on the Australian Research Council College of Experts.



Cynthia Cliff, Board Member

Dr Cynthia Cliff is the Director (Knowledge Transfer & Partnership Development) in the Faculty of Health at QUT where she is responsible for driving innovation at the university—industry interface.

Cynthia joined the RACI as a student member in the School of Chemistry at

ANU. Following a PhD in the UK investigating nitrene insertion reactions, chemistry became a springboard for a career encompassing extensive business leadership experience in university, government, private and not-for-profit organisations engaged in consumer advocacy, publishing, education policy, research, technology and social change, and health.

She is a graduate of the Australian Institute of Company Directors (GAICD) and holds graduate diplomas in business administration (with Distinction) (QUT), outdoor education (BCAE), and environmental studies (Macquarie University), a Graduate Certificate in Academic Practice (QUT), a PhD (Keele University, UK), and a BSc(Hons) (ANU).

Cynthia has served on the Board of Parkrun Australia and chaired its Constitution Review Committee, and served for 10 years on the Board of the Australian Consumers' Association (*Choice* magazine), where she was also a member of the Audit and Governance Committee, and the Finance Committee. She is looking forward to contributing energy and insight to the RACI

Board's role in continuing to build member engagement and organisational strength and vibrancy.

Maree Stuart, Board Member

Maree Stuart is a Fellow of the RACI and has been an active member for over 19 years. She has held various office bearer positions on NSW special interest group committees, on the NSW Branch Committee and on several conference and symposia organising committees. For a short period, Maree also worked in the position of the NSW Branch Coordinator.

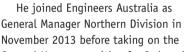


She is currently the Chair of the NSW Consultants and Contractors Group.

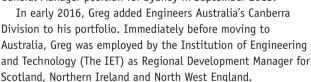
Maree is the founder and leader at MAS Management Systems. Maree is an analytical chemist 'by trade' and a management systems leader by experience. She specialises in business systems and compliance, and metrology of chemical and biological process. Apart from her qualifications in chemistry, Maree holds qualifications in business, politics and international relations, and law.

Greg Ewing, Board Member

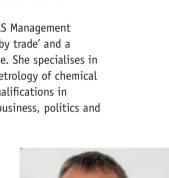
Greg Ewing is the General Manager, Engineers Australia Sydney & Canberra. He is a highly experienced senior executive with an extensive career in the not-forprofit/for purpose and government sectors, both here in Australia and internationally.



General Manager position for Sydney in September 2015.



Most of Greg's professional career was with the Scottish Government, a career that encompassed a variety of positions, including senior management, people development, communications, project management, CPD delivery and relationship management.



2019 FACS Awards and Citations: call for nominations

FACS presents a number of awards and citations to recognise outstanding achievements of chemists in the FACS region.

General rules for all awards

- All awards involve a lectureship delivered during an Asian Chemical Congress (ACC) held in conjunction with the biennial FACS General Assembly (GA).
- The lectureship shall be open to members of member societies of FACS.
- Nominations may be made by member societies of FACS.
- Nominations, together with supporting documentation from the candidate, and/or referees should be lodged with the Secretary General at least 6 months prior to the GA.
- The FACS Executive Committee shall establish an Award Committee comprising the President, the President-Elect and the Immediate-Past President, to select lecturers for endorsement by the GA.
- If in the opinion of Executive Committee there is no candidate among those nominated who has sufficient merit, the Executive Committee may refrain from making an award.
- The successful lecturers shall deliver a lecture at the ACC.
 They shall be provided with \$1000 towards a return economy air ticket to ACC by FACS. The ACC host society shall provide local travel, board and lodging. FACS shall also present a plaque to each of the lecturers.
- The lecturers shall undertake to provide a written manuscript of the lecture to FACS at the ACC. FACS shall reserve the right to publish in any of the publications of FACS or in the Proceedings of the ACC.

FACS Foundation Lectureship

The FACS Foundation Lectureship shall be presented to an eminent chemist who has made distinctive contributions to the profession of chemistry. The Lectureship will be awarded in the field of inorganic chemistry. The nomination shall contain curriculum vitae, contributions to the designated area of chemistry in the past 15 years, a list of important publications and the title of proposed lecture if successful.

FACS Distinguished Young Chemist Award

The FACS Distinguished Young Chemist Award shall be presented to an eminent young chemist of not more than 40 years of age as of the 1st January in the year of the ACC, who has made distinctive contributions to the profession of chemistry. The Award will be awarded in the field of inorganic chemistry. The nomination shall contain curriculum vitae, contributions to the designated area of chemistry in the past 10 years, a list of important publications and the title of proposed lecture if successful.

FACS Award for Distinguished Contribution to Economic Advancement

The FACS Award for Distinguished Contribution to Economic Advancement shall be presented to an eminent chemist who has made distinctive contributions to the economic advancement of the Asia Pacific region through the application of chemical research. This contribution shall be judged on evidence,

including economic contributions, lists of papers and patents, and reports on work submitted to the Award Committee. The work shall cover the period of 10 years preceding the award, the major proportion of the work having been done in a member country of the Federation while the candidate was a member of the member society of the Federation.

FACS Award for Distinguished Contribution to Advancement in Chemical Education

The FACS Award for Distinguished Contribution to Advancement in Chemical Education shall be presented to an eminent chemist who has made distinctive contributions to the advancement of chemical education in the Asia Pacific. This contribution shall be judged on evidence including lists of publications, projects, innovations, patents and reports submitted to the Award Committee. The work shall cover the period of 10 years preceding the award, with the major proportion of the work having been done in a member country of the Federation while the candidate was a member of the member society of the Federation.

FACS Citations for Contributions to Chemistry in the Asia Pacific

There are a considerable number of eminent chemists who have made substantial contributions to chemistry and especially to the progress of the profession over a period of many years. The FACS Citations are to recognise such chemists who have made substantial contributions to chemistry through activities of the Federation.

Rules for FACS Citations for Contributions to Chemistry in the Asia Pacific Region:

- Up to three Citations may be awarded at each GA.
- The substantial contribution will have been made over at least two of the administrative cycles of the Federation (4 years) and will have assisted the development of chemistry in more than one of the countries of the Federation.
- Nominations may be submitted by member societies of the FACS.
- Nominations for the citation shall include a general statement of the nominee's contributions to chemistry and/or the chemical profession together with curriculum vitae and any relevant details of publications, patents and other supporting materials.
- Nominations should be forwarded to the Secretary General at least 6 months prior to the GA.
- The Executive Committee may appoint an adjudication panel to make recommendations to the GA.
- The Executive Committee reserves the right not to make a citation recommendation if no suitable applications are received.

All nominations, together with supporting documentation, should be submitted to the FACS Secretary General, Roger Stapleford (roger.stapleford@raci.org.au), before 15 June 2019.

Australia Day Honours, 2019

Congratulations to the following RACI Fellows, who were recognised on Australia Day by appointment to or award in the Order of Australia for their contributions to Australian science.

Professor Olaf Drummer MRACI CChem was made an Officer (AO) in the General Division for distinguished service to medicine in the field of forensic toxicology, to medical education, and to professional groups.

Dr Wilfred Armarego FRACI CChem, honorary, was made a Member (AM) in the General Division for significant service to biochemistry and molecular biology.

Professor Mary Garson FRACI CChem became a Member (AM) in the General Division for significant service to education, particularly to organic chemistry, and as an advocate for women in science.

Dr John O'Hagan FRACI CChem, honorary was also made a Member (AM) in the General Division for significant service to medical science and innovation, and to the community.

Dr Leonard Fisher FRACI CChem received a Medal (OAM) of the Order of Australia in the General Division *for service to science through a range of roles*.

The Council for the Order of Australia is 'an independent body that considers nominations for appointments and awards in the General Division of the Order and makes recommendations to the Governor-General'.

The Council for the Order of Australia comprises 19 members, including representatives of each state and territory, public office holders (ex-officio) and community representatives. The community representatives on the Council are appointed by the Governor-General on the recommendation of the Prime Minister'.

The Council considers whether nominees have:

- · 'demonstrated achievement at a high level
- made a contribution over and above what might be reasonably expected through paid employment, or
- made a voluntary contribution to the community which stands out from other volunteers.'

With gg.gov.au



The organisers of the Society of Environmental Toxicology and Chemistry (SETAC) Australasia 2019 conference are calling for abstracts to attend this exciting international conference. The RACI Radiochemistry Division is sponsoring a Special Session in Environmental Radiochemistry and Radioecology, which entitles all RACI financial members to register for the conference at SETAC AU member rates (subject to confirmation of their membership status with RACI, which will be conducted by the SETAC AU 2019 PCO).

The theme of the conference is 'Protecting and improving the environment through collaboration – across disciplines and across borders'. The conference will build on the strengths SETAC AU has gained through their tripartite approach and their history of collaboration between industry, government and academia. The society's rich history is laden with achievements that have demonstrated the benefits of their distinctive approach to maximise environmental outcomes through sharing knowledge. This conference will showcase this capacity with workshops, discussion forums and special sessions aimed at addressing the environmental questions that we share. It is also fitting to have SETAC AU's next conference in picturesque Darwin, as the tropical Top-End is a hotspot for biodiversity, natural and cultural wonders. It is also a region that is rich in natural resources and has seen increasing pressures from industrial development and the legacy of historical mining activities. As such, it is a place where knowledge sharing of environmental toxicology and chemistry offers a real opportunity for the long-term sustainable development of northern Australia.

The conference organisers encourage abstracts from all members of the RACI who have an interest in environmental chemistry and look forward to seeing you in Darwin this July.

For more information, visit www.setac-au2019.com.au.

RACI National Awards 2019: call for nominations

MRACI Post Graduate Student Travel Bursary – closes 5 May

The award consists of a certificate and \$2000 to assist the student to collaborate with a research group at another Australian university, or overseas, or to make use of specialised research facilities (e.g. an advanced light source), or to deliver a paper at a meeting overseas. The bursary will not be granted for travel to an Australian-based conference or workshop. Proof of attendance at the overseas conference or research facility must be provided on return. On completion of the travel, the RACI would like each successful applicant to produce a short article for the RACI website, and make themselves available to speak about their experience to science/chemistry students at an RACI Affiliate Member school in their state.

Applied Research

The medal shall be awarded annually to a full member (MRACI and above) of the RACI who, in the opinion of the Board of the RACI, has contributed significantly towards the development of, or innovation through, applied research, or in industrial fields. This contribution shall be judged on evidence submitted to the adjudicating panel.

Centenary of Federation Teaching Awards in Chemistry

The RACI has established a series of annual awards for the recognition and reward of outstanding excellence in the teaching of chemistry in Australia at both primary and secondary school levels.

The award process is two tiered with the branches offering a primary and secondary teaching award on the basis of one each per state annually, with applicants in the Northern Territory being considered with South Australia and those in the Australian Capital Territory with New South Wales.

Any Branch may refer exceptional awardees to the Board for national consideration.

The Board may select one primary and one secondary national award winner from the candidates submitted by the Branches.

Citations

There are a considerable number of chemists – members of the RACI – who make substantial contributions to chemistry and especially to the progress of the profession over a period of many years. To provide recognition of these contributions, the RACI initiated The RACI Citation.

Cornforth Medal

The Board of the RACI awards the Cornforth Medal, a bronze relief medal bearing the words 'For a Thesis on Chemical Research' commemorating the work of Sir John Cornforth AC CBE FRS. The medal is designed to give recognition of outstanding achievement in chemistry and to promote chemical communication.

The medal is awarded to the candidate who is judged to have completed the most outstanding PhD thesis in a branch of chemistry, chemical science or chemical technology under the auspices of an Australian university and whose degree has been approved, but not necessarily conferred, in the previous 13 months. There shall not be a dual award. If the committee considers that none of the theses submitted reach an appropriate standard, no award will be made.

Distinguished Contribution to Economic Advancement – Weickhardt Medal

This award shall be made every year to a full member (MRACI and above) of the RACI who, in the opinion of the judging committee, has contributed significantly towards the economic advancement of the Australian economy through work in the chemistry area. The Award shall consist of the Weickhardt Medal.

Distinguished Fellowship

Inaugurated in 1996, a Distinguished Fellowship is the recognition of highly distinguished contributions to the profession in academia, government or industry and the RACI, and is awarded on, or very close to, retirement from the candidate's principal professional role. Distinguished Fellowships do not carry financial or postnominal implications. Rarely would there be more than three Distinguished Fellowships awarded per year.

This award requires nomination by the Board, Branch or Divisional Committee of the RACI. The candidate is required to be a Fellow of the RACI with a minimum membership of 5 years.

Fensham Medal for Outstanding Contribution to Chemical Education

The RACI introduced the Fensham Medal for Outstanding Contribution to Chemical Education to recognise outstanding contributions to the teaching of chemistry and science in general over an extended period. It is intended that the Fensham Medal be the most senior award for education in the Institute.

Recognition will be in the form of a medal, awarded at the National Awards Dinner. Nominations for the award will be assessed by a committee appointed by the Board.

H.G. Smith Memorial Medal

The medal shall be awarded annually to a member of the RACI who, in the opinion of the RACI Board, has contributed most to the development of some branch of chemical science; this contribution will be judged by research work published or accepted for publication during the 10 years, or equivalent relative to opportunity, immediately preceding the award.

Leighton Memorial Medal

The Leighton Memorial Medal commemorates the distinguished career of A.E. Leighton. The award was established in 1965 through the generosity of his daughter, Miss Anne Leighton. It is the RACI's most prestigious medal. A.E. Leighton CMG, FRIC, FRACI MIChemE, died in 1961 after a distinguished career as a chemist, technologist and administrator, in which he had served Australia's interests in both war and peace.

He was a staunch supporter of the RACI, and during his frequent visits to England in the early years of the RACI he carried out an enormous amount of work to secure the RACI's Royal Charter. He was in the first group of Fellows elected (June 1920), served as Victorian Branch President 1920–22 and was President of the RACI 1952–53.

The Leighton Medal, designed by the internationally famous medallionist Andor Meszaros, is of sterling silver showing a profile of Leighton on the obverse, and a design symbolising chemical industry on the reverse.

The Leighton Medal is awarded in recognition of eminent services to chemistry in Australia in the broadest sense.

Candidates may apply or be nominated. The candidate must be a MRACI CChem with a minimum membership of 5 years.

Margaret Sheil Leadership Award

The award has been established to honour the trail-blazing contributions of Professor Margaret Sheil, Provost of the University of Melbourne (at the time of commencement of this award), former CEO of the Australian Research Council and the first Australian female professor of chemistry. Through these and other roles, she has worked tirelessly to progress the participation, success and recognition of women in chemistry, and science and engineering more generally.

The aim of the award is to recognise an outstanding female leader working in an area of a chemistry-related field, including academia, teaching, and the public or private sector, who has helped to inspire and mentor junior female chemists and/or help to provide a more equitable work place.

Masson Memorial Prize

This award has been established as a memorial to the late Sir David Orme Masson, founder of the RACI. The winner will receive a Memorial Medal, together with a copy of Len Weickhardt's book Masson of Melbourne – the life and times of David Orme Masson and \$500 paid in two equal instalments – the first at the time of the award, the second at the successful completion of the year of study.

The award is open to any financial member of the RACI or to any financial student of the RACI, who has attained the academic qualification of BSc or its equivalent, and who is eligible to proceed for a further year's study of Chemistry at BSc Honours level, either at a university or other approved institution in Australia.

RACI Chemistry Educator of the Year

This award is designed to encourage developing teachers, and is open to tutors, lecturers and senior lecturers (academic levels A, B and C) teaching in undergraduate or postgraduate university courses.

The winner will be required to submit an article for publication in *Chemistry in Australia* on his/her contribution to chemistry teaching.

Rennie Memorial Medal

This medal is awarded by the RACI for research excellence in chemical science. The award requires nomination by a Branch or Divisional Committee of the RACI. The candidate is required to be a current member (for a minimum of 3 years) with less than 10 years professional experience since completing his or her most recent qualification of a BSc, BSc(Hons), MSc or PhD, or, the equivalent.

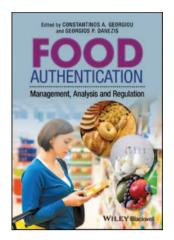
Rita Cornforth Lectureship

The award has been established to honour the pioneering contributions of Lady Rita Cornforth (1915–2012), the wife of Nobel Laureate Sir John Warcup Cornforth (1917–2013) and collaborator on 46 of his papers. In his Nobel Lecture, Sir John paid tribute to his wife's pivotal contributions to their joint work: '... with patience and great experimental skill [she] executed much of the chemical synthesis on which the success of the work was founded.'

The aim of the award is to provide an outstanding female early career chemist with an opportunity to achieve broader recognition of her career achievements to date, and help establish collaborations and networks that will further assist her in establishing an independent career. The award will recognise an outstanding contribution to chemical research in any sphere, including industry, the public sector and academia.

RACI National Award nomination dates and documents

All award nominations, except for the post graduate student travel bursary (closes 5 May), close on **14 June**. Nominations, together with supporting documentation, should be submitted to Robyn Taylor (robyn.taylor@raci.org.au) by the closing date.



Food authentication: management, analysis and regulation

Georgiou C.A., Danezis G.P., Wiley Blackwell, 2017, hardback, ISBN 9781118810262, pp. 568, \$336

Food authentication: management, analysis and regulation is ably edited by Constantinos Georgiou and Georgios Danezis from the Agricultural University of Athens. There are 41 contributors to the book, most from continental Europe, and the entire book hangs together

remarkably well, so you will appreciate my use of 'ably'.

In an era where food is traded internationally, little can be more important than the safety and security of our food, and the necessity to aggressively fight food fraud, which is both common and highly profitable. A trip to your local supermarket will show you myriad ways to sell very expensive water. Currently, there are claims of adulteration of honey with rice, corn or beet syrups, all of which are much cheaper than honey. This also militates against beekeeping, a practice vital for the pollination of many plants we eat.

A complicating factor when discussing food authentication and the term 'authentic' is to get an adequate 'handle' on the terms. In some ways, they are like 'quality': you know it when you see it, and you recognise its absence, but in the middle everything can be a tad blurry. The concepts are multifaceted. And there are no official definitions. The best definition in the book (Santos and Oliveira, Chapter 7, p. 200) is that a food may be considered authentic if it 'complies with existing regulations; has the correct composition to assume its legal name; has the composition, origin and production systems as stated on the label; and has not been adulterated by substitution of cheaper or inferior ingredients to reduce production costs'.

We also bring our own sets of moral and ethical principles to bear on what we see as authentic and unauthentic. For example, you may exclude certain foodstuffs from your selection of purchases for many reasons, including concerns about treatment of agricultural workers in some countries, pesticide use or hygiene, adequacy of government oversight of production, or, simply, a desire to support only Australian organisations.

We are all familiar with a number of recent major food frauds. Perhaps the most serious of these involved the addition of melamine to infant formula in China (to increase the apparent protein content assessed via Kjeldahl nitrogen analysis), resulting in a number of deaths, many hospitalisations and a great wariness among Chinese parents towards buying local formula for their infants. There has also been the recent major European horse meat scandal, not to mention various olive oil scandals about origins, adulteration (in one case with glycerol) and variety. More locally, we have seen recent recalls of frozen berries and frozen vegetables due to contamination.

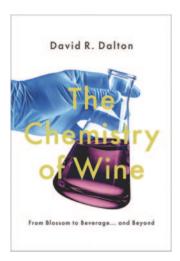
These instances are quite gross violations, but there are many more subtle instances. Palm oil, which is relatively cheap, is commonly substituted for more expensive oils in commercially baked products and confectionary. Are you sure the fish fillets you bought for a premium price are the 'real deal' and not a cheap substitute? Frozen fish should be cheaper than their freshly caught counterparts, so maybe we should all be a bit sceptical about 'thawed for your convenience'. The profit motive is a powerful incentive for all sorts of scoundrels and double dealers to fudge and at times flout the rules and regulations. There are clever people writing rules to ensure authenticity and other clever people trying equally hard to skirt around them. So, while there are rules and regulations and quality and industry standards pertaining to food, there is a lot of money to be made with just a tad of fudging! Caveat emptor indeed!

Food authentication is a very fine book, which I highly recommend. A relatively short opening section explains the concepts of food authentication, both from technical and sociological perspectives. The real power of the book is the detailed coverage of the very advanced and frequently novel analytical and molecular-biological techniques that can be brought to the areas of food authentication, exposure of food adulteration and food fraud. The coverage is comprehensive, erudite and extensively referenced. If you want to know what information almost any technique can tell you about foodstuffs, then this is an excellent place to look. Each chapter is a standalone survey of the literature on the application of a particular technique to foods. That is the great strength of the book: you can readily explore the technique of your interest. It is also, of course, a minor weakness: you need to read the entire book to understand the range of possibilities and see the rounded picture emerging from the combination of several approaches. The third section of the book is, again, of a sociological bent, exploring consumer attitudes and the application of bioinformatics to food authentication.

The book is aimed at analytical chemists interested in food analysis, and food scientists interested in the analytical procedures underlying their research. The book would also be excellent for postgraduate or undergraduate students of food technology. Academics and research scientists in food and allied areas would find it an invaluable reference as well. Finally, this is a book we all ought to read. We have all got a vested interest in food. We cannot last long without it! Even if you do absolutely nothing, the basic human machine requires an energy input of 5–8 MJ/day, directly derived from the food you eat.

Food authentication is full of fascinating 'stuff' and will teach you, if nothing else, to do your food foraging with enhanced caution. As well as (for most of us) enhancing your knowledge of the very clever array of techniques that can be utilised for your wellbeing, you will also increase your awareness of the many cunning ways in which you can be parted from your money!

R.J. Casey FRACI CChem



The chemistry of wine: from blossom to beverage ... and beyond

Dalton D.R., Oxford University Press, 2018, hardback, pp. 560pp., ISBN 9780190687199, \$75

What better than The chemistry of wine: from blossom to beverage ... and beyond, a serious womb-to-tomb discussion of the chemistry underpinning a substantial industry as well as a pleasant tipple for many. Author

David R. Dalton provides a wide-ranging and scholarly account of the area.

The book emerged from a general education course, The Chemistry of Wine, at Temple University (Pennsylvania). However, as Dalton states in his introductory remarks, this is not the text he set out to write, and I can well and truly assure you his book is vastly more sophisticated than anything intelligible to even the brightest 'general education' student. This one is only for proper, serious-minded graduate chemists with a deep interest in both analytical and wine chemistry.

My only (trivial) quibbles are that the entire work is printed in greyscale (a splash of colour here and there would help break up the text, albeit, undoubtedly at extra cost) and slightly larger structural formulas would often be beneficial (again, no doubt, at increased cost).

Wine is as old as civilisation itself. Noah is often credited with the discovery, but what is certain is that Pliny the Elder (23–79 CE) wrote of the Nebbiolo, a type of red grape, in his work on wine, *Naturalis historia*, John the Evangelist (born 15 CE) wrote of the conversion of water to wine at the marriage at Cana, and the Persian mathematician, astronomer and poet Omar Khayyam (1048–1131) waxed lyrical on wine in his *Rubaiyat*. Wine has been gladdening many human hearts for a very long time, as well as alarming many others for whom its consumption is seen as just above drinking methylated spirits, and countless others for whom it has readily and efficaciously lubricated the path to perdition.

Be under no misapprehension, this book contains more wine-associated (structural) formulas than a plethora of feverishly formulating pharmacists could ever conjure up. These range from compounds involved in photosynthesis of the vines, to compounds found in varieties of wine grapes and skins, to species involved in the fermentation process, finishing processes and oak ageing processes. For me, this was a tad overwhelming: making (potable) wine is a complex business. If you think you might get into brewing your own home *grappa*, then reading this book will vastly enlighten and, most probably, deter you from embarking on the venture at all. It is a very complex path from the grapevine to the dining table, best left

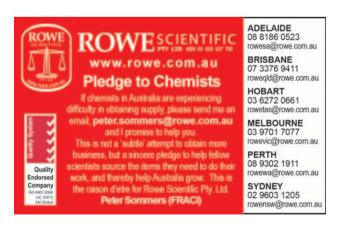
to people who know what they are doing, and there are myriad ways to failure and strictly limited demand from friends for your 'home vinegar'. If you *must* persist, then my only advice, gleaned in my youth from association with winemaking neophytes, using/abusing kits supplied by Boots the UK pharmacy chain, is to add a banana skin towards the end of fermentation. The *cognoscenti* claimed this conferred a more rounded taste to the product. Did it work? It was pretty woeful either way! Dalton, alas, does not appear to have taken this wisdom on board.

Dalton presents an erudite, well-referenced account of everything associated with winemaking. You will learn everything from how grapevines propagate, how the flowers develop and what they contain, how the grapes grow and what they contain, how the yeast works its 'magic', how fining and ageing do their work, right through to what happens when you pull the cork or unscrew the cap! You will learn about special wines, such as sparkling and fortified wines, and biosynthetic pathways relating to odour, colour and flavour compounds in wine. There are extensive, interesting tables in the appendices, as well as a hefty (48-page) 'Chemistry primer'. If by chance you need this (well presented) primer, I suggest you give the book a miss and proceed directly to consumption. Alternatively, if you know your chemistry and want a deep understanding of matters viticultural and oenological, then this is a fine book indeed.

R.J. Casey FRACI CChem

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A picture is worth a thousand words

Many students find chemistry difficult to learn because they need to think at three different levels: the macroscopic (what we can sense), the sub-microscopic (explanations in terms of atoms and molecules) and the representational (code-like symbols, structures and equations). No one has ever seen an individual atom or felt a single molecule. To learn and understand chemistry, we must first believe what we cannot see, touch or taste.

Dr Eryn Newman, from the ANU Research School of Psychology, and other researchers have found that 'people were more likely to believe [a claim] when it is paired with a photo ... even if it is just a stock photo that provides no evidence'. In one set of experiments, test subjects saw names of familiar and unfamiliar celebrities with the claim 'this famous person is alive' or 'this famous person is dead'. Some of the claims appeared with a photograph of the celebrity, while other claims appeared without a photograph. For unfamiliar celebrity names, photographs increased the likelihood that the subjects would believe the claims. In another experiment, subjects found that a claim such as 'macadamia nuts are in the same evolutionary family as peaches' was more believable when it appeared with a photograph of macadamia nuts, even though the photograph provided no information about the truth of the claim.



'Kieran Lim is alive.'

... people were more likely to believe [a claim] when it is paired with a photo.

School-level textbooks are filled with photographs. For example, discussion about gases might be accompanied by photographs of hot-air balloons and scuba divers. Many first-year undergraduate textbooks also have photographs, though fewer than school texts. But it was not always like this. Pauling's *General chemistry* and similar undergraduate textbooks from the 1960s and 1970s only have graphs, chemical structures and equations – no photographs. Photographs might be relevant for Science as a Human Endeavour (see March 2017, p. 40) at school level, but this does not explain their inclusion in first-year undergraduate textbooks. Nor does it explain the lack of photographs in graduate-level and upper-undergraduate textbooks.

Newman again: 'pictures influence belief on all types of topics. It is across the board. We have found the same effect with claims about science, wine, stock markets, general knowledge, or celebrities. It doesn't really matter what the claim is about, as long as there is a related photograph with it, it will nudge people toward believing it.' Extrapolating from the work of Newman and other researchers, photographs in school-level and first-year undergraduate textbooks make it easier for students to believe and learn new concepts.

The lecture slides of one of my colleagues has been described as 'being filled with pictures of old, dead people'. Portraits of deceased pioneering chemists might not be the most engaging choice of photographs, but he has the right idea. In the future, there will be more photographs in my lectures.



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Patents of beauty

Maria Matveenko, Trainee Attorney, FB Rice



The words 'beauty' and 'patents' are rarely used together, unless you are talking to some passionate patent attorneys.

Similarly, advertising the use of 'chemistry' or 'chemicals' in the manufacture of beauty products or cosmetics is rather unlikely. However, the three – chemistry, cosmetics and patents – constitute a successful formula

that has been working for well over a century, resulting in the development of a variety of cosmetic products that we cannot imagine living without (and ones we might not actually need but enjoy nevertheless). For example, an 1888 US patent apparently gave the world the first deodorant, and, following on from the US patent No. 49 561 that claimed the first liquid soap in 1865, numerous patents directed to advances in skin cleaning have been filed around the world. The invention of a lead-free and effective hair dye in 1907 (French patent No. 383 920) by chemist Eugène Schueller launched L'Oréal's path to become a leading beauty company, with research and development that now extends far beyond dyes and pigments to, for example, applying the modern 'omics' approaches to discover new ways to halt or reverse skin ageing.

Why patent?

Patents play an important role in enabling innovations to materialise into usable products. The need for appropriate patent protection exists whenever there is an intention or a potential to derive commercial value from a technological invention. Otherwise, the associated investment into research and development could be lost due to competitors taking advantage of the technology and manufacturing/selling the product themselves. Moreover, funding from investors is often required to translate research developments into commercial products, and having patent protection in place is usually a prerequisite for attracting that investment.

What can be patented?

Patent protection may be obtained for a variety of inventions, formulated as specific claims. Within the beauty industry, the most common category is likely to be compositions or formulations containing a mixture of ingredients, such as sunscreen, shampoo, deodorant, toothpaste, skin cream, fragrance and nail polish. Other common types of inventions are substances (e.g. a protein with hair strengthening properties) or devices (e.g. an electric facial cleansing brush). Methods, such as a method of reducing hair loss, minimising fine lines and wrinkles, or assaying skin condition, can also be patented, although this is an area where the boundaries as to what is/is not patentable vary between countries. Further examples of patentable inventions include the use of a product for a particular purpose (e.g. use of a micellar suspension for skin cleaning); a process for making a product (e.g. a process for preparing hyaluronic acid); a method of administration of a product (e.g. a skin patch for delivery of cosmetic ingredients); or a 'product produced by a process' (e.g. coconut oil obtained without heat). Lastly, numerous patents are filed with regard to packaging, applicators and dispensers, such as lipstick cases, mascara brushes and capsules for serum.

What's next?

According to Forbes magazine, the beauty industry is thriving, with consumers open to exploration, leaving plenty of room for innovation. For example, South Korean cosmetics giant AmorePacific was one of the most innovative companies in the world in 2018. Multiple developments have proven successful in the recent years, such as tissue facial masks based on transdermal patch drug delivery technologies, and products to repair damaged hair by using a Michael acceptor to tie up free sulfhydryls of hair proteins. Personalised cosmetics relying on genomics and artificial intelligence is tipped to be a hot area in beauty research. Whatever the next big beauty hits will be, some of the first people to find out about them will be intellectual property professionals.

For more information, email mmatveenko@fbrice.com.au.





Paracelsus in the marketplace

This chemistry is not exactly fun – you will need to apply some serious concentration, but only a relatively small dose!

About 600 years ago, a Swiss physician, alchemist and astrologer, Philippus Aureolus Theophrastus Bombastus von Hohenheim – known to his mates (and us) as Paracelsus – founded pharmacology. He promulgated this aphorism:

The dose makes the poison. Everything is poisonous at a high enough concentration.

We can explore his statement by scanning labels on supermarket shelves. Consider clove oil. It is sometimes used in food, as an old-fashioned ingredient in pasta sauces. It's often used in commercial products, declared as 'flavour'.

What does the label (see photo) tell us?

Oil of cloves is good for toothache and inflamed gums. The active ingredient, eugenol, not only soothes teeth (it's an antiseptic and analgesic; bit.ly/2QFznyN), it also sedates (it's not sold for this purpose) and, at higher concentration, euthanises cane toads. The Australian Pesticides and Veterinary Medicines Authority is considering an application for the registration of Toad Blitz Cane Toad Killer, containing eugenol, for the humane control of cane toads in the home garden (bit.ly/2SOAo9A).

The same active ingredient is used in all of these foods and products, but why is it sometimes labelled as a poison? The difference is in the concentration. With

increasing concentration, clove oil moves from being a food, to a medicine, to a cane toad killer.

The label warning in the image is for classical (acute) toxicity. It is the dose that determines this type of toxicity. For allergy, sensitivity and carcinogenic potential, the effects occur at much lower levels. Scientists agree that there is still a doseresponse relationship, but it's not linear and it's more complicated.

We accept that taking prescribed medicines should strictly follow the dosage and don't assume that more is better. Why not with all else?

Quinine in tonic water is a food, and as the first drug against malaria it was an effective medicine – at a certain dose. Concentrate it, and it becomes a poison on par with chemical cousins such as caffeine and, more seriously, solanine (in green potatoes).

During World War II, distinguished entomologist Doug Waterhouse was looking at ways of protecting allied troops against malaria-carrying mosquitoes in the tropics:

I tested essential oils ... and an extremely effective repellent was from Huon pine ... containing methyl eugenol ... To my great disappointment half of the army volunteers became nauseated within about 10 or 15 minutes after it was applied to their face. The other half ... was totally unaffected ...

bit.ly/2TJk3mK The natural preservative in Huon

pine is methyl eugenol (see structure), very widely found in nature. It is the major pheromone attractant used in traps to capture (male) papaya and oriental fruit flies, which can devastate Australia's fruit crops, and in higher concentrations in citronella, where it repels and then kills insects. The same Paracelsus pattern.

methyl eugenol

Methyl eugenol has been assessed for the actual risk as well as theoretical hazard (potential for harm, given likely pathways of exposure). Many herbs contain low levels of methyl eugenol (e.g. basil, bay and tarragon), but using them is not considered a problem unless they are concentrated.

Most importantly, in the Australian Poisons Standard, methyl eugenol is a Schedule 6 substance and must be labelled 'poison' at concentrations above 1%. If such a product makes, or deems to make, a therapeutic claim, it also needs registration/listing by the Therapeutic Goods Administration, the regulatory body for therapeutic goods in Australia.

Companies using such chemicals must be registered with the National Industrial Chemical Notification and Assessment Scheme, Australia's regulatory body for industrial chemicals. It notes unanimous agreement (including from the excellent self-regulating fragrance industry, IFRA (bit.ly/2TKV3vr)) that methyl eugenol '... should not be intentionally added to cosmetic products'.

Oil of cloves consists mainly of eugenol, not methyl eugenol, but both substances are classified in Schedule 6 of the Australian Poisons Standard.

Physical chemistry says that the amount of the fragrance released will increase with the surface area of the source that has been exposed and thus with decreased particle size. The release also increases exponentially with temperature. This means that solid wood is safe, while release from oil, shavings and sawdust is indeterminate. Room fresheners can 'trigger adverse health effects' if not strictly (self-) regulated (bit.ly/2RMmHLe). Huon pine carpet fresheners and, alarmingly, Huon-pine-stuffed teddy bears are available for sale to the public (see Jan/Feb issue, p. 5).

Hence, there is strict local and international prohibition of intentional addition of methyl eugenol to consumer products.

Some 'health' supplements contain concentrated extracts of natural products. Paracelsus still applies here! A few cups of green tea is fine, but some people have lost their livers after taking green tea concentrate (https://ab.co/2Rrv2o7).

So, think Paracelsus and concentrate very thoughtfully.

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.

POISON

POISON

POISON

POISON

CLOVES

TOWNSHIP

TOWNSH

Ben Selinger

Feeling the facts

In his last, posthumously published, book Stephen Hawking wrote that the public doesn't believe experts. As examples, he cited the Brexit referendum, and many of the decisions made by the Trump Administration in the USA. He included scientists among the experts, and discussed the implications for the environment of this community distrust.

While the climate change debate is often cited as an example where the science is not understood or believed, I was reminded, during a recent homeward commute, how other matters of environmental interest are also affected by this phenomenon. In separate programs, ABC Radio broadcast two discussions on whether or not to cull wild animals. One was related to control of sharks in the Whitsundays, after a Melbourne man had been killed. The other dealt with feral horses (brumbies) in the Kosciuszko National Park. Scientists were among the interviewees in each report, and both relied on their knowledge of the relevant science to support their case. As it happened, they were on different sides of the 'cull or don't cull' argument in each report. Dr Jane Williamson from Macquarie University's Marine Ecology Unit was against culling sharks, and Dr Jamie Pittock from ANU was in favour of culling brumbies.

The proposed shark cull is intended to improve water safety for visitors in a popular tourist area. While local fishers provided anecdotal evidence of increased shark numbers, Dr Williamson argued that there is insufficient information to demonstrate that shark culls improve safety. She also questioned whether there was any data to support the fishers' observations about shark numbers. Dr Williamson proposed what are, effectively, risk-management approaches to minimise the opportunities for harmful interactions between humans and sharks.

Conversely, Dr Pittock used science arguments to support the culling of brumbies, something that has the backing of the Australian Academy of Science. Dr Pittock cited clear evidence of the damage being done to the National Park. However, opponents of culling were having no truck with the science, and used cultural heritage arguments to support their case. In this, they invoked the 'iconic' status of brumbies in European Australian culture, attributable to A.B. (Banjo) Paterson's poem *The man from Snowy River*. They also argued that the preferred culling method, aerial shooting from a helicopter, was inhumane because of the difficulty in obtaining a clean kill shot. Concern for animal welfare had an element of being science-based, it seemed to me.

However, what was clear in both cases was that the general community was not prepared to meekly accept that the scientific arguments were equally compatible with their own local knowledge, and in response to this, Dr Pittock suggested



that scientists had to engage on the same emotional level as the brumby advocates. He suggested that the beauty of the natural environment, and the damage done by introduced species, become a focus in arguing for a cull.

Control of feral animals, and managing their interactions with humans and the natural environment, was brought closer to home about a month after these broadcasts. There was a dead deer on the side of the main road not far from my home on the outskirts of Melbourne. I was aware that there had been deer sightings in the district, but this was my first encounter. There is a hot debate on local social media about what should be done. One side favours protecting the native bush from the deer; the other side uses the 'don't shoot Bambi' argument. Apart from my sighting of deer road kill, there have been other reports of deer using creek-side bush corridors to travel to less bushy suburbs and running amok by wandering into the path of cars. Locally, deer are stripping bark from native trees. Aside from concerns for the native vegetation, there are risks involved with human interactions with feral deer. A person is unlikely to be injured in a direct encounter, because the deer will avoid the human; injury or death in a traffic accident involving a deer is a more probable outcome.

Shooters' organisations are keen to assist with culling. Licensed shooters would need a police permit to shoot on private land, and authorisation can be obtained from the relevant government department to shoot on public land. The police permit is required because of the proximity of houses, which is understandable, because a stray bullet from a high-powered rifle is not acceptable around residential areas. In all this, it has been apparent to me that there is a key element of risk management to be addressed, and another animal whose behaviour needs to be managed – *Homo sapiens*.



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Gasoline (petrol) additives – update

In the past I have reported on the quality of fuel in Australia and the potential for unregulated chemicals to enter the fuel market to the detriment of the motorist using the fuel (May 2017, p. 36). Here, I will give an update.

The quality of fuel sold in Australia is regulated by the Fuel Standards Act. The Act sets the levels of various components and performance criteria for gasoline (the preferred industry term for petrol), diesel, LPG, ethanol fuels and biodiesel. The Fuel Standards Act complements vehicle design rules that set performance levels for new vehicles sold in Australia, including emission limits.

The introduction of a standard to lower greenhouse gas emissions comes down to improving fuel economy (km/L). This requires higher efficiency engines, which means increasing the octane of the fuel so that higher compression engines can be used. At the time of writing, it is proposed that the minimum fuel octane will be 95RON (research octane number, premium petrol) rather than the current 91RON for unleaded petrol.

Higher RON can be achieved by more severe refining or using chemical octane boosters. Organometallic additives are very effective but are now banned or opposed by vehicle manufacturers. Widely used octane boosters are alcohols, especially ethanol, and ethers such as methyl *tertiary*-butyl ether (MTBE). Ethanol is widely used in Australia but has some issues with vehicle compatibility (especially old vehicles) and is not very compatible with petrol (fungible). Although adding ethanol may achieve the 95RON standard, there may be difficulty in obtaining the higher 98RON grades.

Nitrogen compounds such as amines have been used as gasoline additives to reduce deposits on engine intake valves for some years. Currently, there is active interest in using aniline and aniline derivatives in higher concentrations as octane boosters. Adding relatively small quantities of these materials to a gasoline results in large increases in the octane. Prima facie, the aniline additives are five times more effective than ethers such as MTBE in boosting octane. Like all other nitrogen compounds in fuel, more nitrogen oxides are produced and emitted from the exhaust, which requires advanced catalytic converters to eliminate.

The main drivers for using these unconventional chemicals come from two different points:

- raising the octane of low-octane gasoline to make it suitable for modern high-performance vehicles
- attempting to formulate an aviation gasoline without lead or other organometallic octane boosters.

In many parts of the world, particularly in developing economies, there are simple refineries. *Simple* here is used as a technical term to describe a refinery with few unit processes to produce gasoline, motor diesel and fuel oil. In more affluent parts of the world, the refineries are more *complex* and have unit operations that convert the fuel oil component into gasoline and diesel. A third group of refineries are *very complex*

and are designed to convert the most intractable (cheap) crude oils into specification fuels.

Simple refineries produce the base gasoline from naphtha (a distillation cut of crude oil) and reformed naphtha (reformate), which contains a high level of aromatics, which delivers high octane. The octane of base gasoline depends on the octane of the naphtha cut, which depends on the source of the crude oil – for many operations this is a local crude oil. The point is that many of these simple refineries barely manage to produce 91RON product and have difficulty in producing the 95RON and 98RON grades. Additives based on aniline seem to be gaining traction for this duty.

Aniline as an octane booster has been widely used in Russia since the days of the USSR, when most refining operations were in the simple category and produced a low-octane gasoline, which was used in low-compression engines such as the DDR Trabant. The aniline booster was in the form of aniline itself, *N*-methyl aniline or toluidine or mixtures of these. However, Russia is now moving to improve refinery operations to produce higher quality fuels and the use of these additives is declining as they are being replaced by ethers.

Lead (Pb) is still widely used in aviation gasoline (AVGAS) where high-compression engines demand very high octane – typically, MON of 100 compared to 85 in motor fuel. Furthermore, there are minimum specific energy requirements, which limits the quantity of oxygenates that can be used. The removal of lead in AVGAS is the subject of extensive research by oil majors; for instance, researchers at Shell have proposed a formulation based on toluene, aniline and diethyl carbonate added to alkylate (Shea T.M. et al. US Patent 9,388,358 (12 July 2016)).

One of the problems with aniline additives is that they can easily polymerise. This requires the additive packages to contain anti-oxidants. Recent work by vehicle manufacturers on the use of aniline additives has shown a marked tendency to degrade lubricating oil to produce varnish and form sludge, which damages the engine.

In evaluating the impact of a gasoline on a lubricating oil, it is important to consider how the gasoline and the components of gasoline contact the lubricating oil.

In an internal combustion engine, gasoline enters the hot combustion chamber as a vapour—air mixture in carburetted engines or is mixed and vaporised in hot air in the combustion chamber in fuel-injected engines. The presence of hot air from prior combustion or the compression process as the piston rises in the cylinder overwhelms any anti-oxidant present in the gasoline. The gasoline is ignited by means of a spark.

Lubricating oil from the sump is carried by the pistons up the cylinder wall. There is always some by-pass of the piston and the piston rings; a small amount of lubricating oil is carried into the combustion chamber and clings to the chamber walls, lubricating the piston movement. This oil interacts with the

vaporised gasoline, and the gasoline combustion products and partial combustion products and absorbed materials are carried back into the engine sump by returning oil on the cylinder walls. In this manner, gasoline and gasoline components enter the lubricating oil system and are carried throughout the engine to form varnish and sludge over cooler components remote from the combustion chamber.

Most manufacturers warranty their vehicles for 100 000 km or five years' operation and since we are concerned with fouling of parts and components that are rarely inspected over this period, it is important that fuel and fuel components do not contribute to excessive fouling. This means that even a small quantity of material that contributes to fouling should be eliminated as far as possible from the fuel system. This could be a major obstacle in developing a high-octane AVGAS from aniline and derivatives.

This problem is in addition to the additives causing swelling of O-ring seals, which may result in fuel leaks.

It is now becoming clear that oxygenates in general can act as octane boosters. The well-researched, demonstrated and commercialised are ethers, particularly MTBE and ETBE, and alcohols, particularly ethanol and potentially butanol, which can be produced from renewable sources. Other oxygenates, such as acetone and esters, are of interest to the racing fuels community but the inclusion in retail gasoline is opposed by the original engine manufacturers.

Methanol, which is opposed by the original engine manufacturers, has been widely used in China where it can be produced from local, low-cost coal. Methanol does not mix well with gasoline and probably to help assist with this problem and maintain access to a low-cost blendstock, there has been a rise in the use of dimethoxy methane (methylal). Methylal can be produced by oxidation of methanol or from methanol and formaldehyde.

Another oxygenate of interest is diethyl carbonate, which delivers good octane (101RON) and, in contrast to ethanol, a low-vapour pressure impact. It seems to be a preferred co-additive to aniline compounds for producing high-octane unleaded AVGAS.

One problem shared by most of these octane-boosting additives is that they are more powerful solvents than pure hydrocarbon gasoline. This property leads them to dissolve into seals (O-rings), which causes the rubber to swell and can result in leaks in the fuel delivery system.

It is important that regulations and regulatory authorities remain in control of additives to gasoline and not inadvertently allow materials into the Australian petrol pool that damage vehicles and engines.



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- Professor Helen Sullivan director of the ANU's Crawford School of Public Policy
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Copper(II), hydrogen sulfide and wine - the ongoing saga

Some time after I published a technical paper on the measurement of copper in wine in 1983, I was called by a winemaker who wished to discuss the chemistry of copper additions to remove the aroma of hydrogen sulfide. The winemaker's concern was that after the addition of copper(II) sulfate, the off-aroma of H₂S disappeared, but it returned after about one month in tank. The winemaker said, 'I am trained in chemistry and spent many years working as an industrial chemist. The whole thing doesn't make chemical sense, as I know the solubility product of copper sulfide and it should simply precipitate and be removed'. I agreed and said 'leave it with me and I will get back with an answer'.

It is now about 35 years after that phone call; I have retired, as has the winemaker. Fortunately, Dr Andrew Clark of the National Wine and Grape Industry Centre (NWGIC) at Charles Sturt University has continued working on the copper–sulfide problem and is now unravelling the intriguing chemistry of this wine chemistry issue. Andrew, together with Nikos Kontoudakis and Anque Guo, has examined the complexities of copper sulfide filtration using model wines and white wines. The results take the understanding of the copper sulfide saga into the area of copper sulfide nanochemistry and the association of these nanoparticles with various wine components (see *Aust. J. Grape Wine Res.* 2019, vol. 25, pp. 53–61).

To model industry practice of adding copper(II) (see April 2015, p. 39), the NWGIC group used a tartaric acid/ethanol model wine to which CuSO_4 and Na_2S were added to give a final Cu:S ratio of 1:2. A 10-millilitre syringe filter was used in association with 0.45 and 0.20 μm pore size regenerated-cellulose filters. The copper concentration in the filtrate was measured to reflect the effectiveness of the filtration.

With the model wine, about 4% of the total copper in the system was found in the filtrate, seemingly all good news. However, when as little as 1% white wine was included with the model wine, about 70% of copper made its way into the filtrate, increasing to more than 90% with 10% white wine in the model. In separate experiments, it was found that the copper in the filtrate was present as copper sulfide, which I will write about in my next column. So, at least we have an explanation as to why the H₂S aroma can return to the wine over time: the sulfide is not actually being removed as copper sulfide - rather, it is being seguestered. An explanation in part perhaps, but not overly helpful to the winemaker. None-the-less, the results opened up several areas for research, including the influence of wine components on the filtration step, the size of the copper sulfide particles themselves and what the actual mechanism of filtration is: size discrimination or adsorption.

A search for wine components that influence the filtration step showed that white wine proteins and polysaccharides exerted a major influence on the filtration process. When added to the model wine, these macromolecules allowed close to 100% of the sulfide-bound copper to pass through the filter So, at least we have an explanation as to why the H₂S aroma can return to the wine over time: the sulfide is not actually being removed as copper sulfide – rather, it is being sequestered.

compared to only 4% of sulfide-bound copper in the absence of the macromolecule. Phenolic compounds allowed 30–35% of the sulfide-bound copper to pass through the membrane, a much lower effect than with the wine macromolecules. So, while copper–phenolic chemistry is important for wine oxidation, it is less critical for copper–sulfide chemistry.

Nanoparticle tracking measurements were carried out through a NWGIC collaboration with Agnieszka Mierczynska-Vasilev, Paul Smith and Eric Wilkes at the Australian Wine Research Institute. The results showed that when $\rm H_2S$ (from $\rm Na_2S$) and $\rm Cu^{II}$ were added to the model wine, the particles were much lower than 0.2 μm , markedly smaller than for white wine, where the majority of the particles were just below 0.2 μm with about 20% in the 0.2–0.3 μm range. The existence of smaller particles in the model wine was sufficient for the study authors to conclude that size exclusion was not the mechanism involved in the different filtration results for copper sulfide in model and white wines.

Using different filter materials, it became clear that the removal of copper sulfide is actually by an adsorption process, a process that is hindered by white wine proteins and polysaccharides. The impact of the macromolecules is most significant with the regenerated cellulose filters, while more effective, but not total, copper sulfide removal was observed with nylon and polyethersulfone filters. Differences in the hydrophilicity and/or polar activity of the filters is a question still be explored.

Recognition of the chemistry of copper sulfide nanoparticles in white wine and the interference by wine macromolecules on the filtration process has significantly advanced our understanding of the copper(II)/sulfide problem. The study authors do note that their experiments need to be repeated on a larger scale with selected filter materials, recognising that the type of filter most suitable for copper sulfide removal may not be effective for other wine filtration needs.



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.

DIY artists' pigments

Historic inorganic pigments are still used by painters, alongside the products of the modern chemical industry. The colours are mostly due to the presence of transition metal ions – green from copper; blue from copper, cobalt or iron (remember Prussian blue); yellow from chromium(VI). But one blue pigment is quite different. It occurs naturally in the mineral sodalite (see the photo of my personal sample), and in the gem form of the mineral lapis lazuli. There is a synthetic version, too, known as ultramarine and prepared by heating together various inorganic materials.

As well as its use by painters, ultramarine was applied to cotton clothing to colour-balance the yellowing that follows continual use and exposure to sunlight. The Reckitt company made their money by marketing this 'blue' for use in laundries. These days, many white fabrics are 'dyed' with colourless organic dyes that fluoresce blue-violet in daylight. Known as fluorescent brighteners, they are used to achieve the colour balance. Reckitt's product came in small bags of compressed blue powder that went into the rinse after the washing was complete. Because the bags were about the size of the top joint of a thumb, it was often referred to as 'thumb blue'. Recipes for making it were published in various places but, like most 'well-known' processes, making it work in practice required a certain skill. In the early 19th century, both British and French governments offered prizes for the production of ultramarine.

Attempts to produce a synthetic equivalent of lapis lazuli began in the early 19th century with analysis by European scientists of the natural product. As with most mineral analyses, the results were expressed in terms of oxides: soda 9%, alumina 31%, silica 42.5%, lime 3.5%, and sulfuric acid 5.9%. Fusing sulfur and sodium carbonate at red heat and sprinkling in sodium silicate and sodium aluminate – all in the correct proportions – produced ultramarine of variable quality, depending on the experimenter. Eventually it was found that heating to redness a mixture of kaolin (China clay), sulfur and sodium carbonate was a reliable way to produce a good product that could be regarded as a compound of aluminium silicate, sodium silicate and sodium sulfide. Modern mixtures include some charcoal or coal as a reducing agent.

Replacing sodium with potassium did not produce a blue colour, showing that the sodium is essential to the production of the blue colour. The calcium aluminium silicate lattice structure of the mineral, and presumably of the synthetic ultramarine, was established in 1929 by X-ray crystallography. There are large (on the molecular scale) cavities where sodium ions reside, their charges balanced by chloride, sulfate or sulfide ions. The blue colour is due to the presence of S_3^- ions that contain an unpaired electron.

In the 1860s, somebody in Melbourne had worked it out and started a factory to produce this thumb blue. He was William Sloggatt (1823–1900), a Cornish immigrant who arrived in



1851 at the age of 28 and went into business in the city as a trader. A decade or so later he moved to the then outer suburb of Malvern and began to manufacture 'blue'. His 1861 patent application described:

an invention for the application of a clay known as Kaolin in the manufacture of various articles of commerce not hitherto manufactured in the colony, that is to say, for the manufacture of cements, thumb blue of commerce, also as a substitute for white lead and Paris White in the manufacture of various pigments from the various oxides in the application of this clay or kaolin.

The fact that he called his product thumb blue suggests that he was aiming at the laundry market.

I found more information on the website of the Malvern Historical Society, one of whose members had researched Sloggatt's career. With a partner, Sloggatt became the owner of land in Glen Iris, adjacent to Malvern, and they named the estate 'Valency' after Sloggatt's birthplace in Cornwall. I couldn't find Valency on modern maps, but there is a Valency River that flows north and enters the sea near Boscastle, and closer to home there is Valency Road in Glen Iris, where Sloggatt's house – also Valency – once stood.

Sloggat was an amateur painter and had some of his oil paintings exhibited by the Victorian Academy of Arts, so I wondered if he used his blue (ultramarine) as a pigment in his work. I have been unable to track down any of them, so this has to remain an open question.



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29 April 2019, QUT, Brisbane, Qld ivvy.com.au/event/ELD822

21st Australia and New Zealand Electrochemistry Symposium

30 April 2019, QUT, Brisbane, Qld ivvy.com.au/event/ELD822

VCE Chemistry Unit 2&3: Investigating the Electrochemical Series, Electrochemical Cells and Faraday's Law

5 June 2019, RMIT University, Melbourne, Vic Register by 17 May at https://bit.ly/2toHpTs

Australasian University Safety Conference

25-27 June 2019 Crown Perth, WA ausa.org.au/ausa-conference-2019

NSW Polymer Group Symposium:

Synthesis and Application of Functional Polymers and **Polymer Architectures**

15 July 2019, University of Sydney, NSW markus.muellner@sydney.edu.au

Asian Federation for Medicinal Chemistry International Medicinal Chemistry Symposium

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

International Congress on Engineering and Food

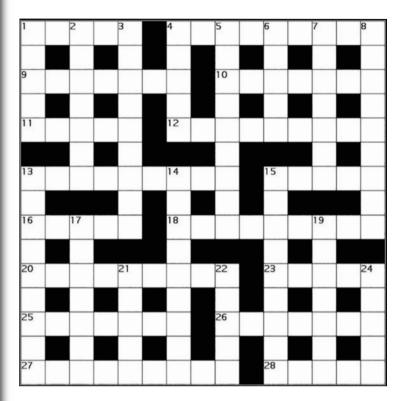
23-26 September 2019, Melbourne Convention Centre, Vic. icef13.com

Chemeca 2019

29 September – 2 October 2019, Sydney, NSW chemeca2019.org



cryptic chemistry



Across

- 1 Dug back to find textile. (5)
- Relocates faster RNS production. (9) 4
- 9 Passionate sounds under canvas. (7)
- 10 Less CrO used in the manufacture of hydroxy-substituted 25 Acrosses. (7)
- 11 Put out in Lake Victoria. (5)
- Handy new 1 Down when water is removed. (9)
- 13 Of late, mimes hold back arsenic, for example (9)
- 15 Ground discipline. (5)
- 16 Three or four elements are fundamental. (5)
- 18 Neutral crude? Hang around! (9)
- 20 Let censor work! Not 18 Across! (9)
- 23 Component of para-aminophenol derivative has been around a bit longer. (5)
- 25 Elute no mixture of C₇H₈. (7)
- Perhaps the 10 Across is around some 26
- 27 Goes down and uses a press?! (9)
- 28 Tables media sections. (5)

- 1 Trip and push. (5)
- Turn! Aim for old eleven. (7)
- 3 Action Mom attacked! Neon perhaps! (9)
- 4 $\theta = 90\eta$. (5)
- 5 Five or six or seven elements containing ethanol! (9)
- Sulfur wet fly. (5)
- 7 2-methyloxirane is one deep oxicompound. (7)
- 8 Pensile delayed. (9)
- 13 Buds eject product brought under control. (9)
- Same tutor makes constitutional isomers of organic compounds that readily interconvert. (9)
- 15 Derived from 2-phenylchromen-4-one of no valid program. (9)
- 17 Call around after she finds resin. (7)
- Immortal Spooner's pet speculation. (7)
- 21 That place for the 75. (5)
- Angular momentum forms sulfur fixes. (5)
- 24 Back selenium and sulfur or flowers result. (5)

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

Periodic Table of Younger Chemists: nominations open

In celebration of the 100th anniversary of IUPAC and of the 2019 International Year of the Periodic Table, IUPAC and the



International Younger Chemists Network (IYCN) are creating a Periodic Table of Younger Chemists. From July 2018 to July 2019, a diverse group of 118 outstanding younger chemists from around the world will be honoured. The resulting periodic table will highlight the diversity of careers, creativity and dedication of the young chemists leading this community into the next century. Each Young Chemist Element is profiled on the IUPAC100 website.

Elements are revealed over time and in order of scientific discovery, and announced monthly at various chemistry events, many being IUPAC-endorsed conferences. More than 40 Young Chemist Elements have already been revealed, including some for RACI members! The final elements will be revealed at the IUPAC World Chemistry Congress in Paris, France, in July 2019.

Nominations are ongoing, and are currently being accepted for the elements below. More information is available on the website, along with detailed criteria and access to the submission form.

If there are younger chemists who inspire you, nominate them now!

https://iupac.org/100/pt-of-chemist

Nominate by 1 April for:

technetium, francium, astatine, neptunium, plutonium, promethium, curium, americium, berkelium, californium

Nominate by 1 May for:

einsteinium, fermium, mendelevium, lawrencium, nobelium, rutherfordium, dubnium, seaborgium, bohrium, meitnerium

Nominate by 15 May for:

hassium, darmstadtium, roentgenium, copernicium, nihonium, flerovium, livermorium, oganesson, tennessine, moscovium

