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cover story

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We need to look at metals in new ways and in new places, to see what commodities are there for the taking, says Dave Sammut.

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From the President

The inaugural Decadal Plan for Chemistry (being coordinated by the Australian Academy of Science's National Committee of Chemistry in partnership with RACI) has been underway for more than a year. The initial phase involved an enormous amount of data collection throughout 2014. Twenty-six open 'Town Hall' meetings were held all over Australia, which were very well attended by RACI members. In addition, many one-on-one interviews and online surveys were held. All sectors of the chemistry community have been involved. This data has now been assembled and distilled, and a draft version of the Decadal Plan for Chemistry is available for public comment (<http://chemistrydecadalplan.org.au>). It's vital that we have as much feedback on this document as possible so the more people who are able to read and comment on it, the better it will be.

The Decadal Plan literally maps out the road ahead for chemistry as a discipline over the next 10 years, and making accurate predictions of where chemistry will be and how it will fit into the world in 2025 is more difficult than ever, given the rapid technological, scientific, economic and political changes that we are experiencing. The Decadal Plan must capture what is most important to us all and deliver strategies that will lead to significant improvements across all sectors. The Decadal Plan working group is only a very small subset of the Australian chemistry community. We don't have all the answers and solutions. We need your input!

Many findings came out of the consultation process. One of the clearest messages is the disconnection between many parts of the chemistry community such as academia and industry, and the secondary and tertiary education interface. Another issue is the general lack of awareness in society (and in politics) of what chemistry is and how reliant we have been on chemistry innovation over recent decades and over centuries before that. Getting our message out to the public is paramount and the chemistry community must take responsibility for this; it isn't good enough to say that 'nobody understands what we do.'

The timeline of the Decadal Plan clearly spans that of several future terms of government, so we dearly need a bipartisan agreement between the major political parties on how chemistry (and science for that matter) relate to our education system, and innovation (and economic prosperity). A long-term policy is

needed that will not simply be reversed by an incoming new government. There are some sobering statistics in the Decadal Plan draft document highlighting Australia's current position among OECD nations on the score of innovation and also investment by industry in academic research. Australia is, on many of these measures, 'holding up the table'. There is no reason why we should be in this position unless we accept (and I don't) that Australia is incapable of doing things as well if not better than comparable OECD nations in terms of translation of chemistry innovation into high-value technology.

The final (and most important) issue that remains, when the Decadal Plan for Chemistry document is tabled, is implementation. How can we ensure that the recommendations from this report are taken up by policymakers and the public? There are many examples of similar documents gathering dust after being written. We cannot repeat the same mistakes here.

RACI is obviously the largest representative organisation for chemistry in Australia and it will be doing all it can to communicate the virtues of this report to those who can help implement these recommendations. At the July 2015 Special General Meeting of RACI, the Constitutional changes proposed by the Board were overwhelmingly accepted. A key change was the ability to recruit up to two Board members from outside the chemistry sector. RACI, an Institute, restricts full membership (with voting rights) to those who hold a recognised chemistry degree (or equivalent). This formerly excluded the involvement of anyone on the RACI Board who did not have a formal chemistry tertiary qualification, yet there are many areas, beyond knowledge of chemistry, that require the RACI Board to make informed and strategic decisions. This restriction is now gone and the Board may appoint up to two non-members (non-chemists) who bring expertise that may not be available to the Board at that time. This will be an exciting opportunity for the Board and may also prove important in the communication and implementation of the inaugural Decadal Plan for Chemistry.



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Neville Currey

I read the June 2015 issue with interest. Ian Rae's column concerning little-known chemist Neville B. Currey was intriguing and I decided to do a little further searching of my own using trove.nla.gov.au. Trove is a valuable resource for lovers of early 20th-century Australian history.

Several entries indicate that he was a businessman and manufacturing chemist, active in the social scene of inter-war Melbourne. Exactly what business he was in is less clear.

It appears that he ran a business using his own name and also the 'Twilight Shoe Dressings Pty Ltd' company. In 1926, he applied for a trade mark, number 43 930, covering Twilight as a 'cleaner for evening shoes and all other forms of footwear', which was granted and renewed up to 2006, so perhaps a reader may recall the brand. In 1930, another application number 54 498 was made regarding 'heel pads for boots and shoes made of velvet, rubber solution and cotton, in which velvet (or cotton) predominates. A poster design displaying a comfort shoe grip'. In 1935, he exported a case of shoe cleaner to Hong Kong, presumably to build his business.

It seems reasonable to conclude that Currey's principal business was boot and shoe polish maker with a sideline in shoe accessories, rather than as a professional chemist of the stature of Professor Masson and the others mentioned by Ian.

Bruce Leary FRACI Hon Life Member

CSIRO's future

Ian Maxwell's analysis of CSIRO (July, p. 18), prompted by his meeting with new CEO Larry Marshall, will no doubt interest many readers of *Chemistry in Australia*. Ian admits to some confusion regarding CSIRO's role and its struggle to 'find relevance'. He sees a leadership seemingly desperate to make CSIRO more profitable or at least generate enough positive publicity to secure government funding. He wonders about its complicated structure and whether all parts suit the Australia of 2015. He suspects that future commercial income growth will be problematic as the market approaches saturation. Most significantly, he questions the emphasis on science when the real growth is in engineering and IT. According to Ian, Larry Marshall is still thinking about future strategy.

Yes, CSIRO can be confusing. It's old and big and carries lots of baggage. The National Flagship structure conveys its current focus easily but also suggests rigidity and excessive coverage. But I spent 30 years in CSIRO and am confident that it still has a role. Larry's challenge is to inject an agile element while ensuring the stable framework that R&D, a notoriously long-term human activity, requires.

CSIRO's strategic purpose should remain as the creation of new knowledge. The tests it should apply are deceptively simple. Does Australia need the new knowledge? Can CSIRO acquire and exploit that knowledge? Is it all worth the cost? But these are hard questions to answer. The results will be fuzzy. Judgements must be made. That's the nature of the business.

Structure follows strategy. Predetermining CSIRO's fields of activity through structures like flagships, or prejudging them as scientific or technological or engineering, can reduce flexibility and responsiveness, though I do acknowledge the need for focus.

Ian describes Larry Marshall as a serial entrepreneur, venture capitalist and private investor. That's a useful background for generating the discipline needed to guide CSIRO's future. Indeed, he may well see every CSIRO project as a kind of personal investment, a risk-laden venture for the funding he controls or can gather. That would be a great starting point but extremely difficult to apply consistently. I wish him luck.

Tom Biegler FTSE FRACI CChem

New coal chemistry

I greatly enjoyed Duncan Seddon's 'New coal chemistry' (July, p. 36). He gives interesting perspectives on the production of chemicals from synthesis gas and related issues, including greenhouse gas emissions.

Duncan mentions the release of carbon dioxide from the production of hydrocarbons from coal. This of course is due to the water gas shift reaction, to which he refers and for which he gives the chemical equation. Carbon dioxide from gasification can be sequestered, as is currently happening on a trial basis in Alberta, Canada. There, synthesis gas is made by underground gasification of coal and nearby geological sites for sequestration are being identified (Olateju B., Kumar A. *Appl. Energ.* 2013, vol. 111, pp. 428–40).

I wish also to draw attention to possible substitution of biomass for coal in making the synthesis gas, to whatever extent local availability of biomass makes this feasible. Carbon dioxide removed from synthesis gas so made would, like the carbon dioxide from combustion of biomass fuels, not contribute to the carbon dioxide level of the atmosphere. It would simply be put back where it came from, which is the basis of carbon neutrality of fuels. It also applies to synthesis gas.

Clifford Jones FRACI CChem

'Your say' guidelines

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

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Leap second keeps Australia on time



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Action taken by the National Measurement Institute (NMI) will keep Australia on time with the rest of the world. You'd be forgiven for not noticing, but every second counts in today's global markets.

At precisely 9:59:59 am (AEST) on 1 July, measurement scientists at the NMI added an extra second to their super-accurate atomic clocks, to account for a very slight slowing in Earth's rotation. In fact, it's thought that four billion years ago, a day on the planet lasted only 22 hours.

Observing this leap second at NMI's Lindfield facility in Sydney, Parliamentary Secretary for Industry and Science Karen Andrews said this was another example of how science and technology underpin daily life.

For more than a decade, NMI has supplied accurate timing systems that have linked the atomic reference clocks to industry, defence, government, law enforcement, telecommunications and financial markets.

The SI definition of the second is '... the duration of 9 192 631 770 periods of the radiation corresponding to the transition between two hyperfine levels of the ground state of the ^{133}Cs atom'. NMI's four commercial primary caesium frequency standards work to this definition.

The need for a leap second is determined by the International Earth Rotation and Reference Systems Services, which keep track of time by comparing the Earth's rotation against an international network of atomic clocks. The leap second keeps the time difference between the two 'clocks' to below 0.9 seconds.

The leap second is introduced to the world's atomic clocks in unison, immediately before midnight on 30 June UTC (Coordinated Universal Time).

DEPARTMENT OF INDUSTRY AND SCIENCE

Canberra researcher's medical discovery heading for market

US chemical company Strem Chemicals Inc. has signed a commercialisation agreement to market a new synthetic catalyst developed by University of Canberra researcher Associate Professor Ashraf Ghanem FRACI CChem that will help make the pharmaceutical manufacturing process more efficient.

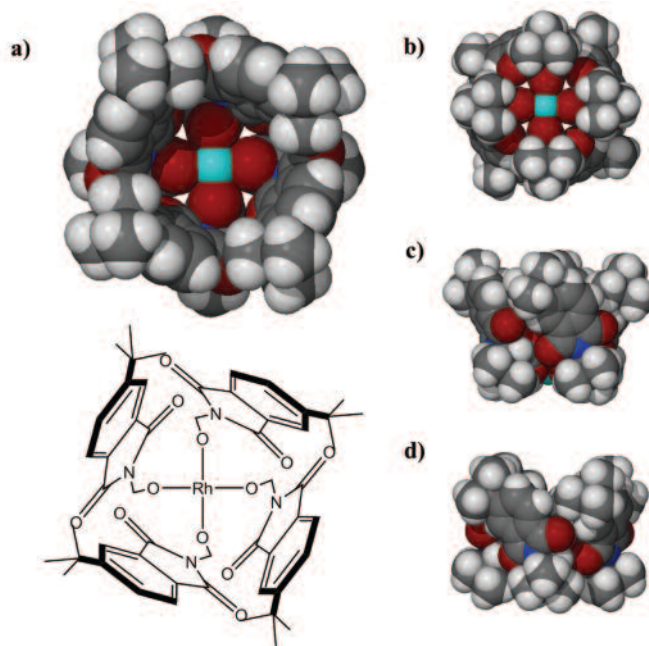
The deal is the University of Canberra's first intellectual property licence for a chemical product that will be sold worldwide.

The catalyst, discovered by Ghanem, will be useful in pharmaceutical processing, particularly in the production of the drug Ritalin (methylphenidate), which is used in the treatment of attention deficit disorder and attention deficit hyperactive disorder.

Ghanem explained that this synthetic catalyst produces a chemical reaction that allows certain molecules to be extracted with a very high level of purity, reducing the need for additional processing and diminishing the risk of unintended side effects.

'This is important because it can help produce more effective pharmaceuticals quickly, at a reduced cost and hopefully in the future that means people are paying less for the medication they need,' he said.

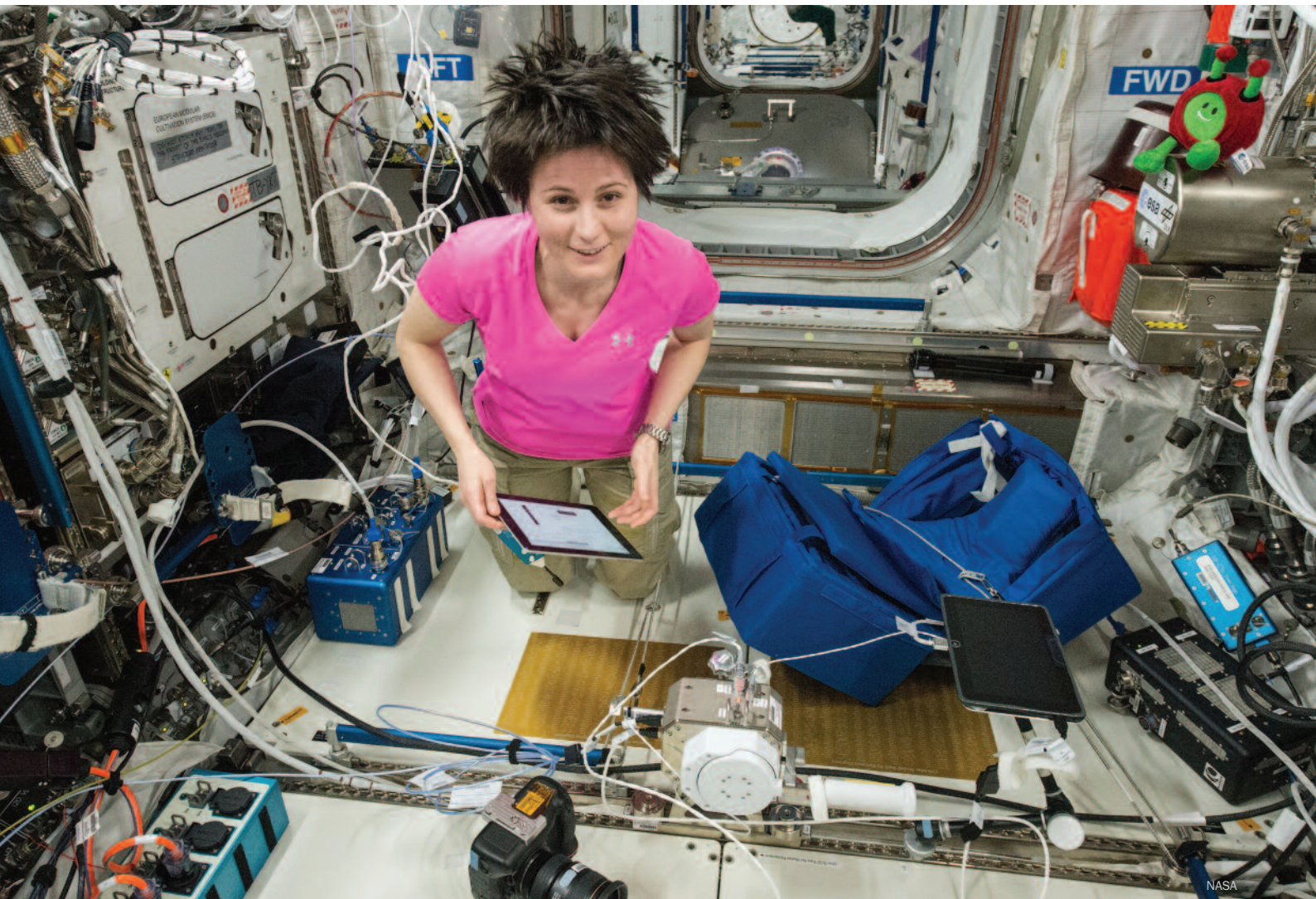
Ghanem said the path to commercialising his discovery has been hard work, but rewarding now that his research is delivering a beneficial outcome to the pharmaceutical field, with great flow-on effects for those depending on their medication.



Molecular structure of bis(THF) adduct of the catalysts $[\text{Rh}_2(\text{S-PTTL})_4]$. Space-filling representation: (a) top view, (b) bottom view, (c) and (d) side.

UNIVERSITY OF CANBERRA

Keeping astronauts in space longer with better air and water



Currently, ISS residents such as European Space Agency astronaut Samantha Cristoforetti must collect air and water samples and send them back to Earth.

As astronauts embark on increasingly ambitious space missions, scientists have to determine how to keep them healthy for longer periods far from Earth. That entails assuring the air they breathe and the water they drink are safe – not an easy task given their isolated locations. But scientists are now reporting in *Analytical Chemistry* (doi: 10.1021/acs.analchem.5b00055) a new method to monitor the quality of both in real time with one system.

Current options for testing air and water for contaminants, including microbes and radiation, require collecting samples and sending them back to Earth for analysis. But for long missions – aboard the International Space Station, for example – this approach could take six months before the astronauts have their results. The International Space Station is also

equipped with some real-time hardware for detecting unwanted substances, but it has limitations. Facundo M. Fernández, William T. Wallace and colleagues wanted to come up with a system to conduct real-time, sensitive monitoring.

The researchers outfitted a kind of air quality monitor already used aboard space missions with a device that can vaporise water samples, turning its contents and any contaminants, into a gas. The gas can then enter the air quality monitor for analysis. Astronauts could also use the same equipment, with a modification, for testing the air. The team says the system could be used in space or for remote locations here on Earth.

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GO Resources and CSIRO sign safflower deal

GO Resources Pty Ltd – a new Australian clean technology company – has entered into an exclusive worldwide licence with CSIRO to commercialise its technology to produce super-high oleic safflower oil for the high-value industrial oil market.

Super-high oleic oil represents a step in the development of plant-sourced alternatives to petroleum-based raw materials and traditional sources of oleic oils. GO Resources' super-high oleic safflower oil will have direct applications as a raw material for bio-based feedstock, with industrial applications including lubricants, solvents, cosmetics, plastic additives, resins and polymers, biofuels, coatings, paints and inks.

The estimated value of the worldwide industrial oils and oleochemical market is in excess of \$30 billion a year.

GO Resources will give Australian farmers access to safflower that produce very high levels of oleic acid (>92%) in the oil extracted from the seed. At the same time, there is a reduction in the levels of less-desirable saturated and polyunsaturated fats. This level of oleic acid is currently the highest of any commercially available plant-derived oil worldwide. Oleic acid is a naturally occurring and industrially significant fatty acid, traditionally sourced at much lower levels from palm, tallow and oilseeds.

GO Resources expects Australian commercial production to begin in 2018 and seeks to expand Australian and international opportunities over time.

GO RESOURCES



Solution to corrosive ocean mystery points to future climate

Researchers have discovered how an abrupt global warming event triggered a highly corrosive deep-water current to flow through the North Atlantic Ocean 55 million years ago.

The findings, published in *Nature Geoscience* (doi: 10.1038/ngeo2430), solve a long-running scientific mystery that also has profound implications for the sensitivity of our current climate to carbon dioxide emissions.

The researchers explored the acidification of the ocean that occurred during the Paleocene Eocene Thermal Maximum (PETM) period when Earth warmed 5°C in response to a rapid rise in CO₂ in the atmosphere and one of the largest mass extinctions occurred in the deep ocean.

This period is considered to closely resemble the scenario of global warming we are experiencing today.

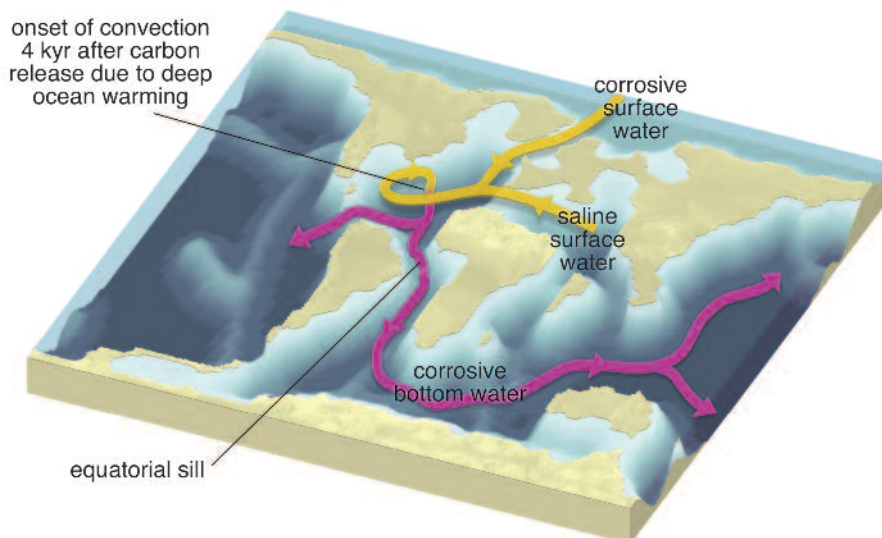
‘There has been a longstanding mystery about why ocean acidification caused by rising atmospheric CO₂ during the PETM was so much worse in the Atlantic compared to the rest of the world’s oceans,’ said lead author from the ARC Centre of Excellence for Climate System Science, Ms Kaitlin Alexander.

‘Our research suggests the shape of the ocean basins and changes to ocean currents played a key role in this difference. Understanding how this event occurred may help other researchers to better estimate the sensitivity of our climate to increasing CO₂.’

To get their results, the researchers recreated the ocean basins and land masses of 55 million years ago in a global climate model.

At this time, there was a ridge on the ocean floor between the North and South Atlantic that separated the deep water in the North Atlantic from the rest of the world’s oceans. It has been described as being like a giant bathtub on the ocean floor.

The simulations showed this ‘bathtub’ filled with extremely corrosive water from



In this bathymetric image, surface currents are yellow, deep currents are purple, shading shows the shape of the ocean floor.

the Arctic Ocean, mixed with dense salty water from the Tethys Ocean and sank to the North Atlantic seafloor where it accumulated. The sediment in this area indicates the water was so corrosive that it dissolved all the calcium carbonate produced by organisms that settled on the ocean floor.

When Earth warmed as a result of a rapid increase in atmospheric CO₂, it eventually warmed this corrosive bottom water. As this corrosive water warmed, it became less dense and was replaced by denser water sinking from above.

The corrosive deep water was pushed up and spilled over the edge of the giant ‘bathtub’ and flowed down into the South Atlantic.

Determining how the event occurred also has important implications for today’s climate and how it might warm in response to increases in atmospheric CO₂. This is because if the high amount of acidification in the Atlantic Ocean was an indication of global acidification, then it would suggest enormous amounts of CO₂ are necessary to increase temperatures by 5°C.

However, these latest findings suggest that other factors made the Atlantic bottom water more corrosive than in other ocean basins.

‘We now understand why the dissolution of sediments in the Atlantic Ocean was different from records in other ocean basins,’ said fellow author of the paper Associate Professor Katrin Meissner from the Climate Change Research Centre at the University of New South Wales.

‘Using all sediments combined, we can now estimate that the amount of greenhouse gases released into the atmosphere causing a temperature rise of 5°C was around the CO₂ equivalent of 7000–10 000 gigatons of carbon. This is similar to the amount of carbon available in fossil fuel reservoirs today.’

The big difference between the PETM and the alteration to the current climate is the speed of the change, said Alexander.

‘Today we are emitting CO₂ into the atmosphere ten times faster than the rate of natural CO₂ emissions during the PETM,’ Alexander said.

‘If we continue as we are, we will see the same temperature increase that took a few thousand years during the PETM occur in just a few hundred years. This is an order of magnitude faster and likely to have profound impacts on the climate system.’

UNIVERSITY OF NEW SOUTH WALES

On-board laboratory for Otago research centre



The new Class 100 clean laboratory is lifted onto the RV *Tangaroa* for its maiden voyage.

The University of Otago/NIWA Research Centre for Oceanography has turned a brand-new shipping container into a clean laboratory for use on board research vessels – keeping New Zealand on the map internationally for research on marine biogeochemical cycles of trace elements.

The Centre, which was established in 1996 by a memorandum of understanding signed between NIWA and the University of Otago, won the Prime Minister's Science Prize in 2011.

Centre Director Research Associate Professor Sylvia Sander of Chemistry says the Class 100 clean laboratory was funded through the Prime Minister's Science Prize money.

It recently finished its maiden voyage – a three-week sampling trip on board the NIWA RV *Tangaroa* with Dr Rob Middag – taking samples from the Hauraki Gulf and over the shelf to the east as part of a Marsden-funded research project.

Sander says while the Centre has used modified shipping containers as onboard laboratories previously, this is the first time it has had a new container fitted out professionally and for this purpose.

'The benefits are huge, because now we can be absolutely sure our samples aren't becoming contaminated. We spend weeks cleaning our bottles in acid before the trip, and then some intense weeks working on board. We don't want to find the samples are tainted.'

Preventing contamination is as vital as it is difficult, she said. Trace metals are present in the water in such minute

amounts, that any particle from the ship, the container or air could jeopardise the results. The new container is internally totally metal-free and the air is fully HEPA-filtered, removing all airborne particles.

Sander said the container laboratory keeps the University of Otago/NIWA Research Centre for Oceanography at the same level as its contemporaries across the globe.

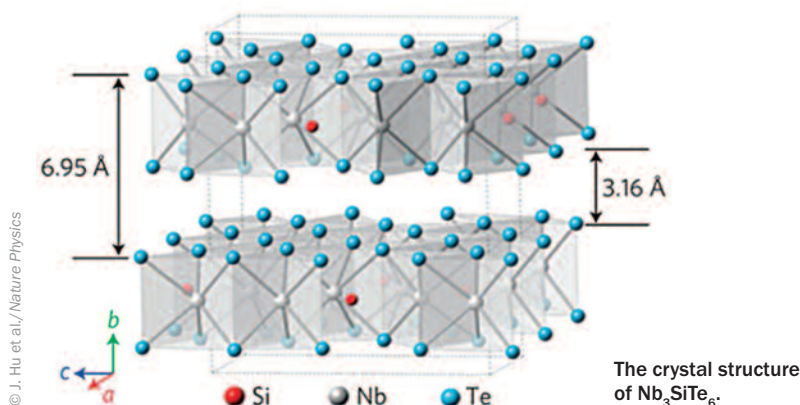
'This is especially important as we are a partner in the international GEOTRACES research program, which aims to improve understanding of biogeochemical cycles in the oceans,' she said. 'By mapping the distribution of trace elements and isotopes in the ocean, we can begin to understand the processes controlling this distribution – and to establish the sensitivity of these distributions to changing environmental conditions, such as climate change and ocean acidification. All results are rigorously quality controlled and we would not want to embarrass ourselves with results from contaminated samples.'

The container will be used for coastal as well as open ocean work on the micronutrients iron, copper and zinc, but also most other trace elements.

One of the next missions will be to the Kermadec Arc in 2016/17 on the German RV *SONNE*, where the Otago group is leading the trace metal sampling and analysis. Several other voyages including work in the Southern Ocean and Antarctic are also likely.

OTAGO BULLETIN

Transition from three to two dimensions increases conduction



Scientists from the Moscow Institute of Physics and Technology (MIPT) Department of Molecular and Chemical Physics have for the first time described the behaviour of electrons in a previously unstudied analogue of graphene, two-dimensional niobium telluride. In the process, they uncovered the nature of two-dimensionality effects on conducting properties. These findings will help in the creation of future flat and flexible electronic devices.

In recent decades, physicists have been actively studying so-called two-dimensional materials. Andre Geim and Konstantin Novoselov received the Nobel Prize for their research on graphene. The properties of such materials, which can be described as sheets a few atoms thick, strongly differ from their three-dimensional analogues. For example, graphene is transparent, conducts current better than copper and has good thermal conductivity. Scientists believe that other types of two-dimensional materials may possess even more exotic properties.

A group of scientists from Russia and the US recently conducted research on the properties of the crystals of one such material, Nb_3SiTe_6 . In their structure, the crystals resemble sandwiches with a thickness of three atoms (around 4 Å): a layer of tellurium, a layer of niobium mixed with silicon atoms and then another layer of tellurium. This substance belongs to a class of materials known as dichalcogenides, which many scientists view as promising two-dimensional semiconductors.

The scientists synthesised Nb_3SiTe_6 crystals. They then separated them into two-dimensional layers, taking samples for further analysis by transmission electron microscopy, X-ray crystal analysis and other methods. Their goal was to investigate electron-phonon interaction changes in two-dimensional substances.

Quasi particles, quanta of crystal lattice oscillations, are called phonons. Physicists introduced the concept of phonons because it helped simplify the description of processes in crystals, and tracking of electron-phonon interaction is fundamentally important for description of the different conducting properties in matter.

'We developed a theory that predicts that electron-phonon interaction is suppressed due to dimensional effects in two-dimensional material. In other words, these materials obstruct the flow of electrons to a lesser extent,' said Pavel Sorokin, a co-author of the study, from MIPT. US colleagues confirmed this prediction in related experiments.

Full details of the research can be found in an article published in *Nature Physics* (doi: 10.1038/NPHYS3321).

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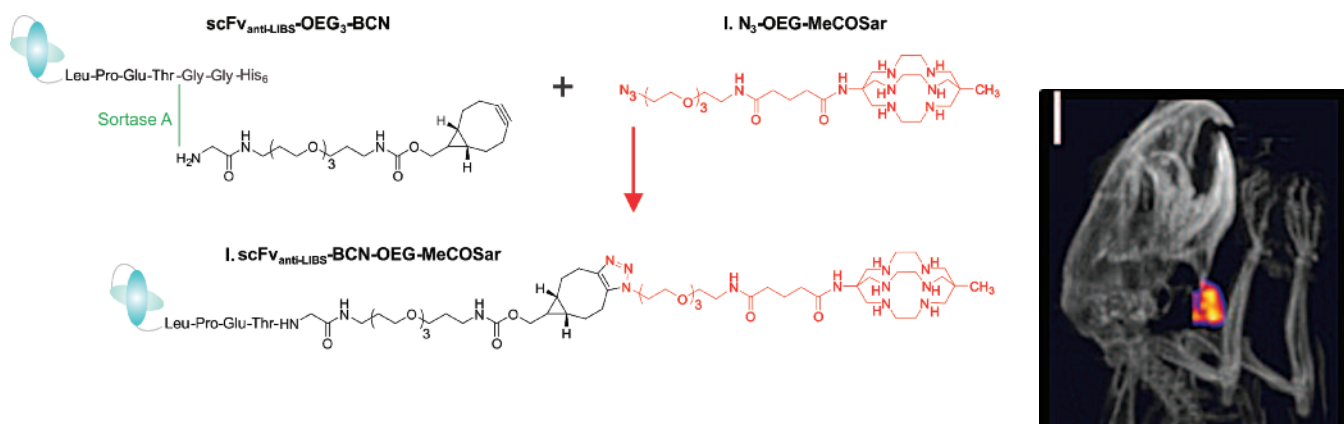
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Clicking imaging probes on to antibodies

A versatile two-step modular process for site-specific antibody modification and conjugation has been reported in *Angewandte Chemie* (Alt K., Paterson B.M., Westein E., Rudd S.E., Poniger S.S., Jagdale S., Ardipradja K., Connell T.U., Krippner G.Y., Nair A.K.N., Wang X., Tochon-Danguy H.J., Donnelly P.S., Peter K., Hagemeyer C.E. *Angew. Chem. Int. Ed.* 2015, **54**, 7515–19). In the first step, enzymatic bioconjugation with the transpeptidase sortase A is used to incorporate a strained cyclooctyne functional group

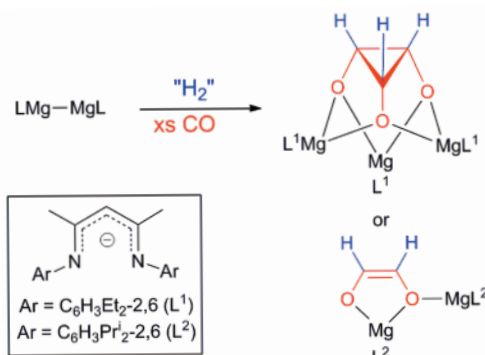
into an antibody. Functional molecules bearing an azide functional group are then added by an azide–alkyne cycloaddition click reaction that completes the site-specific bioconjugation. The team, led by Associate Professor Paul Donnelly and Dr Brett Paterson from the University of Melbourne and Professor Christoph Hagemeyer, Professor Karlheinz Peter and Dr Karen Alt from Baker IDI, demonstrated the versatility of the two-step approach by selectively incorporating fluorescent dyes and a

positron-emitting copper-64 radiotracer into a single-chain antibody fragment that targets activated platelets. The resulting constructs could be used for fluorescence or positron-emission tomography imaging of activated platelets and thrombi. This approach could be readily adapted to incorporate a large array of tailor-made functional groups using reliable click chemistry while preserving the activity of the antibody or other sensitive biological macromolecules.

Magnesium gets its snout in the Tropsch

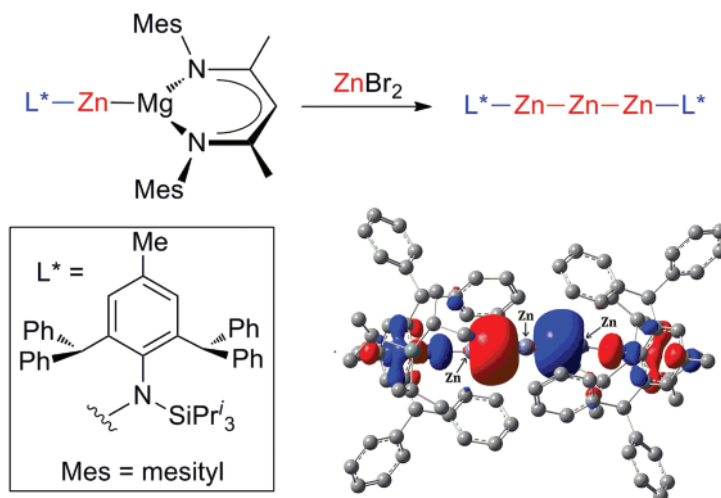
The heterogeneously catalysed transformation of synthesis gas (CO/H₂) to hydrocarbons and oxygenates, via the Fischer–Tropsch (F–T) process, is carried out on an industrial scale. However, such transformations are very energy intensive and offer low product selectivity. Accordingly, considerable efforts are currently directed towards developing homogeneous d-block metal catalysts that enhance F–T selectivity. Until now, such ‘F–T-like’ reactivity has not been observed for s-block metal compounds. In a recent paper, Professor Cameron Jones of Monash University and his collaborators (Maron, Toulouse; Stasch, Monash) have achieved this for the first time (Lalrempuia R., Kefalidis C.E., Bonyhady S.J., Schwarze B., Maron L., Stasch A., Jones C. *J. Am. Chem. Soc.* 2015, **137**, 8944–7). They showed that the formal hydrogenation of magnesium(I) dimers in the presence of CO leads to C–C bond-forming reactions and the selective formation of unprecedented cyclopropanetriolate or ethenediolate complexes, depending on the steric bulk of the magnesium reactant employed. A

computational investigation showed the mechanisms of the reactions to be very similar to those previously proposed for related processes involving f-block metal hydride compounds. This study highlights the potential of cheap and non-toxic magnesium compounds for transforming feedstock gases to value-added oxygenate products.



New zinc supplement

The chemistry of compounds containing unsupported post-transition metal-metal bonds has rapidly expanded since the landmark preparation of the first zinc(I) dimer, $\text{Cp}^*\text{ZnZnCp}^*$ ($\text{Cp}^* = \text{C}_5\text{Me}_5^-$), in 2004. Subsequent computational studies have suggested that extended metal chain analogues of this system would be thermodynamically unstable, and hence not synthetically accessible. The team of Professor Cameron Jones at Monash University has turned this view on its head, with the synthesis of the first mixed-valence, two-coordinate, linear tri-zinc complex, $\text{L}^*\text{ZnZnZnL}^*$ (Hicks J., Underhill E.J., Kefalidis C.E., Maron L., Jones C. *Angew. Chem. Int. Ed.* 2015, doi: 10.1002/anie.201504818). This compound is kinetically stabilised by a 'super bulky' amide ligand developed by the group. It was accessed by first preparing a formally zinc(0) complex by reduction of L^*ZnBr with a magnesium(I)

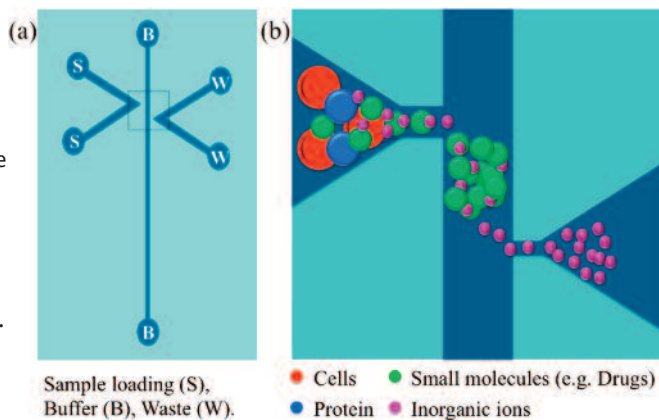


dimer, also developed at Monash. This zinc(0) species contains the first example of a Zn–Mg bond, and was used as an 'inorganic Grignard reagent' in its reaction with ZnBr_2 , yielding the target tri-zinc complex. Computational studies reveal that this compound is best viewed

as a covalently bonded $[\text{Zn}_3]^{2+}$ dication that is stabilised by two anionic amide ligands. The Jones team is currently exploring the reactivity of $\text{Zn}^{0/1}$ compounds towards small-molecule activation processes.

New approach to on-site therapeutic drug monitoring

Better health can be achieved through personalised medicine. In particular, low-cost and easy-to-use point-of-care devices that provide quick and accurate results for on-site therapeutic drug monitoring would help clinicians to adjust dosing regimens for individual patients. An entirely new way to extract, isolate and concentrate drugs from body fluids suitable for disposable point-of-care devices has recently been developed by Aliaa Shallen, a PhD student from the Breadmore and Guijt group in the Australian Centre for Research on Separation Science (ACROSS) at the University of Tasmania (Shallen A.I., Guijt R.M., Breadmore M.C. *Angew. Chem. Int. Ed.* 2015, **54**, 7359–62). An electrokinetic size and mobility trap based on two sequential nanojunctions with different pore sizes is used to capture pharmaceutical targets prior to a rapid electrophoretic separation for identification and quantitation. Levels of the antibiotic ampicillin were determined in 5 min directly from 40 μL of whole blood. The linear-response regime for the device of 2.5–20 $\mu\text{g/mL}$ covers the recommended levels for treating sepsis, a critical condition with 30–50% mortality for which treatment is complicated by unpredictable drug



levels. This new method is simple, applicable to a wide range of pharmaceuticals, and compatible with low-cost microfabrication, and hence has the potential to bring therapeutic drug monitoring within the reach of many.

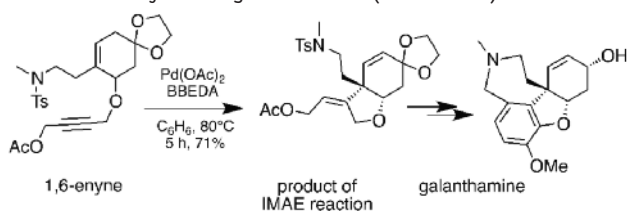
Compiled by **David Huang** MRACI CChem (david.huang@adelaide.edu.au). This section showcases the very best research carried out primarily in Australia. RACI members whose recent work has been published in high impact journals (e.g. *Nature*, *J. Am. Chem. Soc.*, *Angew. Chem. Int. Ed.*) are encouraged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

Aust J Chem

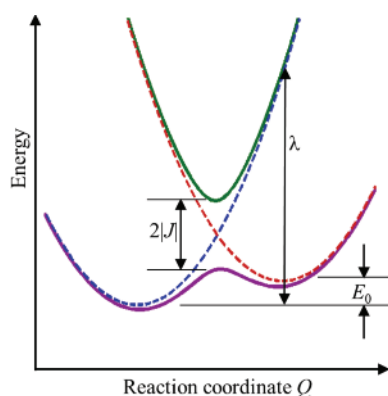
The August issue contains several papers and accounts by the 2014 RACI award winners announced in Adelaide last December.

Dave Winkler (CSIRO, Clayton), the winner of the Adrien Albert Award for medicinal chemistry, describes new computational modelling tools capable of exploring large chemical spaces, extracting meaning from large data sets, designing new bioactive molecules, and making predictive, quantitative models of the properties of materials for use in therapeutic and regenerative medicine.

Martin Banwell (ANU), winner of the H.G. Smith Memorial Award, reports on the use of Pd^{II} -catalysed intramolecular Alder-ene (IMAE) reactions of *C*-, *N*- and *O*-linked 1,6-enyne-type compounds in the preparation of various carbo- and hetero-cyclic compounds, including total syntheses of the alkaloids hamayne and galanthamine (see scheme).



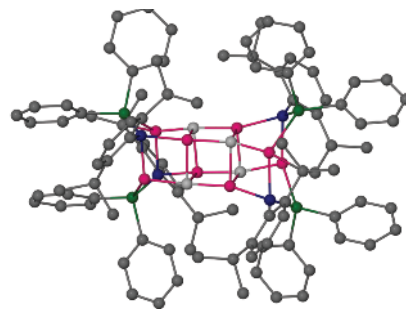
Jeff Reimers (University of Technology Sydney), winner of the Physical Chemistry Division Medal, elaborates the concept of reaction coordinate – a well-known quantity used to define the critical motions in chemical reactions, but many other motions – often ignored – always accompany it. Spectral measurements that one may assume are dominated by the reaction coordinate could instead be dominated by other, accompanying modes. The assignment of the visible absorption spectrum of chlorophyll-*a* was debated for 50 years, with profound consequences for the understanding of light-



harvesting. In Reimers' new assignment, the centrepiece is the determination of the reaction coordinate for a previously unrecognised photochemical process. The notion that spectroscopy and reactivity are closely connected

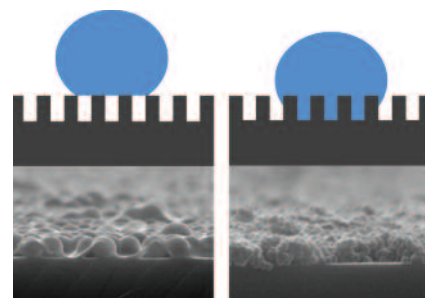
follows from Hush's adiabatic theory of electron-transfer reactions. These ideas are applied to isomerisations, hybridisation, aromaticity, hydrogen bonding and understanding why the properties of first-row molecules such as NH_3 (bond angle 108°) are so different from those of PH_3 – BiH_3 (bond angles 90 – 93°). In the new approach, all chemical processes are described using the same theory.

Andreas Stasch (Monash), winner of the Organometallic Chemistry Award, reviews the synthesis and characterisation of well-defined alkali metal hydride complexes and the principles governing



their generation and stabilisation. The properties of the familiar alkali metal hydrides such as LiH and NaH are dominated by ionic NaCl -type structures. Stable, soluble and well-defined LiH and NaH complexes are obtained by metathesis and β -hydride elimination reactions and by using bulky ligands coordinating to multiple metal ions. The structure of $(\text{DipNPPH}_2)_4\text{Li}_8\text{H}_4$, where $\text{Dip} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$, is shown. The reactivities of these novel hydride complexes are higher than, and different from, those of the familiar ionic solids.

David Lewis (Flinders), winner of the Applied Research Award, used silica nanoparticles to investigate the effect of surface roughness of hydrophobic films



on contact angles and sliding angles for water droplets.

Superhydrophobic materials are of much interest due to their self-cleaning, antifouling, stain-resistant and ice-repellent properties. On a rough surface, the droplet can reside in one of two states, either resting on the surface summits, with small pockets of air underneath, or filling the grooves and thus gaining direct contact with the solid substrate surface as indicated in the figure. The 'Cassie state' (left) is desirable in order to achieve low sliding angles because a smaller contact area results in less adhesion. The water contact angle increases from 105° for a smooth surface to 140° for the roughened surfaces, and it then remained approximately constant for all nanoparticle-roughened surfaces.

Additional papers by Chris McErlean (University of Sydney), winner of the Athel Beckwith Lectureship (chemistry of the synthetic strigolactone mimic GR24), Anthony O'Mullane (QUT), recipient of an RACI Citation (electrochemical restructuring of copper surfaces using organic additives and its effect on the electrocatalytic reduction of nitrate ions), and this author, winner of the Arthur J. Birch Medal (acetylenes from aldehydes) complete the awards section.

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http://uq.edu.au/uqresearchers/researcher/wentrupc.html?uv_category=pub

Chocolate

A moveable feast

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BY **EAGRANIE YUH**

The next time you snap a piece off a chocolate bar for afternoon tea, consider the polymorphic behaviour of cocoa butter.

Chocolate. Once reserved for emperors and royalty, this edible luxury is now within the reach of most people. Legend has it that Aztec warrior Montezuma demanded 50 chalices of *chocolatl* – drinking chocolate spiced with annatto (a natural colouring agent), which would stain the drinker's lips blood-red – before retiring with his harem of wives. (No word on what his wives thought of the brew.)

Chocolate is made from cacao beans, which are obtained from the pods of *Theobroma cacao*, a tree that grows 20° above and below the equator. When ripe, each pod is sliced open and its mucilaginous fruit are

removed and fermented, a process that converts the fruit sugars into a soup of ethanol, acetic acid and lactic acid. At this point, the cacao bean is not particularly tasty, but it contains flavour precursors with the potential to express the chocolate flavour that many of us seek. Next, the resulting cacao beans – a misnomer, as botanically, they're actually seeds – are dried to a maximum of 8% humidity, and then shipped to a chocolate maker.

The chocolate maker winnows the beans to remove their papery husks, and roasts them to transform flavour precursors into full-blown flavours. The Maillard reaction creates roasty pyrazines, floral oxazoles, and even

vegetal pyridines. Other pathways can result in fruity esters, nutty furans, butterscotchy diacetyls, and more. Depending on the roasting temperature, acetic and lactic acids can persist, as do some of the bitter alkaloids that provide chocolate's much-touted health benefits.

Once roasted, the cacao beans are ground into a paste called cocoa liquor, cocoa mass, or unsweetened chocolate. Subjected to temperature and pressure, the paste can be separated into its two constituent components – cocoa solids and cocoa butter. Cocoa solids are the dry portion of the cocoa bean, much like cocoa powder used in baking. Cocoa butter is a solid fat at room temperature and melts just below body temperature.

To make high-quality dark chocolate, chocolate makers combine cocoa liquor and sugar, often adding vanilla and lecithin (an emulsifier). Milk chocolate contains the same, plus milk powder. White chocolate contains no cocoa solids, and is a combination of cocoa butter, sugar and milk powder. A good test for your chocolate's quality is a quick scan of the ingredients list: if sugar comes first, you are buying candy, not chocolate. Another cue is the presence of vegetable fats, which offer cheap substitute for the more expensive cocoa butter.

In fact, it's cocoa butter that is responsible for much of the pleasure associated with eating chocolate. In addition to creating chocolate's luxurious melt, cocoa butter provides a vehicle for all of chocolate's estimated 600 flavour molecules to reach our taste and olfactory receptors.

Like other fats, cocoa butter is a mixture of triglycerides. The primary fatty acid components are oleic acid, an 18-carbon chain with one *cis*-double bond; stearic acid, a saturated 18-carbon chain; and palmitic acid, a saturated 16-carbon chain. Trace amounts of linoleic acid and arachidic acid can also be found, but typically

comprise less than 5% of cocoa butter's make-up. An estimated 80% of cocoa butter is of the form saturated–unsaturated–saturated (SUS) and 5–20% is saturated–unsaturated–unsaturated (SUU). A very minor proportion is composed of the all-saturated (SSS) or all-unsaturated triglyceride (UUU).

The relatively simple composition of cocoa butter belies the complexity of its crystallisation behaviour. In the realm of edibles, sodium chloride is your reliable, stalwart friend – barring the introduction of any interloping cations, it will always adopt a simple cubic crystal structure. Cocoa butter, then, is a rebellious and rambunctious stepchild, a polymorphic substance that can adopt up to six crystalline forms – the melting points of which nearly overlap. These are, most originally, labelled form I (the least stable, with a melting point of 16–18°C) through to form VI (the most stable, with a melting point of 34–36°C).

Six crystalline forms may be possible, but only one is desirable: form V, which offers the shiny and snappy chocolate that is so readily moulded into bars, bonbons and barks. The process of obtaining form V crystals is called tempering.

The first step to tempering is to heat chocolate over a double boiler, to melt any and all cocoa butter crystals that may be present. This may seem counterintuitive, given that commercial chocolate is already tempered, but unless you are serving your guests chocolate chips, melting is a must. In culinary school, I was taught to heat the chocolate to at least 40°C to provide a blank slate of liquid chocolate. (There is nothing magical about 40°C, except that it is safely above the melting point of all cocoa butter crystals but not so hot that the chocolate will burn.)

Next, transfer one-third of the chocolate to a marble countertop and spread it thinly using a long, offset spatula. Using a spackle knife (yes, the



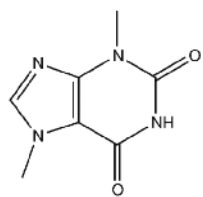
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kind you would use on a wall), scrape up the chocolate, then repeat the process of spreading and scraping until the chocolate thickens and becomes slightly pasty, like a nut butter. Heat transfer from the chocolate to the marble speeds cooling, encouraging the formation of the less stable crystal forms I and II. Conveniently, these crystals are highly unstable; form I crystals quickly give way to form II, which rearrange to form III, and so forth.

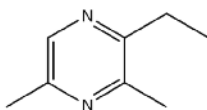
In addition to creating chocolate's luxurious melt, cocoa butter provides a vehicle for all of chocolate's estimated 600 flavour molecules to reach our taste and olfactory receptors.



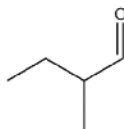
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theobromine



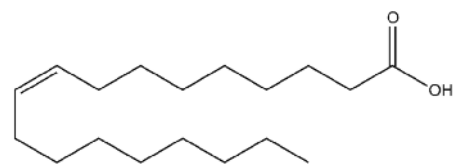
3,5-dimethyl-2-ethylpyrazine



2-methylbutanal

The complex tastes, aromas and flavours of chocolate come from a wide range of chemical compounds.

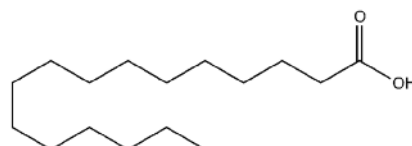
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oleic acid



stearic acid



palmitic acid

The primary fatty acid components of chocolate.

Chocolate inevitably morphs from form V to form VI crystals. The latter is ugly, but safe to eat.

Next, add the thickened chocolate back to the main bowl and stir to incorporate. The crystals created by table-cooling will propagate through the bulk chocolate. Even still, the chocolate will likely be a muddle of crystal forms I–V, with its exact composition depending on its temperature and the extent of mixing. (Form VI crystals are formed by a solid–solid rearrangement, and are not obtained from liquid chocolate.)

Finally, re-heat the chocolate to a temperature of 30–32°C. This temperature range is above the melting point of the crystal forms I–IV, but below the melting point of the form V crystal. In short: all the unstable crystals melt, and only form V crystals remain. Further stirring and time will encourage propagation of the form V crystals through the liquid chocolate, providing you with a bowl of tempered chocolate.

However, as I have learned from experience, tempering requires more than just cycles of heating and cooling. French chefs in towering paper hats taught me a mnemonic for tempering: TMT, or temperature, movement and time. Temperature, as we have seen, controls the types of cocoa butter crystals. Movement and time, however, are equally important. Within the liquid chocolate, fat solidifies onto seed crystals – in an ideal system, onto form V crystals – and adopts the same form, helping the crystals propagate through the bulk material. Therefore, it is important to stir the chocolate, in order to spread the seed crystals among as many fat particles as possible. And while the conversion from forms I and II crystals is quite rapid, form V crystals are the slowest to form. Therefore, you must allow time for the form V crystals to make their way through the bulk chocolate.

There are other methods for tempering chocolate. The method described above is the tabletop method, but the seeding method is also widely used. With the seeding method, a bowl of chocolate is melted completely and then seeded with a small portion of form V crystals. This is typically in the form of finely chopped or grated commercial chocolate, and some companies now offer form V powdered cocoa butter for this purpose. The principle is similar to the tabletop method: melt all the crystals, seed with form V, and hold the temperature at 30–32°C to encourage propagation of the form V crystals. Most chocolate shops use industrial tempering machines with various temperature-controlled compartments and mechanised stirrers, but the basic principles of using temperature, movement and time still hold.



(Top row left to right): Half-melted chocolate in a bowl.
Pouring one-third of the liquid chocolate onto marble.

Continuing to scrape up the chocolate. The cycles of spreading and scraping continue until the chocolate starts to thicken.

(Bottom row left to right): The chocolate has thickened to a point where it can sit on the scraper and not run off; it would feel cool to touch. This is the consistency you want before adding it back to the bowl of chocolate.

The different viscosities of the chocolate in the bowl (especially at about 2 o'clock) and the cooled chocolate, pooled on the spatula. Chocolate that has been heated to about 30°C. With more stirring and time, the form V crystals will propagate throughout to result in a bowl of tempered chocolate.

If this rigmarole seems excessive, consider the consequences of a chocolatier not using tempered chocolate. For example, to create a hollow Santa, chocolatiers typically use polycarbonate moulds: they fill them with chocolate, tap out the excess and allow the chocolate to set. Here, the crystal-packing behaviour of cocoa butter comes in very handy. Crystal forms I–IV are more loosely packed than forms V and VI. Consequently, as properly tempered chocolate sets, it shrinks by approximately 2% in each dimension. This shrinkage makes it easy for a chocolatier to remove their products from a mould. Once the chocolate sets, it's a matter of a

confident rap on the bench to dislodge it from the mould. Pity the chocolatier who has not used tempered chocolate – it will stick to the mould, no matter how hard they try to extricate it.

Properly tempered, plain chocolate has very low water activity and if stored in a cool, dark place, will keep for at least a year. Any 'best before' dates are mostly for enjoyment, rather than food safety. This is due to the slow rearrangement of form V crystals to the more stable form VI, which can result in a more brittle, less melty chocolate. This solid–solid rearrangement occurs slowly, over the course of many months. Because form VI crystals are packed more closely than form V, the change

causes interstitial liquid cocoa butter to be squeezed from the interior onto the surface, resulting in a slightly yellow sheen called fat bloom. The issue is exacerbated in systems with other fats, namely milk chocolate and anything with nuts or nut fillings. It can also occur if chocolate is not stored properly – that is, if it is subjected to variable temperature or humidity. Notably, while fat bloom looks like mould, it is not. So, go ahead – that chocolate Santa is still safe to eat.

Eagranie Yuh is a freelance writer and editor who teaches people how to taste chocolate. She was previously an organic chemist and a chocolatier. She is the author of *The chocolate tasting kit* (Hardie Grant) and lives in Vancouver, Canada. Learn more at thewelltemperedchocolatier.com.



Groundbreaking work

Smart ways to seek metals PART I

We need to look at metals in new ways and in new places, to see what commodities are there for the taking, says
DAVE SAMMUT.

Almost 50 years ago, the Club of Rome published a notorious text, *The predicament of mankind*, which made dire predictions about the limited availability of non-renewable resources, most particularly oil. Subsequent versions – peak oil, peak copper, peak helium – have been desperately overblown.

Although those predictions have been repeatedly wrong – failing to properly consider advances in technology, replacement, and supply and demand – basic mathematics says that sooner or later their underlying principle has to be correct. Perhaps more critical than the absolute quanta of resources available versus those required to serve the growing population and per-capita consumption, the *rate* at which resources can be gathered and distributed is likely to become a key

factor in global geopolitics. With scarcity comes competition. When nations compete for resources, war is too frequently the result.

Crude oil resources are becoming deeper and more sour (higher sulfur content). Miners are increasingly required to turn to deeper, lower grade, more complex (often polymetallic) resources, often in less politically stable regions. Barring incremental improvements in efficiency and scale, production costs across many metals industries are rising.

I have spent much of my career working on ways to improve the efficiency of metals extraction and processing, most particularly in step-change new technology for base metals (copper, lead, zinc and nickel). Throughout this time, the opportunity for any new technology has been closely linked to the global prices of

these commodities, but not always in straightforward ways. It has often been that the greatest pressure to bring forward advances has been when the prices were trending downwards, and therefore when margins were under threat. Of course, there comes a time in such a cycle when the innovative money simply dries up and all progress slows or stops, but the underlying message has always been 'if your new technology can get into the bottom quartile of the industry cost curve, then it might have legs.'

Clearly, if new technology can extend the life of existing mines, if it can rework old ground to more thoroughly exploit what has already been disturbed, then the need to open new mines to satisfy demand is deferred.

This is the first of a two-part discussion of some clever ideas in the technology pipeline that might one day play their part in the global metals cycle. None is yet truly competitive, but the whole point of the supply-demand equation is that the situation will always be fluid. As the pressures shift, one company's problem will become another's opportunity.

Above-ground resources

The best form of metal resource is metal that is already above ground. For this purpose, scrap recycling is a thoroughly established ideal. Metallic lead, for example, is one of the most recycled metals on Earth, far more than even copper or aluminium. According to the International Lead Association, more lead is recycled each year than is mined, and used lead-acid batteries are 'the world's most recycled consumer product', at nearly 100% in North America and Europe.

Reworking old mine tailings is another established practice. With advancements in technologies, old tailings dumps can be an incremental source of metal sitting at-surface (without the costs and impacts of going deep). In simple terms, the older the

former mine, the more likely it is that the tailings can be usefully re-worked, both because of the improvements in extraction and because older mines were generally higher grade. Some new mines being opened have lower grades than some early tailings dumps. For example, at the Migori Project in Kenya, the Macalder tailings has a grade of 1.7 g/t, while the Mikei shear zone (ore) has a grade of 1.3 g/t.

In a similar fashion, multiple proposals have looked at mining old municipal waste dumps, particularly those dating from the mid-20th century and particularly in North America. Such 'urban mines' have often decomposed much of the putrescible material (making the residue easier to reprocess), but were formed during an

era when the intensity of metals consumption had risen sharply and therefore have high metal grades.

Metals in sewage and wastewater sludge

For the past several years, a sewage treatment facility in the Nagano prefecture north-west of Tokyo has been recovering gold from incinerated sewage sludge. The gold levels in this ash have been world-class, with 1890 g/t of gold in the ash, as compared to <20 g/t for a typical gold mine. The prefecture reportedly expected to receive about 15 million yen from the recovered gold in its first fiscal year (2009), subject to gold prices ... and these went up considerably after the GFC.

According to the International Lead Association, more lead is recycled each year than is mined, and used lead-acid batteries are 'the world's most recycled consumer product', at nearly 100% in North America and Europe.



Lead-acid batteries continue to play a significant role in the automotive industry, and are a major source of metals.



Biosolids: a golden opportunity.

The gold content in the Nagano ash is somewhat higher than might generally be expected, reportedly because of a substantial local presence of high-tech industry, which is presumably somehow permitted to dispose of metalliferous waste to the sewers (this would attract heavy penalties in most regions of Australia).

More widely, metals are generally known to concentrate in sewage. This is due to their ubiquitous presence in household products, plus the effluents of local industry, storm run-off particularly from roads – which have levels of platinum group residues from automotive catalysts – and anything else that gets flushed down the drain.

A recent study (doi: 10.1021/es505329q) estimated that the sewage sludge from a typical US city with a population of one million could contain metals worth up to US\$13 million annually, including US\$2.6 million in gold and silver.

That metal value is an enticing economic 'pull' factor for recovery, but society should also be applying a 'push' factor to waste sludge. In many urban wastewater and sewage plants, including in Australia, the metals that are contained in the sludge are not stabilised in any way prior to the current disposal routes, often landfill, agriculture or oceanic outfall. Typical facilities rely on the greater bulk of the

organic residues to reduce metal content to levels deemed acceptable by regulatory regimes – a classic example of 'dilution as the solution to pollution'. In terms of the otherwise-reusable metals being thrown away, it makes the waste wasteful. Between the lost opportunity for reuse and the environmental effect of disposal, it's a double negative.

The key to the metal sludge studies has been the initial incineration of the sludge, which first removes the organics that would hinder most conventional metals extraction techniques, and second concentrates the (non-volatile) metals into the ash for easier recovery.

However, incineration creates its own potential problems, both technical and societal. Incineration of sewage sludge may generate limited calorific value, but the bulk of the energy is lost due to the heat of evaporation of water, so that fuels are actually added in some cases to incinerate the sludge. Some attention is being paid to alleviating this problem, mostly for developing nations. The Bill & Melinda Gates Foundation has, as an example, put its weight behind the Omni Processor, designed by a US firm to treat sewage on a thermally self-sustaining basis to yield clean drinking water.

Another obvious problem is that halogens are ubiquitous in waste and

sewage, through the extensive use of chlorinated and brominated plastics, and the natural processes that leach and distribute low levels of chlorine quite widely. When incinerating anything with significant organic levels and even low levels of halogens, persistent organic pollutants (POPs, particularly dioxins and furans) form readily between 250°C and 400°C. Incinerators may operate at higher temperatures, but the off-gases need to be rapidly quenched to prevent POP formation.

Incineration also has a reputational problem. Commonly practised in the mid-20th century, incineration of municipal waste was a convenient way of reducing mass and putrescible organic content. This was sometimes coupled to heat utilisation, but with limited or no emission controls, those practices were clearly problematic and were mostly phased out.

So the legislation and regulations governing the recovery of metals and energy from waste, in the case of materials with high calorific value, still carry the legacies of the old problems. Similarly, the social and environmental groups that are necessarily involved in the permitting of proposed waste to energy and waste recycling facilities tend to hang on to the negative connotations of the old paradigms. This is understandable, but it is an impediment to newer, clean facilities that can recover the useful components of sewage and/or other organic sludge.

New frontiers

In the second part of this series, I will explore seabed mining and asteroid mining as novel ways to address the world's future problems with metals supply. Each is technically fascinating, and both are massively challenging with potentially global environmental, societal and legislative consequences.

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

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A new element *in* teaching

Using apps in chemistry education

BY **OLIVER A.H. JONES** AND
MICHELLE J.S. SPENCER

Uni students are rarely without a tablet or smartphone. Although they can distract from learning, mobile devices can be useful educational resources.



Teachers, you have all been there: keen and ready to inspire young minds, you look out over the classroom only to see a good proportion of students playing with phones instead of paying attention, and becoming disengaged before you have even started talking.

You might take heart to know that you are not alone and that, while tablets and mobile phones may be relatively new, distractions in class are certainly not. This letter from a medieval father to his son studying at university (amzn.to/1dkqG90) reminds us that procrastination has always been with us, both outside and inside the classroom.

I have recently discovered that you live dissolutely and slothfully, preferring license to restraint and play to work and

strumming a guitar while the others are at their studies, whence it happens that you have read but one volume of law while your more industrious companions have read several. Wherefore I have decided to exhort you herewith to repent utterly of your dissolute and careless ways, that you may no longer be called a waster and your shame may be turned to good repute.

Eh Zaydel (trans), *Vagabond verse: secular Latin poems of the Middle Ages*, 1966

In 1845, at the insistence of the famous resident university, the railway station in Cambridge was built more than a mile from the centre of the town (where it is still located). Concerned that easy access to London would distract students from their studies, the university repeatedly blocked construction of a more central station



iStockphoto/4774344sean

over the years, and even (many years ago) restricted undergraduate travel (bit.ly/1KgPWf2). (Some have suggested that the dons may also have been worried that the station would spoil the view.)

Distractions are not always a bad thing. Railway trips to London enabled students from Cambridge and elsewhere to attend public lectures at the Royal Institution, for example. In the 21st century, smartphones and tablets are not going away, and while technology can be disruptive it can also be harnessed in the chemistry classroom to help teach and reinforce key ideas.

A surprisingly large number of chemistry-based apps are available for university and college students, chemistry professionals and teachers. These range from relatively simple but fun memory-based tests such as Andrey Solovyev's Molecular Games series (bit.ly/1fLNiaJ), e.g. Hydrocarbons, to extremely advanced systems, such as SpinDrops

(apple.co/1Hme9jp) for the interactive simulation of the dynamics of coupled spin systems (see screenshot on p. 26).









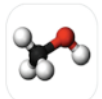
Some apps enable chemists to practise their basic skills, access a huge range of chemistry-related data, sketch and rotate small and large molecules and search online databases such as ChemSpider (apple.co/1RFsQxH). Some of these sorts of apps could be integrated into practical classes to replace, say, the SI chemical data book, or to share the results of an experiment with the entire class (to show variation in replicate measurements, for example) fairly easily. There are also apps to allow students to practise chemistry experiments safely at home. The Chemical Heritage Foundation's ChemCrafter app allows you to encounter fire and smoke, release various gases, and shatter equipment, all from the comfort of your own home (and without increasing your insurance premiums).

A review covering 30 or so of the more popular (and mostly free apps)

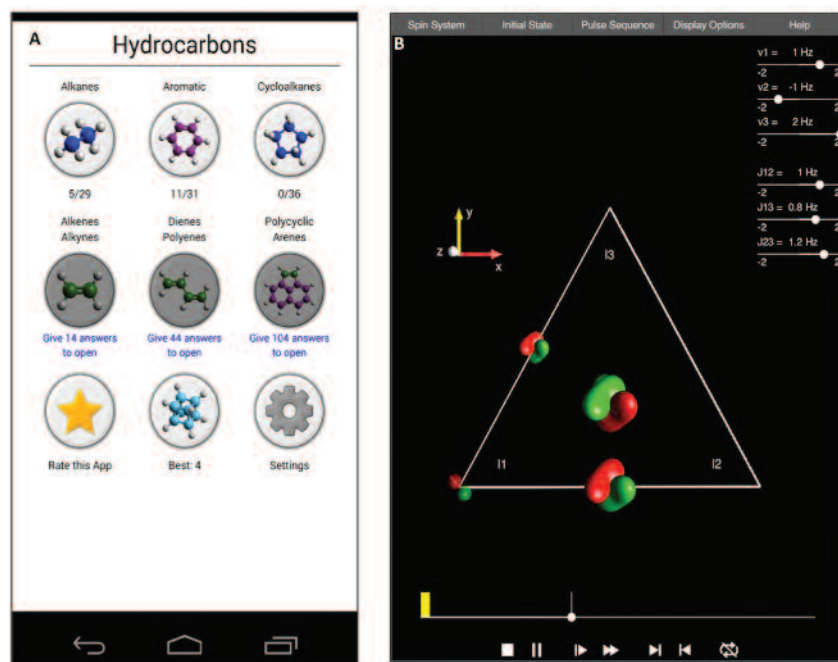
that can be used to learn chemistry and/or serve as reference or research tools was recently published in the *Journal of Chemical Education* (bit.ly/1SRFZ9a). A list of 'top 10' free chemistry apps for teachers, including descriptions, can be found at abt.cm/1Ktj0P5.

While some apps are free, some need to be purchased and some are free to download but offer and/or require in-app purchases to work, or at least work at a reasonable speed and allow you to progress through the levels. Cost can be an important factor to consider with apps and games, particularly for use in a classroom setting. In-app purchases are a significant drawback and source of annoyance in ChemCrafter for example.

Many chemistry apps provide an experience similar to traditional textbooks and papers, and the use of connectivity and interactivity possible with mobile devices is usually fairly minimal. This means that the user still

Chemistry Concept	App Name (Developer) and Summary	
Periodic Table/ Elements	Elementi (Marco Avizzano)  Search list of elements by name, symbol or atomic number. Gives links to the Wikipedia for each element.	Periodic Table (Usha Bhandari)  A single tap shows the information on each element. A double tap gives information from Wikipedia.
	Elemental (Dotmatics Limited)  Draw chemical structures, calculate cheminformatics properties, and even tweet your molecule.	Cmol (Helen Ginn)  Advanced molecular viewer. Allows control over representations & colours for individual chains, residues & atoms.
Chemical Formulas	Chemical Substances (Andrey Solov'yev)  One of a series of fun, quiz based games that test chemical knowledge.	Chemistry Allie (Overpass Limited)  Flashcard based chemistry memory game. Designed to help you brush up on your chemistry and periodic table knowledge.
Chemical Reactions	ChemCrafter (Chemical Heritage Foundation)  A virtual, high school chemistry set, relatively simple experiments and in app purchases are required to progress.	Chemical Reaction Lite (Blue Whale Web Solutions, Inc.)  A chemistry puzzle game. Possibly more suited to younger chemists.
Naming/determining chemical structures	Chemical Detectives (Pinion Systems)  Use data from mass spec, NMR and IR spectroscopy for different molecules to solve their structure.	

Some popular free chemistry apps; nearly all are available on both Apple and Android operating systems.



Screenshots from the Hydrocarbons (panel A) and SpinDrops (panel B) apps.

has to want to access and read the material and to be kept engaged while doing so. The lure of Facebook and Twitter are after all just as strong, if not stronger, on a tablet as they are in a lecture. How then can we encourage students to engage with the material? One approach might be through the use of gaming principles in apps meant for teaching.

Gamification is the use of game-thinking and game mechanics to engage users and solve problems. Although not without its critics in educational circles, if done well it can be a useful learning tool. The advantages of using games for teaching are that learning can be made active, goal-oriented, contextualised and interesting. Additionally, students tend to be drawn to systems where they can receive

rewards for proficiency and/or compete against their peers, and such features are easily implemented in a game – via the use of leaderboards and/or internet connectivity, for example. Games also have the advantage of potentially making learning fun and so they offer a powerful tool for learning through doing and enhancing student interest in the subject as a whole.

Chemistry and science in general are becoming increasingly popular in computer games, including best sellers such as Portal, Portal 2 and the Half-Life series. However, good game design is not just about having an idea. The idea is probably the easiest part; what counts is making it work. The role of a game designer is to take the initial idea and work from the early prototype stages of the game design through to the final product. The mark of a good game designer is their ability to attract and keep the attention of the person playing the game (Angry Birds being a good example).

Many books and university courses cover game design in detail. Good examples are Scott Rogers' *Level up! The guide to great video game design* and *What video games have to teach us about learning and literacy* by James Gee. David Kushner's *Masters of Doom: how two guys created an empire and transformed pop culture* is also well worth reading for the human aspect. A fun game should have a narrative and consequences, and players should be offered meaningful choices (e.g. 'Is doing X a better choice than doing Y and if so, why?') without being afraid to make decisions or feel as though they're missing out. Good design can make learning interactive, provide ongoing feedback,

Academics are in an ideal situation to help develop these systems by incorporating their background knowledge with personal experiences in lecturing and teaching science.

grab and sustain attention, and have appropriate and adaptive levels of challenge. Bad design will mean the game is never used. For both video game makers and educators, failing to engage the user is not an option.

RMIT University's Trouble Tower is an example of a game that follows good game design principles and is designed to assist students learning occupational health and safety (OH&S) for construction at RMIT (bit.ly/1CAcz6a). In this game, you are confronted with increasingly more complex OH&S situations related to building sites. Your task is to identify the hazards and select the appropriate solution; in doing so you learn OH&S principles and can compete to see who can work out the solution the fastest. The design team did several follow-up studies and found that students who played the game were engaged, and felt that, through playing the game, they had learned something new. Trouble Tower is now part of the curriculum of construction induction courses at RMIT. So in this case at least, it is possible to learn and have fun at the same time.

Of course, no technology is a panacea, and many of the traditional problems associated with educating students will remain, no matter how amazing the game or sophisticated the smartphone. However, educators

shouldn't shy away from testing the abilities of technology to enhance and encourage learning. Academics are in an ideal situation to help develop these systems by incorporating their background knowledge with personal experiences in lecturing and teaching science. Trouble Tower is a good example of this: it was developed by a team of people with expertise in electronic games development as well as OH&S and construction. Each part of the design team added something; if the game designers had not been involved, then it would have been no fun to play, and if the OH&S and construction people had not been involved, then the app would not have been useful for teaching. This two-party approach should help in the design of future game-based teaching apps.

Electronic games and apps have great potential for teaching and learning fundamental chemistry concepts, particularly if both chemists and game designers are involved from the start. It will be interesting to see how these systems are further developed in the future; in the meantime, happy gaming.

Dr Oliver Jones MRACI CChem and **Dr Michelle Spencer** MRACI CChem are senior lecturers in the School of Applied Sciences at RMIT University in Melbourne, who promise that the science gets done and they don't spend all their time playing games on their iPads.

Jim Shannon

Mass spectrometrists

Jim Shannon's name is inextricably associated with mass spectrometry, as his scientific career was devoted to its development and applications to organic, biological and coordination chemistry. Jim was born in Adelaide on 11 July 1926 and studied at the University of Adelaide, graduating in 1949 with first class honours in Chemistry. After some further postgraduate work, in 1952 he went to Imperial College London for his PhD, as the recipient of a British Council Fellowship. He returned to Australia in 1955 to a research position at CSIRO in what was to become the Division of Coal Research in Sydney.

Charged with elucidating the chemical structure of coal, Jim realised the need for the latest analytical instrumentation, including mass spectrometry and nuclear magnetic resonance. Consequently, a German Atlas CH4 mass spectrometer was installed in Sydney in 1961 and was the first in Australia that was devoted to the elucidation of the structures of organic compounds. Jim was promoted to the level of senior principal research scientist in 1963. His generous services to other chemists around the country were widely used and appreciated, especially as he continued to develop and understand new and valuable applications.

In 1968, CSIRO transferred the Mass Spectrometry Unit to Canberra. Jim's stay in Canberra was rather short-lived, as he was appointed Professor of Chemistry at the University of New South Wales in 1969 and stayed there until his retirement in 1986. Jim's role in the development of the School of Chemistry at the University of New South Wales was immense; furthermore, his wider contribution to the university cannot be overemphasised. Scientifically, Jim established a strong group in chemical ionisation mass spectrometry, and successfully masterminded the transfer from La Trobe University not only of Peter Derrick, but also of Peter's grand-scale double-focusing mass spectrometer. The negotiations were significant because they resulted in the conversion of substantial areas of teaching laboratories into state-of-the-art mass spectrometry research laboratories. Jim's scientific output was justly recognised by the award of the H.G. Smith Medal for 1967 by the RACI. Also in 1967, he was awarded the degree of Doctor of Science by the University of Adelaide.

On the administrative side, Jim's broad vision, unwavering integrity, sound judgment and diplomatic skills were quickly recognised and highly valued. He served as Head of the School of Chemistry in 1976–7 and again in 1980–4. He served on innumerable committees of the Professorial Board of the University and chaired the Research and Higher Awards



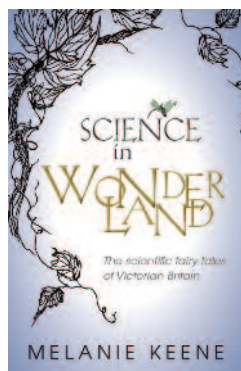
Charged with elucidating the chemical structure of coal, Jim realised the need for the latest analytical instrumentation, including mass spectrometry and nuclear magnetic resonance.

Committee, and the Board of Studies in Science and Mathematics. He was elected to the University Council where he represented the Faculty of Science.

There are many scientists who have benefited from Jim Shannon's innovative science, wise leadership and friendship, and they are deeply indebted to him.

Jim died on 3 May 2015. He is survived by his devoted wife Vois, to whom he was married for 59 years.

David Black FRACI CChem



Science in wonderland: the scientific fairy tales of Victorian Britain

Keene M., Oxford University Press, 2015, hardcover, ISBN 9780199662654, 227 pp., \$34.95

Science in wonderland explores the curious intersection of fairy tales and science in Victorian Britain. Author Melanie Keene illustrates the integration of 18th-century fairies, goblins, giants and sundry other

mythical entities into children's stories, exploring aspects of the science that emerged from the Industrial Revolution and associated era of scientific discovery and reinterpretation.

All societies have their myths and legends. We all strive to make sense of our world and find meaning in existence. In times past, explanations of the unknown were frequently rooted in superstition, invoking the influence and agency of specially endowed not-of-this-world creatures. Perhaps nothing much has changed. Santa Claus, the Easter Bunny and the tooth fairy are still very much alive and well, provided, of course, you *believe*! And sundry important people apparently think the climate-change good fairy will save our bacon!

Against this pseudo-spiritual world, 19th-century Britain was engaged with new technology driving the 'satanic' mills and a rapid expansion of scientific theory. Fossils were no longer objects of awe, but merely the remains of long-dead creatures; tiny species seen under the microscope were seen for what they were rather than begging arcane explanation; astronomy was starting to make sense to the emerging middle classes; and physics, chemistry and microbiology were directing society away from the magic and make-believe towards evidence-based explanation. Education strove to present a strictly rational world view, free from fairies and the like.

Did this rationalist mechanistic view succeed? No, not totally. Apparently the love of fairies runs deep. At the end of the 19th century, butterflies were still pretty much seen as fairies; Kingsley's *Water babies* melded 'scientific' water with fairies; and Gilbert and Sullivan had fairies galore, illuminated with twinkling lights no less, courtesy of (chemical) batteries. No danger of tipping out the baby fairy with the bathwater. Children's authors kept the fairies and fitted the science round the edges.

Overall, this is a delightful little book. It is interesting and engaging, reasonably inexpensive and good bedtime reading. You'll enjoy it!

Good gracious! A little fairy has just lightly tripped right past my house. I think she is probably on her way to ballet with her mother (apparently a mere mortal).

R. John Casey FRACI CChem

Microwave-assisted sample preparation for trace element determination

de Moraes Flores É.M. (ed.), Elsevier, 2014, ISBN 9780444594204, 412 pp., \$235.95

Microwave-assisted sample preparation for trace element determination is ably edited by Érico Marlon de Moraes Flores. There are 12 chapters and 36 authors, so it must have seemed like herding cats to get them lined up and pointing in more-or-less the same direction! Many of the authors are associated with universities throughout Brazil, a fair sprinkling come from the University of Aberdeen's Chemistry Department (Trace Element Speciation Laboratory, TESLA), while the US, Germany, Austria, Poland and Libya are represented to make up the numbers. *Ably* edited, indeed!

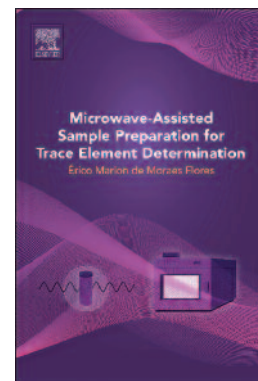
The book is a *tour de force* of every-which-way you can visualise using microwaves to prepare samples and a few more you maybe haven't thought of. Each chapter concentrates on one aspect and is a complete, stand-alone review with its own comprehensive referencing. If your interest lies in the topic of a particular chapter, then you've probably found a very useful review. If, on the other hand, your interests broadly relate to whether you ought to move towards microwave techniques for sample preparation in your laboratory, then you will surely find your answer in this book, but you'll have to dig it out.

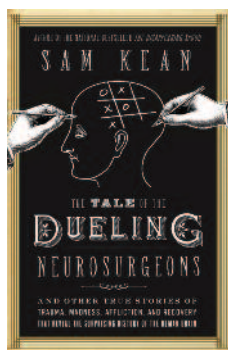
The strength of this book is its comprehensiveness plus some very useful tables in a number of chapters, which will rapidly point you in the direction of methods for particular analytes. Its weakness is the isolation/segregation of the chapters from each other; there is no cross-referencing and pulling together into the rounded 'story' the title implies. This is a pity because the book is quite expensive.

The introductory chapter, 'Introduction to sample preparation for trace element determination', is a clear and insightful definition of the process and goals of trace elemental analysis. Compulsory reading for all tyro analysts! The quality of the remaining chapters is variable, ranging from so-so to very good, mainly at the latter end. For most of the authors, English is not their mother tongue, so in places the English is not quite correct, although the meaning is always quite clear. I know leaping to conclusions based on surnames can be a dangerous game to play; I have an acquaintance with a lengthy, hard-to (OK, impossible-to) pronounce Polish name and an accompanying Glaswegian accent reflective of his Scottish ancestry! However, I think I'm on *terra firma* stating this book has a strong Brazilian flavour.

In summary, if you are looking for a series of comprehensive reviews about microwaves in trace analysis, or a competent literature review about one of the review topics (as of a couple of years ago), then look no further. If by contrast you are looking for a rounded review of the area, then it is mostly here, but you'll need to work at it and draw your own conclusions. Finally, if you just want to get a feel for how you might use microwaves in analysis, then you could do worse than eyeball the table of contents, but you could probably do better elsewhere.

R. John Casey FRACI CChem





The tale of the dueling neurosurgeons: the history of the human brain as revealed by true stories of trauma, madness, and recovery

Kean S., Little, Brown and Company, Hachette Book Group, 2014, hardcover, ISBN 9780316182348, 407 pp., \$16.63 (Amazon)

The tale of the dueling neurosurgeons is another exciting book by Sam Kean. While neurosurgery may not at first sight appear to be strictly chemistry, the book is not bereft of the development of the chemistry of neurotransmitters, synapses, neurons and prions; and the importance of dopamine and vitamin B₁, along with the 'wiring of the brain'. It is, however, the epic stories of discovery that make the book compelling reading.

The story behind the title covers the tale of French King Henri II, who was involved in a jousting accident in 1559. The tale is really about two prominent surgeons of the day, Ambroise Paré (of France) and Andreas Vesalius (of Brussels). The former was a barber-surgeon with substantial battlefield experience, the latter was initially a self-taught anatomist involved in dissecting deceased remains, following the ancient physician Galen (CE 129). The surgical team could do little for the dying king, who drifted in and out of consciousness, even getting up and walking. The underlying philosophy at the time posited if the skull remained intact, then death was a consequence of the visible injuries. Indeed, Henri had large splinters of jousting pole through one eye-socket (which were removed), but he ultimately succumbed. Vesalius and Paré convinced the French Court an autopsy should be performed on Henri. They predicted what they might find, and their predictions were confirmed – pools of blackened fluids at the rear of the brain 'antipodal to the blow' – and the brain itself had yellowed and putrefied at the back. They also found that the 'splinters' at the front of Henri's head had not entered his brain.

This story serves two purposes. First, early neurological research is based on observing a pattern of 'misfortune' as a mechanism to study how a victim's brain may cope (sometimes quite miraculously and at other times not so), followed by a post-mortem analysis of the sites of disorder; and second the brain is a lump of loosely anchored tissue floating around in a soup of fluids within a solid skull.

Our author cashes in on what Henri's autopsy shows in today's context. Namely, brain trauma can occur even if the skull remains undamaged, a lesson we still appear to be learning in the domain of our gladiatorial sports such as boxing, football (body and head impact codes), ice-hockey and even warfare (no blood, no harm?). The recent story of two Australian servicemen in Iraq describes a bomb explosion, where one soldier remained relatively unaffected

(although seriously injured) but his colleague with fewer injuries was designated in an advanced state of Alzheimers – all related to directional location from the blast.

Another story from 1957 concerns the disease kuru, suffered by the *Fore* people and their neighbours (some 40 000 people) in the eastern mountain highlands of Papua New Guinea (PNG). Typically the diet of the PNG highlanders was mostly fruits and vegetables, plus a few sweet potatoes gathered from the poor mountain soils. A few villages kept pigs and hunted rats, possums and birds (mostly consumed by the men), but protein for the women and children came from so-called 'funeral feasts', where the dead were cooked and consumed. Choice bits like genitals, buttocks and brains were provided to relatives of the deceased first. The symptoms of kuru commence with lethargy, headaches and joint pain, and progress through victims stumbling about, flailing their arms and within months being unable to stand or sit up straight without support. Along the way many start to laugh uncontrollably. The lucky ones die of pneumonia before they starve, while the unlucky ones just whittle away.

The neuroscientist and adventurer Carlton Gajdusek was attracted to the highlands in the late 1950s. From 1957, Gajdusek started to gather data on kuru victims and noted it was mainly women and children who succumbed to the disease. He found some 200 people were dying of the disease each year. Gajdusek also started to perform autopsies on the brains of victims. This work attracted the attention of other neurologists as well as some *nair-do-well* local sorcerers. The upshot was the initial damage caused by kuru was traced to the cerebellum – the brain's movement centre. It was speculated by some that the disease might be genetic but this was dismissed since unrelated adults often had the disease.

In the 1960s, Gajdusek's lab in the US also demonstrated that the diseases kuru, scrapie (a similar disease in sheep) and Creutzfeldt-Jacob disease in rodents had some common elements. All resulted in 'spongyform' brain damage, which can remain dormant for long periods. Coincidentally, funeral feasts had become rarer in the 1960s because cannibalism was frowned upon by Christian missionaries. Nevertheless, it took until 1975 for kuru to be all but eliminated.

Stanley Prusiner, a San Francisco-based neurologist, then detected some 'rough proteins' at the blood-brain barrier of victims of the above diseases, which he called prions (proteinacious infectious particles). Prions prove immune to cooking and digestion and unfortunately cross the brain-blood barrier. Prions, consumed by the *Fore* women and children at funeral feasts, proved to be the source of kuru disease. By analogy, the outbreak of mad cow disease in the 1990s is basically a case of 'bovine kuru'. Possible links of prion-type proteins to Alzheimer's and Parkinson's disease are currently being investigated.

If I were to be critical of the author, then it would be because he mentions the colonial power of Australia in a somewhat dismissive manner, while neglecting the critical contributions made to the kuru story by Australian medico Professor Michael

Alpers. Alpers, who among other things directly collaborated with Carlton Gajdusek, has continued to monitor one of the critical aspects of the disease – its incubation period. The last case of what is now called the degenerative prion disease kuru was reported in 2005, not 1975 as suggested in this book (see www.youtube.com/watch?v=vw_tClcS6To).

Beriberi and vitamin B₁ appears to be a worthy place to conclude this review. For as long as people have eaten rice in Asia, doctors there have reported outbreaks of beriberi. This was accentuated in the early days of rice milling when the outer husks were removed from rice grains, producing so-called 'white' rice. During the Russo–Japanese war alone some 200 000 Japanese soldiers fell victim to beriberi. The disease was particularly common in Changi during World War II, where two doctors, de Wardener and Lennox, collected tissue samples from the brains of beriberi victims. These samples (another story of intrigue) ultimately enabled the link to be drawn between vitamin B₁ deficiency, beriberi and Wernicke–Korsakoff syndrome, which expresses itself through 'confabulation' (telling plausible lies), and arises from frontal lobe damage of the brain.

The book includes numerous other stimulating stories that open our understanding of functional aspects of the brain, often through dysfunction.

Dr Alan J. Jones FRACI CChem

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Science Next Collaborative: a new approach to the commercial challenges of early career research

It cannot be disputed that Australian scientists are facing challenging times. Perhaps 'challenging' is an understatement. Australia is producing an ever-increasing number of scientific PhD students, yet government funding of the sciences is at a record low. EMCRs – early-to-mid-career researchers who are looking to take the leap from postdoctoral position to a permanent placement in academia/industry – are arguably the most affected.

Professor Carver, Director of the Research School of Chemistry, ANU College of Physical and Mathematical Sciences, says there is a 'huge demand or need for trying to encourage EMCRs in the development of their careers ... it's a pretty tough time at the moment for anyone doing research, particularly people in those age brackets'. I doubt that any of us would disagree.

Professor Carver has been selected as an Ambassador of the Science Next Collaborative (SNC). Launched in mid-May of this year, the SNC is an Australian-first industry initiative, led by Sigma Aldrich, that aims to better enable Australian scientists to successfully translate their research through to commercialisation.

The initiative will focus on the challenges faced by EMCRs, particularly the transition from basic and promising research discovery to translational research and its commercialisation.

'A thorough examination of the Australian scientific research sector uncovered that many researchers are struggling to achieve the final steps in their research continuum: successful commercialisation', that is, according to Ms Reich Webber-Montenegro, Director – Marketing, Inside Sales and Shared Services, Sigma Aldrich Oceania. Ms Webber-Montenegro identifies the issue as a gap in the knowledge and know-how of EMCRs as opposed to their more senior colleagues, and that this is a worthy area for Sigma Aldrich to focus on.

Ms Webber-Montenegro considers that the commercial challenges faced by EMCRs 'may discourage them from pursuing meaningful and ongoing scientific endeavours ... If this risk becomes a reality, Australia may see a huge dip in the innovation ecosystem and associated returns generated by a dynamic research industry.'

Associate Professor Derek Richard, Director of Research, School of Biomedical Sciences, Queensland University of Technology, and also an SNC Ambassador, has stated 'it's usually difficult for young researchers to take their discoveries through to commercialisation, possibly due to a lack of experience in intellectual property protection, market research, lodging patents and gaining working capital, which are all fundamentals in the commercialisation of research.'

The SNC is led by Ms Webber-Montenegro, who is passionate about the program and what it can potentially offer to EMCRs. Sigma Aldrich has recruited seven key scientists across

Australia, and together they constitute the SNC ambassadors, also known as the 'think tank'. Sigma Aldrich became familiar with each of the ambassadors through their dealings with the company, and subsequently approached them for their expertise.

Key to selecting the ambassadors was that they must be influential opinion leaders in their field, be at a point in their career where they can lay claim to having successfully commercialised research, and, importantly, now be willing to give back to the field and mentor the next generation of Australian scientists. Further, it was essential to Sigma Aldrich that the ambassadors come from a good representation of Australian research institutions, in both the chemical and biological fields.

From my own investigation, it appears that the SNC Ambassadors have vastly varied commercialisation track records. Professor Carver considers that each of the SNC Ambassadors offer different areas of expertise. In Professor Carver's instance, while his commercialisation experience may or may not be as strong as other Ambassadors, through his leadership roles at both the University of Adelaide and Australian National University, he has mentored EMCRs, encouraging them to further their careers in research. His experience in mentoring EMCRs is a strength that he will be bringing to the SNC.

There is often a direct conflict between commercialising and publishing research, and this is a problem. Research grants are heavily dependent on the number and quality of publications produced, yet commercialising research often requires the information to remain out of the public domain. When I spoke with Professor Carver about this, I was reassured to learn that the SNC Ambassadors had discussed this competing interest at length, and that the content of the forums will reflect this. Professor Carver considers that 'academics are geared to outputs in terms of research publications in prestigious journals', and consequently, 'academics are routinely measured in this way'. He states there is 'little room, in many ways, for people who have a different approach'. Quite simply, commercialisation output does not fit the standard model that we currently have in place, and this will need to change.

The initiative will materialise as a series of forums held in Brisbane on 26 August, Sydney on 3 September, and Melbourne on 8 September 2015. There is no cost to attend the forum, though there will be no financial support available for those who do not reside in these key cities. The Ambassadors will present their commercialisation experience, guiding EMCRs through the process. A session on intellectual property and its relevance to EMCRs is also on the agenda. At this stage, the forums are not limited to particular EMCRs, and are not exclusive to particular institutions.

The SNC online 'hub' (sciencenextcollaborative.com) includes



Attendees at the Science Next Collaborative Think Tank Meeting, 11 May. Back row (left to right): Associate Professor Derek Richard (QUT), Professor Peter Currie (Monash University), Professor Mark Baker (Macquarie University), Professor John Carver (ANU). Front row (left to right): Irfan Beig (Scientific Liaison, Sigma-Aldrich), Arlene Burton (Product Initiative Manager, Sigma-Aldrich), Reich Webber-Montenegro (Director – Marketing, Inside Sales & Shared Services Oceania, Sigma-Aldrich), Associate Professor Kaylene Simpson (Peter MacCallum Cancer Centre), Rachael Rose (Marketing Communications Assistant, Sigma-Aldrich), Farhad Shafiei (Product Manager, Sigma-Aldrich).

information about commercialising research as relevant to EMCRs and will be expanded to include a variety of educational resources. Forum dates are advertised at the hub and through major institutions. The SNC intends to have the forums posted as videos online, with the opportunity to stream the sessions in real time for those who cannot attend.

The first of the objectives to be met by the SNC Ambassadors is the publication of a positioning paper, which is available via the SNC hub. The paper captures the current situation faced by EMCRs, key challenges, and ways to better enable scientists to secure economic returns for their research.

The feedback received from EMCRs along the way will be used to direct future SNC efforts. Professor Carver considers it a dynamic process in which the program will continue to evolve to meet EMCR needs.

What is the value of the SNC to an EMCR? First and foremost, an EMCR's commercialisation knowledge will benefit from participating in the SNC. Second, so will their resumé. Would an employer value an EMCR who has participated in the SNC? Absolutely, according to Professor Carver, who is well versed in

hiring for academic positions. He states that employers are 'looking for distinguishing characteristics ... It's not just about the ability to do research; it's about the ability to interact, it's about the ability to have a variety of skills ... this initiative would be another aspect to that.'

What's in it for Sigma Aldrich? The answer is 'stakeholder engagement'. This is highly valued by Sigma Aldrich, and is the 'main goal' in terms of measurable return; Sigma Aldrich wants to engage with key leaders in industry and academia, as well as up-and-coming EMCRs. Perhaps I'm naïve, but I believe this response. Australian science is a relatively small community where word spreads quickly. Altruistic acts do not go unnoticed, and the initiative will surely fair favourably for Sigma Aldrich. We should be encouraged to see an industry-led initiative, such as the SNC, aim to directly address the issues faced by Australian scientific researchers.



Dr Brittany Howard MRACI completed her PhD in medicinal chemistry at the Monash Institute of Pharmaceutical Sciences before undertaking a postdoctoral position with the National Institutes of Health (US), and has since commenced as a trainee attorney with Watermark Patent and Trade Marks Attorneys.

The smell of rain: how CSIRO invented a new word



Are you one of those people who can smell when the rain is coming? Ever wondered then what you're actually smelling?

Australia's CSIRO has come up with some pretty amazing inventions over the past 86 years of research, from polymer banknotes to insect repellent and the world-changing Wi-Fi. But we can also lay claim to something a little more esoteric – we actually invented a whole new word.

And no, we're not talking about one of these new-fangled internet words like 'YOLO', 'selfie' or 'totes'.

The word is 'petrichor', and it's used to describe the distinct scent of rain in the air. Or, to be more precise, it's the name of an oil that's released from the earth into the air before rain begins to fall.

This heady smell of oncoming wet weather is something most Australians would be familiar with – in fact, some scientists now suggest that humans inherited an affection for the smell from ancestors who relied on rainy weather for their survival.

Origins

Even the word itself has ancient origins. It's derived from the Greek 'petra' (stone) and 'ichor', which, in Greek mythology, is the ethereal blood of the gods.

But the story behind its scientific discovery is a lesser-known tale. So, how is it that we came to find this heavenly blood in the stone?

'Nature of Argillaceous Odour' might be a mouthful, but this was the name of the paper published in *Nature* of 7 March 1964, by CSIRO scientists Isabel (Joy) Bear and Richard Thomas, that first described petrichor.

Thomas had for years been trying to identify the cause for what was a long-known and widespread phenomena. As the paper opened:

That many natural dry clays and soils evolve a peculiar and characteristic odour when breathed on, or moistened with water, is recognised by all the earlier text books of mineralogy.

The odour was particularly prevalent in arid regions and was widely recognised and associated with the first rains after a period of drought. The paper went on to say:

There is some evidence that drought-stricken cattle respond in a restless manner to this 'smell of rain'.

The smell had actually been described already by a small perfumery industry operating out of India, which had successfully captured and absorbed the scent in sandalwood oil. They called it 'matti ka attar' or earth perfume'. But its source was still unknown to science.

Joy and Richard, working at what was then our Division of Mineral Chemistry in Melbourne, were determined to identify and describe its origin.

By steam-distilling rocks that had been exposed to warm, dry conditions in the open, they discovered a yellowish oil – trapped in rocks and soil but released by moisture – that was responsible for the smell.

The diverse nature of the host materials has led us to propose the name 'petrichor' for this apparently unique odour which can be regarded as an 'ichor' or 'tenuous essence' derived from rock or stone.

The oil itself was thus named petrichor – the blood of the stone.

Bring on the humidity

The smell itself comes about when increased humidity – a precursor to rain – fills the pores of stones (rocks, soil etc.) with tiny amounts of water.

While it's only a minuscule amount, it is enough to flush the oil from the stone and release petrichor into the air. This is further accelerated when actual rain arrives and makes contact with the earth, spreading the scent into the wind.

According to the *Nature* paper:

In general, materials in which silica or various metallic silicates predominated were outstanding in their capacity to yield the odour. It was also noted that the odour could be obtained from freshly ignited materials rich in iron oxide, with or without silica.

The smell itself comes about when increased humidity – a precursor to rain – fills the pores of stones (rocks, soil etc.) with tiny amounts of water.

It's a beautiful sequence of events, but one that may be hard to visualise.

Thankfully, in a testament to the ongoing scientific fascination with this finding, a team of scientists at the Massachusetts Institute of Technology have just this year released a super slow motion video of the petrichor process in motion.

Using high-speed cameras, the researchers observed that when a raindrop hits a porous surface, it traps tiny air bubbles at the point of contact. As in a glass of champagne, the bubbles then shoot upwards, ultimately bursting from the drop in a fizz of aerosols.

The team was also able to predict the amount of aerosols released, based on the velocity of the raindrop and the permeability of the contact surface, which may explain how certain soil-based diseases spread.

Lasting legacy

There's a small body of research and literature on petrichor that's fascinating in its own right, including Thomas and Bear's subsequent paper 'Petrichor and Plant Growth' a year after they first named the smell.

So what happened to Joy Bear and Richard Thomas?

Richard had actually retired from CSIRO in 1961 when he was First Chief of the Division of Minerals Chemistry. He died in 1974, aged 73.

Joy, aged 88, a true innovator and pioneer in her field, retired from CSIRO only in January this year, after a career spanning more than 70 years.

The joint discovery of petrichor was just part of a truly remarkable and inspiring career that culminated in 1986, with Joy's appointment as a Member of the Order of Australia for services to science.

We are thankful to both for the lasting legacy on giving a name to the smell of rain and to Joy for the role model she has been to so many women in science.

Howard Poynton, Research Group Leader – Materials Characterisation, CSIRO. First published at *The Conversation* (www.theconversation.com).

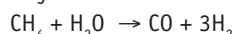
Declining refineries

It now seems likely that Australia will be one of the first (if not the first) major industrialised countries to close all of its oil refinery operations. An old and outdated refinery in Adelaide (Port Stanvac) closed in the 1990s. The two refineries in New South Wales (Shell at Clyde and Caltex's refinery at Kurnell) have closed in the past years, BP's Bulwer Island near Brisbane is slated to close and there are persistent rumours that the BP refinery at Kwinana in Western Australia will follow suit. This leaves the two refineries in Victoria (Viva Energy, formerly Shell, near Geelong, and ExxonMobil's refinery at Footscray in Melbourne) and Caltex's refinery at Lytton near Brisbane. Whether these refineries will survive their scheduled major shut-down and maintenance times over the next few years, when new capital is usually required for upgrades or replacing major equipment, is a moot point.

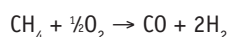
The duty of a refinery is to convert crude oil, which has a hydrogen to carbon stoichiometric ratio of 1.5 or less, into refined fluids for motor transport, which have hydrogen to carbon ratios of over 1.8 for gasoline (petrol) and the best-quality diesel. This role is performed in refineries by either rejecting carbon in the crude oil or adding hydrogen.

In Australia, carbon rejection is the favoured method via fluid catalytic-cracking (FCC). In this process, hot solid-acid catalysts react with heavy oils ($H/C < 1.5$) to form gasoline, olefins and a low-quality diesel with H/C ratios of 1.8 or more. The reaction is very rapid and the catalyst becomes coated in carbon (coke). The catalyst is regenerated by separating it from the hydrocarbons and burning the coke off the catalyst to form carbon dioxide and reheating the catalyst to the required reaction temperature.

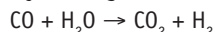
An alternative to FCC is hydrocracking, which is used at the Bulwer Island refinery (and at New Zealand's refinery at Marsden Point). For this operation, hydrogen is required; it usually comes from natural gas by the steam reforming reaction:



or, as is used for the Bulwer Island operation, by partial oxidation:



more hydrogen is made by water-gas-shift:



The carbon dioxide is removed and emitted to atmosphere.

For completeness, another method for rejecting carbon, which is not used in Australia, is to form coke by liquid-phase pyrolysis of heavy components. This makes a low-quality gasoline and diesel, which require further hydro-treatment, and petroleum coke, which can be used to make anodes for smelting aluminium.

One of the main effects of increasing the ratio of hydrogen to carbon in the products is that the density of the products is significantly lower than that of the crude oil feedstock. This results in an increase in the total volume and because oil products are universally sold on a volume basis, this results in



increased product volumes and sales (the so-called refinery gain).

In modern refineries producing fuels to the latest quality standards, more hydrogen is required to hydro-treat diesel fuels to virtually eliminate sulfur (less than 10 ppm). This is required to minimise the tailpipe emissions of particulates from diesel as required by the latest vehicle engine technology.

A significant issue is the economy of scale. Refineries have a good response to economy of scale (unit production costs fall with increasing size of the refinery). Recently in our region several refineries have been built with outputs near or exceeding Australia's total refinery capacity. Some of the major export refineries in the region are given in the table.

These refineries are export-oriented refineries in that they take crude oil from the Middle East, including Iran, and convert it into products that are exported to the region. These refineries use the latest technology to produce high-quality fuels now being adopted throughout Asia. Also they use heavy oil hydro-cracking so that high-density, high-sulfur crude oil (i.e. cheap) can be used rather than the more expensive light crudes that Australian refineries require; the graph shows the persistent price differential between heavy oil ($sg < 0.933$; API gravity < 20) and the lighter crude oils ($sg > 0.876$; API > 35.1). This benefit is increased by a larger refinery gain because of the relatively higher density of the feedstock oil.

Major export refineries in the Middle and Far East with output similar to Australia's total refinery capacity

Company	Location	Country	Capacity (bbl/day)
SK Innovation	Ulsan	South Korea	840 000
GS Caltex Corp	Yeosu	South Korea	785 000
S-Oil Corp	Onsan	South Korea	669 000
Reliance Industries	Jamnagar	India	660 000
ExxonMobil	Jurong/Pulau Ayer	Singapore	592 000
Reliance Industries	Jamnagar	India	580 000
Saudi Aramco	Ras Turana	Saudi Arabia	550 000
Formosa Petrochem.	Maliaw	China Taiwan	540 000
Kuwait National Petroleum	Min Al-Ahmadi	Kuwait	466 000
Shell Eastern	Pulau Bukom	Singapore	462 000
BP PLC	Kwinana, WA	Australia	136 698
Viva Energy Australia	Geelong, Vic.	Australia	120 000
Caltex Australia	Lytton, Qld	Australia	108 600
BP PLC	Bulwer Island, Qld	Australia	96 850
ExxonMobil	Footscray, Vic.	Australia	77 000
Total Australian refinery capacity			539 148

Closure of Australian refineries has resulted in the facilities being refurbished as import terminals importing high-quality specification fuels from these export refineries.

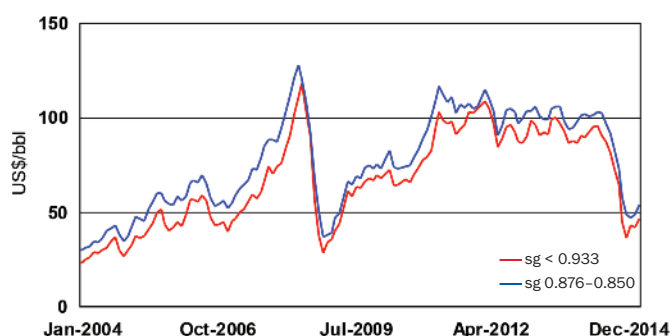
As well as the smaller scale, one of the major issues for Australian refineries competing with these facilities is that coastal shipping in Australia (cabotage) is very expensive compared to shipping from foreign ports using foreign flagged vessels. It is cheaper to service an Australian port from Singapore (say) than from an expanded refinery somewhere else in Australia. Also, from the above equations, it is evident that refinery operations are major emitters of carbon dioxide. The enthusiasm for taxing or proscribing such emissions in Australia increases the investment risk versus investments in countries with little enthusiasm or even hostility to carbon emission taxes and the like.

One of the major issues for the chemistry profession is that as refineries close, there is less opportunity for chemists and chemical engineers both working for and servicing refinery operations. But it is worse than this because refineries also supply many downstream chemical manufacturers with feedstock. This ranges from propylene for making high-valued polymers to sulfur for the fertiliser and agricultural industries.


Compared to the furore over the demise of vehicle manufacturing, there has been little concern expressed about the demise of hydrocarbon processing in Australia. This is a very worrying situation as it leaves the country exposed to the vagaries of international supply of high added-value products and further reduces exports to basic minerals and LNG, which have minimal added value.



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



Relative cost of oil at varying density.



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Measuring arsenic in rice – an Australian reference material

In the next few years, it is likely that specific legislation will be introduced for inorganic arsenic concentrations in rice in Australia, Europe and elsewhere, with the acceptable levels for inorganic As set at 0.2–0.3 $\mu\text{g/g}$. This will require producers of rice in Australia to certify that their rice has acceptable inorganic As concentrations.

Inorganic As is a class one carcinogen and at high exposure levels causes cancer of the bladder, lung and skin. Worldwide, drinking water and foodstuffs are the two main sources of inorganic As. In Australia, rice consumption is an exposure

well below the current maximum levels permissible for arsenic in cereals in Australia (1 $\mu\text{g/g}$) (Australian and New Zealand Food Standards Code, Standard 1.4.1 Contaminants and Natural Toxicants 2011C). Inorganic As concentrations are below 0.2 $\mu\text{g/g}$.

Measurement of inorganic As in food is difficult. First, inorganic As must be quantitatively extracted and separated from other arsenic species such as monomethylarsenic and DMA, to avoid overestimation of inorganic As. Commonly, HPLC

coupled to inductively coupled mass spectrometry (ICPMS) is used for this purpose, but care must be taken that co-elution of arsenic species and/or losses from adsorption to column packing material doesn't occur. Arsenic analyses by ICPMS can suffer from carbon enhancement in the ICP torch and isobaric interferences in the mass spectrometer, leading to an overestimation in arsenic concentration. Precautions must be taken to ensure the quality of results.

Accurate measurements of inorganic As in rice are required because inaccurate analyses will result in substantial inconvenience, lost production and costs to the rice industry. At the Ecochemistry Laboratory at the University of Canberra, we have produced a rice reference material to assist those undertaking inorganic As analyses of rice. Rice flour was sterilised by gamma irradiation and extracted with 2% nitric acid; total arsenic was measured by ICPMS and inorganic As and DMA by HPLC-ICPMS by a method verified by analysis of eight international rice flour reference materials and XANES. The rice flour contains $0.192 \pm 0.006 \mu\text{g/g}$ dry mass total As, $0.040 \pm 0.004 \mu\text{g/g}$ dry mass As^{III} , $0.068 \pm 0.003 \mu\text{g/g}$ dry mass As^{V} and $0.085 \pm 0.004 \mu\text{g/g}$ dry mass DMA.

Homogeneity tests were conducted using a suite of other elements present in the rice flour. The analysis of reference material and obtaining satisfactory results gives confidence in arsenic concentrations being reported.

The reference material is available, free of charge, by sending a stamped, self-addressed envelope to Ecochemistry Laboratory, University of Canberra, Bruce, ACT 2601. For more information, email Bill.maher@canberra.edu.au.

Professor Bill Maher is at the Institute for Applied Ecology, University of Canberra.



A range of rices ready for analysis. Brown rice normally contains more arsenic than white rice. Polished rice has less arsenic than rice with husks.

route of inorganic As. Arsenic is a natural component of soils and when paddocks are flooded, arsenic can become available for uptake by plants. Historically, lead arsenate was also extensively used in sheep dips and dimethylarsinic acid (DMA) used as an insecticide in orchards. Some of this legacy arsenic will also be present in rice-growing areas.

A recent survey of arsenic in rice available in Australian supermarkets (Maher W., Foster S., Krikowa F., Donner E., Lombi E. *Environ. Sci. Technol.* 2013, vol. 47, pp. 5821–2) has shown that rice contains less than 0.4 $\mu\text{g/g}$ arsenic, which is

Prediction of astringency

The capacity to predict astringency has been the subject of considerable research. In our review of red wine astringency in 2011 (*Trends Food Sci. Nutr.* vol. 27, pp. 25–36), we summarised six different approaches that have been used. In reality, most of these studies were not ‘predictive’. Rather, they simply determined the correlation between the taster-assessed astringency and a chemical assay for astringency. One approach towards a predictive model has used the measurement of the turbidity that resulted following the addition of mucin to a wine and the consequent formation of a mucin–polyphenol precipitate. While the authors initially used grapeseed extract to develop their method, they found a high correlation ($r^2 = 0.95$) between the measured turbidity and astringency rating for 18 wines (Condelli et al., *Food Qual. Pref.* 2006, vol. 17, pp. 96–107).

Irrespective of the apparent success of some approaches to assess astringency, there are numerous factors that make the link between prediction and consumption a challenge. First, a wine’s phenolic composition can change over time through a range of polymerisation and hydrolysis reactions. Second, the conformation of the phenolic compounds is important in determining interactions with salivary proteins as I discussed in my August column. Changes in conformation as a wine ages would change the perception of astringency.

Third, recent work by Aurélien Furlan and colleagues from the University of Bordeaux (*Langmuir* 2014, vol. 30, pp. 5518–26) has raised new questions relating to phenolic compound interactions with lipids, particularly oral cavity membranes. The work used deuterium and phosphorus solid-state NMR to examine the interactions between phenolic compounds and micrometric liposomes, as a model for oral cavity membranes, and nanometric bicelles to represent food lipid droplets. Catechin, epicatechin and epigallocatechin gallate caused disordering of the membrane’s hydrophobic core as well as destabilisation of the bicelles. While the authors recognise that the models used in their study were somewhat simplified, the approach provides a new strategy for examining the complex interactions that occur in the mouth when wine is consumed.

For some time, I have been reflecting on the role of what I call molecular assembly in the structure of red wine and this is a fourth issue that can influence attempts to assess or predict astringency. Molecular assembly is now commonly accepted in foods, but only recently has it started to gain traction in red wine. The concept was first proposed in 1966 by Dr Chris Somers, then at the Australian Wine Research Institute. Chris suggested that his gel filtration experiments on red wine implied that the pigmented molecules were ‘physically and not chemically bound in a three-dimensional tannin structure’.

The procyanidin association studies that I described in my August column provide more recent evidence for molecular

assembly and help interpret conflicts in the literature about compounds that contribute to astringency. The flavan-3-ol monomers catechin and epicatechin, as well as some procyanidin dimers, have been proposed to contribute to astringency. The experimental approach used in the study involved additions of the compounds to a model and then assessing by taste the increase in astringency. The concentrations used in the addition study, however, would have exceeded the critical micelle concentration for some of the flavan-3-ols leading to molecular aggregates and even colloidal particles. Some estimates of particle size suggest diameters of 300 nm or more can be obtained. Particles of this dimension are likely to induce friction in the flow of saliva, which could possibly be interpreted as astringency.

To add to the complexity of aggregate formation, Drazen Zanchi and colleagues (*J. Phys.: Condens. Matter* 2008, vol. 20, 494224; doi: 10.1088/0953-8984/20/49/494224) have shown that under conditions of high supersaturation, conditions that may be achieved when compounds are added to wine, the perturbation of the wine matrix can be significant and lead to the formation of fractal, rather than spherical, aggregates. This then opens up a new research area of the relationship between geometric characteristics and changes in mouthfeel response.

For some time, I have been arguing that the assembly processes in wine could lead to frictional effects as this seems more relevant when tasters use terms such as *gritty* or *sandpaper*. It would be fair to say that my position has not gained much credence with the traditionalists in wine sensory work. However, the work of Zanchi and others is suggesting that larger fractal aggregates may induce changes in textural characteristics rather than a change in lubrication that would be the traditional view of the astringent response. And in 2013, Gibbons and Carpenter (*J. Texture Stud.* vol. 44, pp. 364–75) argued that ‘astringent stimuli alter the salivary bulk, saliva rheology and the saliva pellicle leading to an increase of friction in the oral cavity’. So, I am not alone!

When next at a wine tasting, if you find your assessment of astringency differs from the rest of the group, you could comment that ‘clearly the combination of my salivary flow together with the phenolic conformer interactions with my saliva as well as the phenolic interactions with the lipids in my oral cavity means that my assessment will be different’. Or you can simply say, as I do, ‘I am right and the rest of you are wrong’! That usually starts a good argument, especially after a day of tasting.



Geoffrey R. Scollary FRACI CChem (scollary@unimelb.edu.au) was the foundation professor of oenology at Charles Sturt University and foundation director of the National Wine and Grape Industry Centre. He continues his wine research at the University of Melbourne and Charles Sturt University.

Plagiarism is a dirty word

Recently, the national media has reported incidents of plagiarism and cheating by year 12 and university students. Plagiarism is not just practised by students; nor is it new. There have been reports of scientists, politicians and others engaging in plagiarism and other forms of cheating. There is even a Retraction Watch website.

The internet, electronic resources, books and other resources provide an information-rich environment, in which it is extremely easy to copy information. Sometimes such copying constitutes misconduct but at other times copying is not misconduct. For example, discussion about occupational health and safety probably requires the inclusion of the exact wording of the relevant legislation. Whether copying is or is not misconduct can be confusing.

According to a widely used classification suggested by Oxford Brookes University, there are six ways to use sources.

- 1 Copying a paragraph verbatim from a source without any acknowledgment
- 2 Copying a paragraph and making small changes, e.g. replacing a few verbs, replacing an adjective with a synonym; acknowledging in the bibliography
- 3 Cutting and pasting a paragraph by using sentences from the original but omitting one or two and putting one or two in a different order, no quotation marks; acknowledging in the text and bibliography
- 4 Composing a paragraph by taking short phrases from a number of sources and putting them together using words of your own to make a coherent whole with in-text acknowledgments and a bibliographical acknowledgment
- 5 Paraphrasing a paragraph by rewriting with substantial changes in language and organisation; the new version also having changes in the amount of detail used and the examples cited; citing source in bibliography
- 6 Quoting a paragraph by placing it in block format with the source cited in text and in bibliography

At senior secondary and tertiary levels, point 1 is plagiarism; point 6 is not. What is considered plagiarism depends on the culture of the community. For example, it is the cultural practice in some disciplines to quote verbatim, sometimes without citing the source if the source is extremely well known. What is considered well known depends on the particular community.

Teachers and educators are often reluctant to discuss plagiarism. They are afraid that discussion in a public forum may help the small number of dishonest or lazy students to plagiarise (cheat) and to avoid detection procedures. This silence also causes problems. A few years ago, a north American study of two university student cohorts found that the students in this sample generally considered themselves honest and that most of them stated that cheating was never acceptable, or acceptable only in rare circumstances. However, a number of them did report that they had engaged in practices that many academic staff considered as cheating, suggesting that these practices were partially due to ignorance of what was considered acceptable academic practice. The silence also means that teachers and educators often have inconsistent notions and expectations of acceptable academic practice, by drawing the line between acceptable practice and plagiarism at different points in the classification of the use of sources.

A further problem is that plagiarism can affect staff morale. In common law, Blackstone's formulation says that it is better that ten guilty persons escape than one innocent suffers. Since academic misconduct depends on whether it was an honest mistake or whether there was an intention to cheat, often school and university authorities only issue a warning without further penalty or consequence, in applying this legal principle. Teachers and educators can then feel that the institution does not care about plagiarism, which serves to discourage them from tackling plagiarism.

A previous column (February 2014 issue, p. 38) discussed the importance of including ethics as an essential part of chemistry education. What is needed to reduce plagiarism and other forms of cheating is better education and clarification of what is considered acceptable and unacceptable practice, reducing the opportunities and motivations for cheating, and obviously acting to detect and penalise all forms of cheating. But we can all start by discussing the issue and modelling what is ethical professional practice.



Kieran F. Lim (林百君) FRACI CChem (kieran.lim@deakin.edu.au) is an associate professor in the School of Life and Environmental Sciences at Deakin University. The content of this column has been influenced by, and partly based on, the work of other authors. Full citations are available on request.

Ever heard of carbazotic acid?

The exploitation of Australian natural products has a long history, in which the *Xanthoroea* or blackboy turns up from time to time. The earliest reference I found was in the *Memorials and Proceedings of the Chemical Society* (of London) in 1845 (vol. 3, pp. 10–13). It was a paper entitled ‘Observations on the Resin of the *Xanthoroea hastilis*, or Yellow Gum-resin of New Holland’ by John Stenhouse, Esq., PhD.

Stenhouse was born in Glasgow in 1809 and after a long career ‘down south’ he died in London in 1880 and his body was returned to his native town for burial. Since the PhD did not appear in Scotland or England until much later than 1845, he must have earned this degree on the continent, probably in the time he spent with Justus Liebig, 1837–9, in Giessen. Returning to England, he took up an appointment as professor in St Bartholomew’s Hospital and remained there until 1857, during which time he was elected a Fellow of the Royal Society in 1848. A stroke in 1857 terminated his hospital career but after recuperating at a Mediterranean resort, he set up shop as a consultant chemist with rooms in London. Laboratory work was out of the question but his assistants performed well and in 1865 he was appointed as assayer to the Royal Mint, a titular appointment that did not require actually doing the assaying. His chemical work, which included other natural products, dyeing, waterproofing, textile chemistry, glues, tanning and the use of wood carbon in deodorising and in respirators earned him the gold medal of the Royal Society in 1871.

In his 1845 paper, Stenhouse described it as ‘this remarkable resin, which is known in commerce as the yellow gum or acaroid resin of Botany Bay’ that ‘exudes from the *Xanthoroea hastilis*, a tree which grows abundantly in New Holland, especially in the neighbourhood of Sidney (sic)’. He went on to observe that the ‘resin was first described in Governor Phillip’s Voyage to New South Wales in 1788’ and that Phillip believed that it was ‘employed by the natives and first settlers as a medicine in cases of diarrhoea’.

By repeated crystallisation from aqueous alcohol, Stenhouse isolated a small amount of an acid that carbon and hydrogen analyses suggested was a mixture of cinnamic and benzoic acids. The presence of cinnamic acid was consistent with the production of ‘oil of bitter almonds’ when it was treated with manganese dioxide and sulfuric acid. The benzaldehyde was presumably identified by smell, since Stenhouse gives no details.

When the resin is treated with moderately strong nitric acid, Stenhouse wrote, ‘a violent action ensues with the evolution of nitrous fumes’, and evaporation of the solution produced ‘a mass of fine yellow crystals, consisting chiefly of carbazotic acid, but mixed with some oxalic acid and a little nitrobenzoic

acids’. No evidence is produced about the identities of the by-products, but carbazotic (= picric) acid was identified by combustion analysis of the acid and its silver salt. We can speculate that the complex structure of the resin was broken down by oxidation by nitric acid, and then nitro groups were added to the carbon skeleton, replacing hydrogen or carboxyl substituents.

The yield of picric acid was high and it was easily purified from the reaction mixture, causing Stenhouse to opine that ‘this resin seems likely to prove the best source of that substance’. He did not discover the explosive potential of picric acid, which had to await the researches of Sprengel in 1863, and he would not have imagined its use in warfare under the name ‘Lyddite’. In 1849, Stenhouse did discover a nitrate ester that was extremely shock sensitive. It was formed from ‘erythromannite’ that he had extracted from a lichen, by reacting it with a mixture of sulfuric and fuming nitric acids, and was apparently a pentanitrate. He was working by analogy with the work of French chemists who had, two years previously, converted mannite (mannitol) into its pentanitrate. The French chemists described their compound as ‘a curious detonating compound’ that ‘possesses the remarkable property of detonating so violently when struck with a hammer’ and others observed that it might be used as a substitute for fulminate in percussion caps.

Stenhouse reported the results of his combustion analyses in detail, and they match pretty well for the $C_4H_{10}O_4$ formula of erythritol but with the hydrogen result a little high. However, such was the state of chemical knowledge at the time that he took the atomic masses of carbon and oxygen as 6 and 8, respectively, so he calculated that erythritol was a C_{11} compound and in like vein he accepted that mannitol, which we now know is a hexitol, was a C_{12} .

Later in the century the *Xanthoroea* resin found use in varnishes, and quantities of it were exported from Australia, ostensibly for that purpose. By the early 20th century, however, suspicious minds noted that the major destination for the exports was Germany, and memories of the production of picric acid were stirred. The eventual result, as war neared, was an embargo on such exports. Phenol from coal tar and later from benzene, courtesy of the burgeoning chemical industry, became the major source of picric acid for explosives.



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

22nd International Clean Air and Environment Conference

20–23 September 2015, Melbourne, Vic.
<http://casanz2015.com>

11th Australasian Conference on Vibrational Spectroscopy and 5th Asian Spectroscopy Conference

29 September – 2 October 2015, Sydney, NSW
<https://acovsandasc.wordpress.com>

Medicinal Chemistry and Chemical Biology Vic Symposium

30 September 2015, Parkville, Vic.
<http://wired.ivvy.com/event/BOD501>

4th Federation of Asian Polymer Societies – International Polymer Congress

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

2015 Sustainable Industrial Processing Summit and Exhibition

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

HAZOP Study for Team Leaders and Team Members

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

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

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

Australia and New Zealand Magnetic Resonance Society Conference

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

Pacificchem 2015

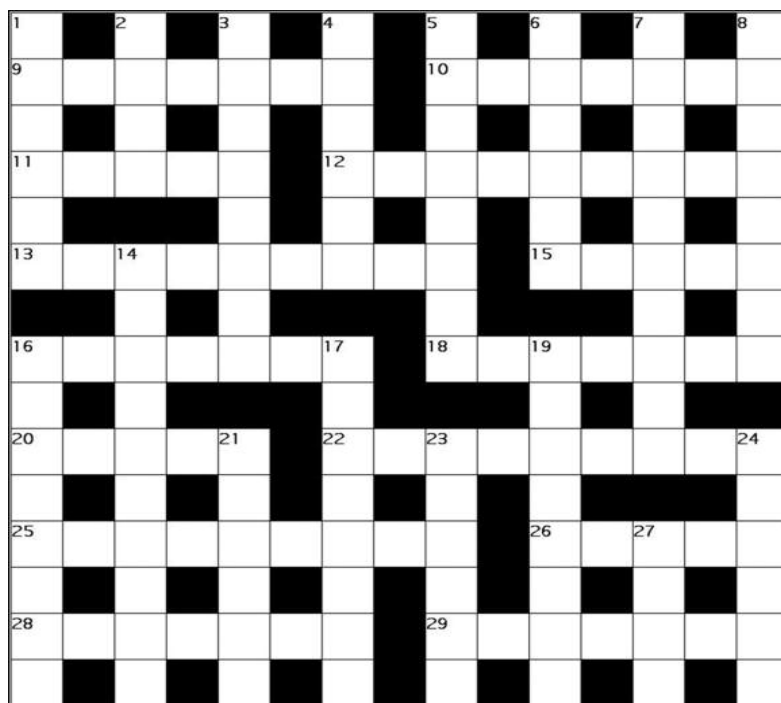
15–20 December 2015, Honolulu, Hawaii
www.pacificchem.org

RACI events are shown in blue.



Coming up

- Salmon and their strontium signatures
- Regulating e-cigarettes
- Public perceptions of chemistry
- Stay tuned for November's public edition!

**Across**

- 9** Opening for if I centrifuge in it. (7)
10 Make it item A. Copy? (7)
11 Two letters sounded out collapse. (5)
12 Supplies apparatus. (9)
13 Thought about it and gave it back. (9)
15 10^{24} holding somewhat to yellowcake inversion. (5)
16 Dog split present. (7)
18 So cap uranium and sulfur at the temperature at which melting begins. (7)
20 Extract electron tube. (5)
22 Relocates decals. (9)
25 Airing may damage abstract. (9)
26 Capacity to make it. (5)
28 One sound compound! (7)
29 Use of solvent to extract line-out restart?! (7)

Down

- 1** Hydrogen with aged supporter. (6)
2 30 = last in 6. (4)
3 First lemon extract with lysine used to make a reactive intermediate which contains a neutral divalent silicon atom. (8)
4 Choose, sulfur. Choose! (6)
5 We object after three pound the temperature at which melting is complete. (8)
6 Does sulfur indicate plainly? (6)
7 $C_{20}H_{19}N_3$ -HCl made. Get any reaction? (7,3)
8 True! Sulfur, aluminium and nitrogen combine to form unaligned states. (8)
14 Prepared four malted concoctions. (10)
16 Revolutionary claim about one of our substances. (8)
17 Used 16 Down analytical method bird assessed. (8)
19 Shiny excitement with sour mixture. (8)
21 Stand two effects of drug use. (6)
23 Yes! Ran around the compounds. (6)
24 Enigma: 16151537 unknown. (6)
27 A 10 is a point about which it all revolves. (4)

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

Bringing bubble mania to Victorian schools

The RACI's 'Chemistry is Everywhere – Bubble Mania' Schools Program has been bringing the fun and excitement of science to schools across Victoria.

The new program has been designed to highlight the role that chemists play in the development of everyday products. Students look at the maths, physics and chemistry of bubbles before taking on the role of formulation chemists trying to develop the formula for the ultimate bubble. Along the way, they learn about the chemistry of water, detergents and the various industrial applications of bubbles.

There is some serious science in bubbles. Students look at how something as seemingly simple as a bubble is actually very complex and how bubbles have fascinated scientists and mathematicians from Newton to Einstein and Joseph Plateau.

Learning science and chemistry is seen by many as difficult or boring, but this program strives to break down those barriers and highlight the wonderful world of science through fun hands-on activities. After all, everybody loves bubbles.

According to Esha at St Patrick's Primary School in Stawell: 'It was the most exciting science lesson I have ever had and I can relate it to what may be ahead when I partake in science at secondary school.'

Ashley H at Irymple Secondary College said he 'can't believe how much there is to know about bubbles. Such a simple activity contains so much complexity.'

The program is suitable for upper primary years 5 and 6 to secondary year 10 with the chemistry adjusted at each level to match the students' science level. It is a hands-on program with the students actively involved in preparing and testing their formulas. It is serious science and a lot of fun. The program can be used to introduce a range of science-related topics and investigations and is mapped to the AusVELs science standards.

The program is self-contained and



Liam of Alexandra Secondary College with his bubble and St Patrick's Primary School, Stawell, students Kobe and Ajay working on their bubble geometry.

does not require anything from the schools other than space and students. Each session can cater for up to 36 students and runs for 100 minutes. Each student receives theory and workbooks. The RACI is committed to making the program accessible to schools across the state.

For further information, details or costs or to organise a program for your school, contact the RACI Victorian Branch Coordinator on (03) 9328 2033 or at raci-vic@raci.org.au.

Matthew Corkhill

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