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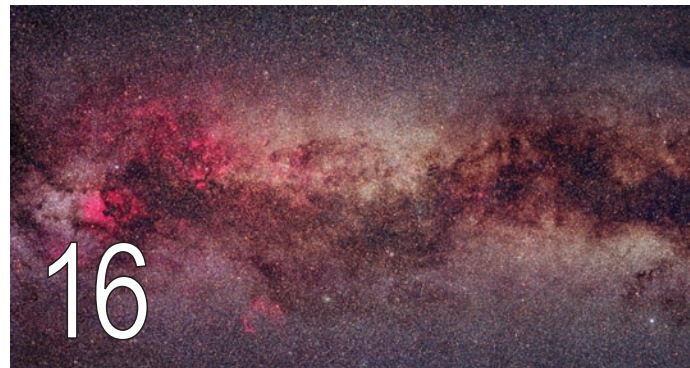
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From the President

I have been part of the Working Group for the inaugural Decadal Plan for Chemistry, an initiative of the Australian Academy of Science's National Committee of Chemistry, which is supported by the RACI. At dozens of open 'Town Hall' meetings during 2014, chemists from all sectors have given their opinions on the best way ahead for chemistry in our country. The initial findings and recommendations are currently being assembled and a Green (consultation) Paper will appear in early 2015 for public comment (see <http://chemistrydecadalplan.org.au>). Every meeting I've attended has brought out new issues and ideas.

The Decadal Plan project focuses on two questions: 'Where do you want chemistry to be in 2025?' and 'How will we get it there?' In Australia, we have not tackled these questions before and the current generation of newly educated chemists in particular need to buy into them.

Most at the meetings agreed on the need for improvement in the public's perception of chemistry. The word 'chemical' is used pejoratively and the loosely phrased expression 'chemical free' pervades non-chemistry-literate society. Even young children are warned of the dire consequences of going near the (usually locked) cupboard with the 'chemicals' in it. Some of these chemicals, which could be anything from cleaning products to pharmaceuticals, are potentially harmful if ingested, but we all rely on them, or why did we buy them? Chemists know how to safely live with chemistry – we survey the information and assess the potential hazards. We don't fear the chemical.

Organic produce is an interesting example of 'chemicals' being given a bad name in spite of the longstanding successes of agrochemicals. The organic food industry is based on the premise that produce grown without (or with a minimum of) (synthetic) chemicals is inherently better for you. The exclusion of synthetic chemicals in favour of 'natural' products is a peculiar distinction – synthetic pesticides are generally at odds with the principles of organic farming yet 'natural' pesticides may be allowed. A natural product is not intrinsically less harmful than a synthetic product – a point that is rarely made,

leaving society with a distorted view of the worth of chemicals and chemistry in general.

The Organic Federation of Australia (OFA) acknowledges that obtaining accord on the criteria for organic produce in Australia remains a challenge and there is still no mandated regulatory system for organic products. So there are currently various degrees of 'organic' produce on the market. The term 'organic chemistry' must have members of the organic produce industry perplexed. Perhaps it's seen as an oxymoron. Where does 'inorganic chemistry' sit (a double whammy)?

The word 'chemical' (and 'chemistry') needs advocates in society. You can help by pointing out to friends and relations that nothing on Earth is actually chemical-free (in spite of countless examples to the contrary – Google 'chemical-free' if you dare). Although nobody denies the damage that has been done to the chemistry 'brand' by past unregulated and irresponsible handling of some harmful compounds, we should point out that this does not represent a balanced view of chemistry. All around, we can see evidence of chemistry's positive impact. To go (synthetic) chemical-free would limit much of what we currently do.

The Chemistry Decadal Plan open meetings also highlighted that the 'grand challenges' are harder to define for chemistry than for biology or physics (e.g. origin of life, unification of the laws of physics). However, chemistry will continue to permeate the other sciences and will share the accolades and rewards that come from its interactions on the fringes, although these boundaries are even more diffuse than ever. The challenges we face in energy, food and water supply and materials for a rapidly growing world population will involve chemistry and chemists at the forefront.

Can we please have our word back now?



Paul Bernhardt FRACI CChem (president@raci.org.au) is RACI President. He was educated at the University of Newcastle where he joined RACI as a student in 1986. After postdoctoral fellowships in Basel and at ANU, he joined the University of Queensland where he is currently Professor of Chemistry.

chemistry
in Australia
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ISSN 0314-4240 e-ISSN 1839-2539



Viability of warm-bloodedness

I refer to the June 2013 article 'When the going gets hot' (p. 20) wherein Ronald Clarke explains a mechanism whereby warm-blooded mammals, which include humans, will have trouble living in warmer climates, a circumstance that he relates to climate change.

Whilst I think that he may be being a bit tongue in cheek, a highlighted statement in the article says '... if global warming continues, warm bloodedness will eventually become unviable ...', but he does not tell us at what temperature and when this may occur.

Without any quantification of his hypothesis, his statement is unworthy of publication in our journal. Any figures that I have seen on global warming are quite minute, being of the order of tenths of a degree over decades; in fact, over the last two decades the records show cooling, if any change at all. Australians, with their fine warm blood, have no problem living in Melbourne or Brisbane with an average temperature difference of 5°C.

There is no scientific case for claiming that current global warming predictions will threaten human life. We live in the Arctic and the tropics, and such a proposition should not be perpetrated in our journal without valid evidence.

As an organic chemist, I find this article interesting in terms of the importance of environment upon mammals, but the global warming inference is just plain offensive.

Richard Corbett MRACI CChem

Mr Corbett objects to the statement 'If global warming continues, warm-bloodedness will eventually become unviable ...'. However, this statement is simply a logical application of the laws of thermodynamics, to which the Earth as a whole and every human being on it are subject. If the rate of heat inflow to an object remains constant, but the rate of heat outflow is inhibited, as it is in the case of the Earth via the greenhouse effect, then the undeniable consequence is an increase in temperature of the object concerned, i.e. in the Earth's case an increase in the average global temperature. If the temperature of the Earth increases, this naturally inhibits the ability of all animals on it to dissipate body heat to their surroundings. Thus, if the rate of heat dissipation is reduced, just as in the case of the Earth, body temperature must eventually rise, thus impacting on an animal's viability.

Of course, this is all based on the hypothesis that global warming is occurring, which Mr Corbett doubts. In contrast, he states that records (uncited) show that the Earth is actually cooling. However, this is in clear disagreement with the consensus of results published by the International Panel on Climate Change (established by the United Nations Environment Programme and the World Meteorological Organization) in their 2013 Climate Change Report, which show an increase in the globally averaged combined land and ocean surface temperature of 0.65–1.06°C over the period 1890–2012 and an increase in the average decadal temperature for every decade since the

1970s. It is clear that Mr Corbett is correct that Australians have no problem in living in Melbourne or Brisbane. However, what is equally true is that in France, a country in which air-conditioning is much less widespread in homes than in Australia, almost 15 000 heat-related deaths were recorded in the summer heatwave experienced there in 2003.

Of course, this author hopes that global warming never gets to the stage that the survival of the human species or any other warm-blooded animal is threatened. But rather than wait and take the gamble that it never happens, I would suggest it be advisable for the world community to take concerted action to ensure that it doesn't.

Ronald J. Clarke MRACI CChem

Swelling jelly babies

The illustration of Smarties immersed in water in the November issue (p. 39) reminded me of some work of my own from a decade ago (Jones J.C. 'Looking swell, baby', *Phys. Educ.* 2004, vol. 39, p. 25). I published a similar illustration of jelly babies immersed in water. We were interested not in colour effects but in swelling. This was part of a program of work in which the swelling of polymers in organic solvents was investigated, and we also made the brief study of the water-induced swelling of gelatinous foodstuffs.

A reader performing the Smarties test might care to consider swelling as well as the migration of colouring agents. Swelling of the jelly babies was quite sufficient for visual detection. It could of course have been measured quantitatively by use of a travelling microscope.

J.C. Jones FRACI CChem

'Your say' guidelines

We will consider letters of up to 350 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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Climate change: chemistry + cofactors = complexity + chaotic confusion

'Carbon dioxide reduction', the climatologists'/physicists' slogan for reversing the claim of climate change, but where are the chemists? In my opinion, the world's chemists must join the discussion to demonstrate that climate change is not resolvable with a simple one-factor solution.

The chemistry involved in any chemical reaction, which includes every single process in the entire world, is rarely if ever the result of reacting substances creating a new entity without any other outside influences/cofactors.

The background to this personal opinion was a comment by Ben Selinger in a climate change article (December 2010) in which I, surprisingly, discovered that, as opposed to media information/hype, carbon dioxide and methane were not the only 'greenhouse' gases contributing to 'climate change' – water vapour was the most abundant and equally important, while not being mentioned in the public media and rarely in climate change scientific literature.

The greenhouse gas 'water vapour' can be transformed into highly unpredictable/difficult-to-model clouds; hence the demise of the 1980's 'nuclear winter' panic.

Virtually each drop of rainwater in clouds contains a 'seed', aka generic 'dust', in the atmosphere due to unpredictable cofactors, e.g. wind, volcanoes, bushfires, earthquakes, aerosols, human activities.

Other natural, unpredictable cofactors involved in climate change, and of which humans have limited knowledge and even less control, include oceans, seas and currents, sun cycles, sunspots, solar winds, the roiling Earth's core etc. which are rarely mentioned, as they are not attributable to humans and then politically taxable.

I agree humans can do a lot to improve or change our outputs to reduce any generated minor effects that actually affect 'climate change', if it is really occurring, but it is mostly due to a complex mixture of non-human induced/uncontrollable cofactors.

This is a call to RACI members to contemplate cofactors and discuss with colleagues, friends and families. Chemists possess the education and expertise to rationally influence this debate; it is not as simple as the media and pressure groups portray. The truth is more complex than just human outputs; cofactors must be elucidated and included in education curricula.

Tony Zipper FRACI CChem



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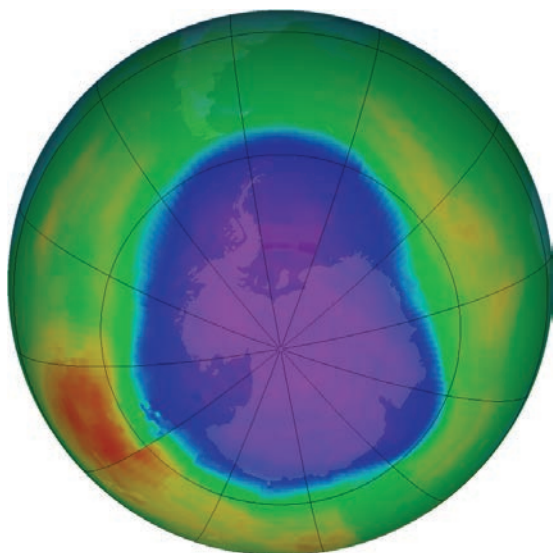
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Ozone layer recovering but remains threatened



The deepest ozone 'hole' occurred in 1994, when concentrations fell to just 73 Dobson units on 30 September. Purple and dark blue areas are part of the ozone hole.

NASA Earth Observatory

The Earth's protective ozone layer is on track to recover by the middle of the century, the United Nations reported in September, urging unified action to tackle climate change and curb continued fluctuations to the composition of the atmosphere.

That is according to the assessment of 300 scientists in the summary document of the Scientific Assessment of Ozone Depletion 2014, published by the UN Environment Programme (UNEP) and the UN World Meteorological Organization (WMO).

'International action on the ozone layer is a major environmental success story,' WMO Secretary-General Michel Jarraud said. 'This should encourage us to display the same level of urgency and unity to tackle the even greater challenge of climate change.'

The ozone layer, a fragile shield of gas, protects the Earth from the harmful portion of the sun's ultraviolet rays, thus helping to preserve life on the planet. Its recovery, according to the scientists, is attributed to the collective action through the Montreal Protocol, which since 1987 has led countries to carry out policies to reduce and then phase out their use of ozone-depleting chemicals.

Without the Montreal Protocol and associated agreements, atmospheric levels of ozone-depleting substances could have increased tenfold by 2050, according to the report. 'However, the challenges that we face are still huge. The success of the Montreal Protocol should encourage further action not only on the protection and recovery of the ozone layer but also on climate,' said UNEP Executive Director Achim Steiner.

Secretary-General Ban Ki-moon recently hosted, at UN Headquarters in New York, a summit in an effort to catalyse global action on climate change.

'The Montreal Protocol community, with its tangible achievements, is in a position to provide strong evidence that global cooperation and concerted action are the key ingredients to secure the protection of our global commons,' Steiner added.

Among the key findings of the report, the authors noted that what happens to the ozone layer in the second half of the 21st century will largely depend on concentrations of carbon dioxide, methane and nitrous oxide – the three main long-lived greenhouse gases in the atmosphere.

UNITED NATIONS

Mexican plant could help 'green' perfume industry

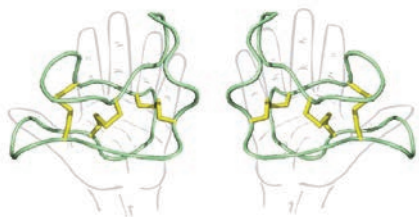
The mere whiff of a dreamy perfume can help conjure new feelings or stir a longing for the past. But the creation of these alluring scents, from the high-end to the commonplace, can also incur an environmental toll. That could change as scientists, reporting in *Sustainable Chemistry & Engineering*, examine a more sustainable way to produce a key perfume ingredient and supply it to fragrance makers around the world.

José M. Ponce-Ortega and colleagues explain that out of the three main ingredients in perfumes, the fixatives, which allow a scent to linger on a wearer's skin rather than quickly dissipate, are often pricey. A particularly coveted fixative comes from a rare whale digestive excretion called ambergris. Not only is its cost exorbitant, but its use in perfumes in many countries is illegal. That's why many perfumeries long ago turned to a synthetic version. Although not as costly, the substitute still commands a high price, and requires considerable time and energy to make. A simpler way to make synthetic ambergris exists, but the catch is that the starting material is a flowering plant found in Mexico. That means the plant would have to take a fuel-consuming, environmentally unfriendly journey across the ocean to Europe, where many perfumes are made. So Ponce-Ortega's team wanted to see whether the process would be worth it.

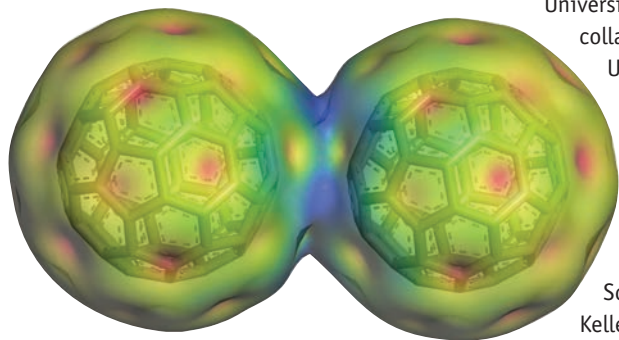
To find out, the researchers conducted a supply-chain analysis. They found that producing the fixative using the Mexican plant would generate considerable local profits to the tune of \$20 million per year and create hundreds of jobs along the supply routes. They did find an environmental cost to the process, but that could be mitigated by using renewable energy sources to produce the fixative.

AMERICAN CHEMICAL SOCIETY

Helping hand for crystallography

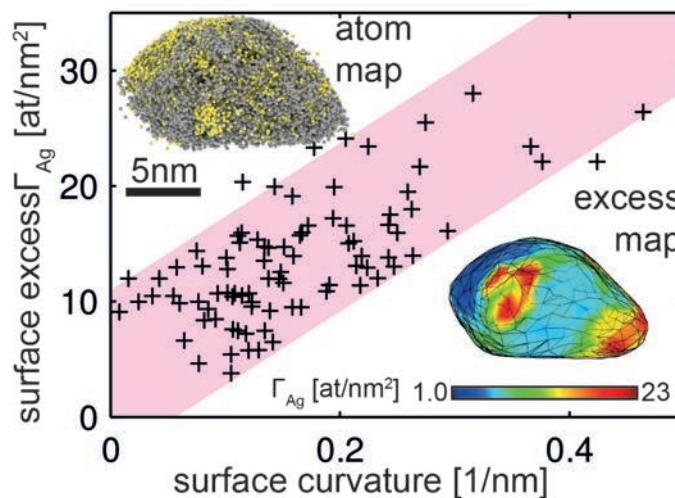


Cyclic disulfide-rich peptides have been the subject of intense scrutiny over the past decade because of their exceptional stability and potential as drug design scaffolds. Despite this interest, obtaining high-resolution X-ray data on their structures has been challenging because crystallisation of disulfide-rich peptides is notoriously difficult. The team of Professor David Craik, at the University of Queensland, has explored the use of racemic crystallography, in which crystals are grown from a mixture containing a peptide and its mirror image, to facilitate crystal formation (Wang C.K., King G.J., Northfield S.E., Ojeda P.G., Craik D.J. *Angew. Chem. Int. Ed.* 2014, **53**, 11236–41). L- and D-forms of three prototypic cyclic disulfide-rich peptides – SFTI-1 (14-mer with one disulfide bond), cVc1.1 (22-mer with two disulfide bonds), and kB1 (29-mer with three disulfide bonds) – were synthesised and the racemic mixtures were crystallised, allowing their structures to be solved at resolutions ranging from 1.25 Å to 1.9 Å. The racemic crystallography approach is currently being further explored at the University of Queensland.



Mapping atoms in bimetallic nanoparticles

To be able to correlate the catalytic properties of nanoparticles with their structure, detailed knowledge about their make-up on the atomic level is required. The teams of Professors Thomas Maschmeyer and Julie Cairney, from the University of Sydney, have, for the first time, demonstrated how atom-probe tomography (APT) can be used to quantitatively determine the three-dimensional distribution of atoms within a Au@Ag nanoparticle with near-atomic resolution (Felfer P., Benndorf P., Masters A., Maschmeyer T., Cairney J.M. *Angew. Chem. Int. Ed.* 2014, **53**, 11190–3). They reveal that the elements are not evenly distributed across the surface and that this distribution is related to the surface morphology and residues from the particle synthesis. The technique allows the determination of the role and influence on performance of the ‘spectator species’, such as the anions used in the synthesis of the particles. The effect of curvature and general morphological features on the assembly of the growing particle can also be addressed. Application of this research will provide a basis for the rational design of (multi)metallic nanoparticles to generate a spread of desirable reactive sites.



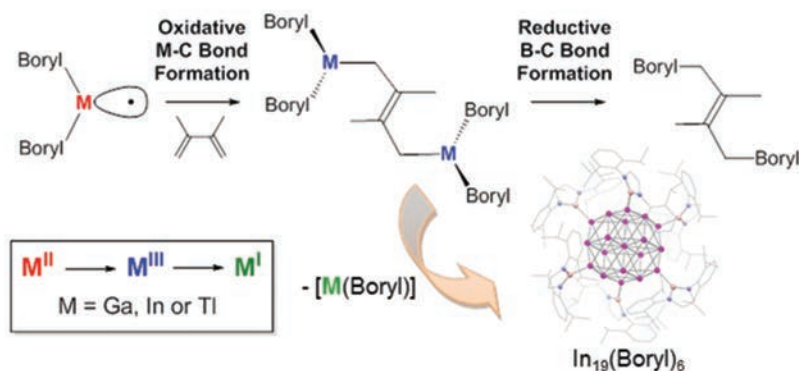
Electrons trapped between fullerenes

C_{60} fullerenes are cage-molecules that resemble soccer balls, which can trap atoms or small molecules inside the cage. In contrast, electrons are usually trapped within the molecular π -system on the surface of the fullerene. Professors Paul Keller and Stephen Pyne, from the University of Wollongong, in collaboration with scientists from the University of Erlangen, Germany, have now discovered that fullerenes can accept electrons far more readily when they are non-covalently in contact with a second fullerene molecule (Shubina T.E., Sharapa D.I., Schubert C., Zahn D., Halik M., Keller P.A., Pyne S.G., Jennepalli S.,

Guldi D.M., Clark T. *J. Am. Chem. Soc.* 2014, **136**, 10890–3). The resulting molecular ion corresponds to a $(C_{60})_2$ -van der Waals dimer: a stable arrangement of the two molecules held together by an electron between the two C_{60} molecules (i.e. two fullerenes can form a ‘bond’ using the extra electron). The figure shows the electrostatic potential on the surface of such a dimer. The strongly negative (blue) potential caused by the electron is clearly visible between the fullerenes. This research should have major impact in the understanding of fullerenes as n-type semiconductors, which can be used, for instance, to fabricate flexible transistors with very low power requirements on plastic sheet.

Radical approach to reversible M–C bond formation

The forming and breaking of metal–carbon bonds by facile oxidative addition/reductive elimination processes is the cornerstone of numerous transition metal-catalysed transformations. In contrast, such chemistry is extremely rare for main group metal systems. As part of an ongoing collaboration between the groups of Professors Cameron Jones (Monash University) and Simon Aldridge (Oxford University), the first stable group 13 metal(II) radicals (see May issue, p. 13) have been shown to react with dimethylbutadiene, via oxidative M–C bond formations, to give metallo-butenediyl complexes (see figure). These systems can undergo subsequent reductive elimination under mild conditions, yielding B–C bonded products (Protchenko A.V., Dange D., Blake M.P., Schwarz A.D., Jones C., Mountford P., Aldridge S. *J. Am. Chem. Soc.* 2014, **136**, 10902–5). In one instance, the



eliminated indium(I) fragment, In(Boryl) Boryl = B(diazabutadienediyl), undergoes partial disproportionation to give the remarkable mixed valence ‘metalloid’ cluster, In₁₉(Boryl)₆. The ‘naked’ metallic In₁₃ core of this cluster exhibits an idealised cubic close-packing structure, similar to that found for nanoparticulate

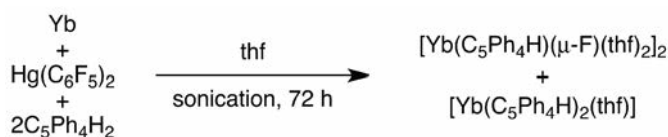
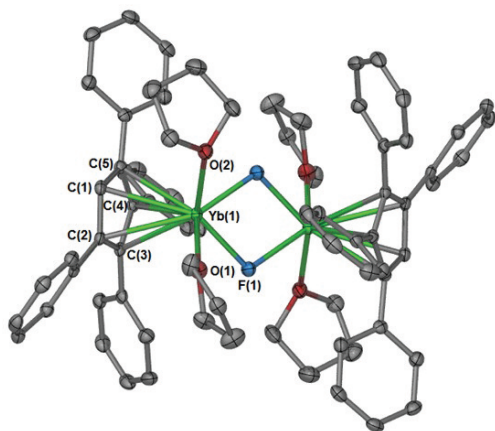
indium metal. The ‘transition metal-like’ reactivity displayed by the group 13 metal radicals highlights the potential low-valent p-block complexes hold for use as catalysts in organic transformations. This potential continues to be developed by Jones’ team.

Is bigger always better? Depends how you use it

Lanthanoid complexes bearing the bulky pentaphenylcyclopentadienyl (C₅Ph₅) ligand are difficult to synthesise due to reactivity and purification problems. However, redox–transmetallation/protolysis (RTP) reactions carried out in tetrahydrofuran (thf) between ytterbium metal, HgPh₂ and C₅Ph₅H afforded the solvent-separated ion pair [Yb(thf)₆][C₅Ph₅]₂, which can be desolvated to yield [Yb(C₅Ph₅)₂]. Although the latter complex is

structurally intriguing, its poor solubility hinders reactivity studies. In order to improve solubility, researchers at Monash and James Cook Universities have turned their attention to the tetraphenylcyclopentadienyl (C₅Ph₄H) ligand (Deacon G.B., Jaroschik F., Junk P.C., Kelly R. *Chem. Commun.* 2014, **50**, 10655–7). RTP reactions yielded the first divalent octaphenylcyclopentadienyl lanthanoid complex, [Yb(C₅Ph₄H)₂(thf)]. Given that reactions with HgPh₂ can be sluggish, the use of Hg(C₆F₅)₂ was explored,

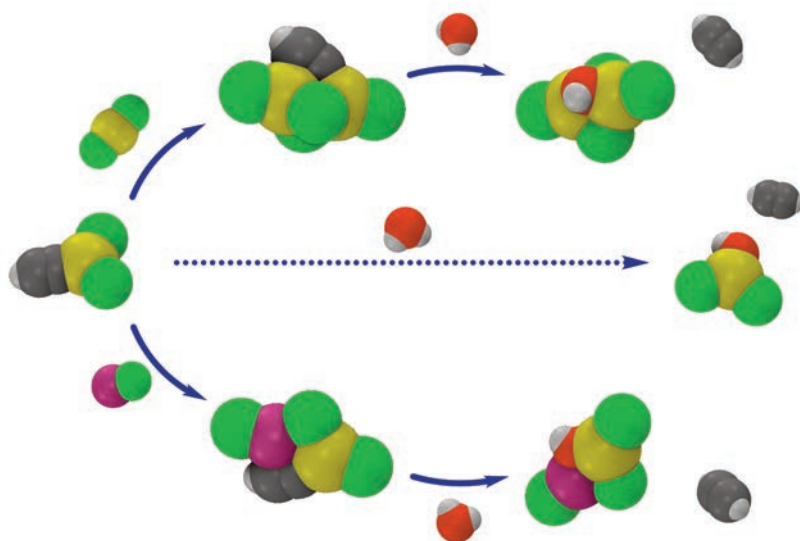
unexpectedly leading to the isolation of the first heteroleptic divalent lanthanoid fluoride complex, [Yb(C₅Ph₄H)(μ-F)(thf)₂]₂ (see figure). This complex forms from reduction of the C₆F₅H generated during the RTP process by ytterbium metal, rather than from [Yb(C₅Ph₄H)(C₆F₅)(thf)₂] (an implied intermediate), which is reluctant to form the fluoride species even after prolonged heating. ¹⁹F and ¹⁷¹Yb NMR studies show the dinuclear fluoride-bridged species maintains its integrity in solution.



Why salty Grignard reactions fail

The mystery of why water and salt contaminants destroy organometallic reagents has been solved thanks to new research conducted by scientists at the University of Melbourne (Khairallah G.N., da Silva G., O'Hair R.A.J. *Angew. Chem. Int. Ed.* 2014, **53**, 10979–83).

Organometallic compounds, such as the ubiquitous Grignard reagents, are powerful tools used to help create new organic molecules both in the laboratory and in commercial chemical plants, although careful management by the chemist is required to avoid contaminants in the reaction. The research team of Professor Richard O'Hair, Dr George Khairallah and Dr Gabriel da Silva has used a powerful combination of electrospray ionisation coupled with multistage mass spectrometry and theoretical simulations to study how simple magnesium and lithium acetylides

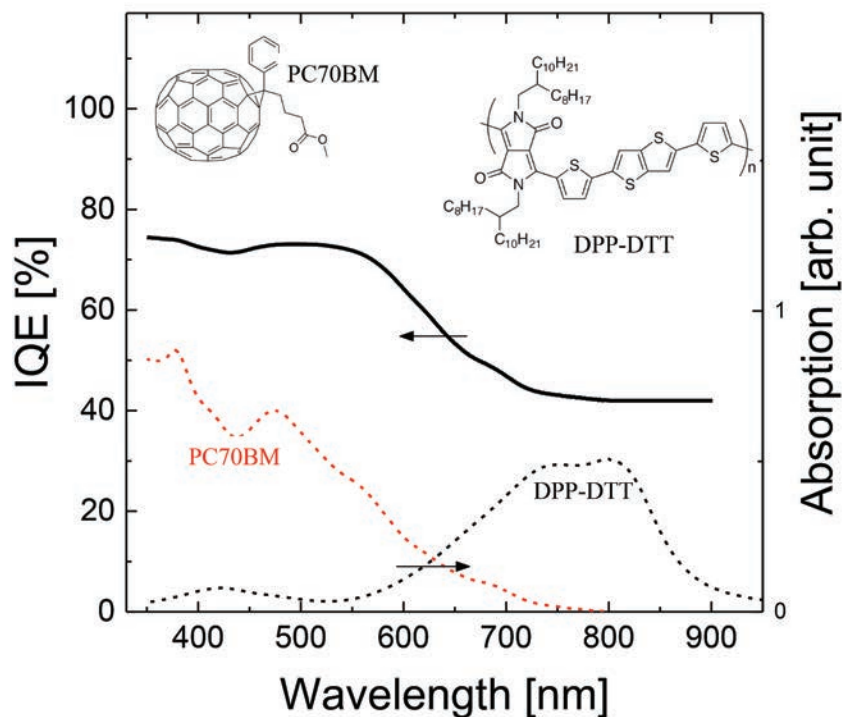


react with water when isolated under idealised near-vacuum conditions, and tracked the effect of adding individual salt molecules (e.g. a MgCl_2 ion trio (top) or LiCl ion pair (bottom) in the figure) on the reaction rate. This approach allowed the researchers to clearly see that the addition of an individual salt molecule to

an organometallic reagent dramatically enhances its reactivity towards water. Interestingly, theory showed how the salt molecule provides a second metal centre, which plays an active role to alter the fundamental chemical transformations taking place when water attacks these organometallic compounds.

The importance of channelling your energy

Researchers from the Centre for Organic Photonics & Electronics, University of Queensland, have shown that the mechanism of charge generation in organic solar cells (OSCs) can be significantly different depending on the combination of active materials used (Armin A., Kassal I., Shaw P.E., Hamsch M., Stolterfoht M., Lyons D.M., Li J., Shi Z., Burn P.L., Meredith P. *J. Am. Chem. Soc.* 2014, **136**, 11465–72). The conventional picture of photocurrent generation in bulk heterojunction (BHJ) OSCs containing a blend of a conjugated polymer donor and fullerene acceptor involves photoexcitation of the electron donor, followed by electron transfer to the acceptor – the Channel I mechanism. Less well studied is the mirror-image process of acceptor photoexcitation followed by hole transfer to the donor – the Channel II mechanism. The team showed that a BHJ layer comprising a narrow optical gap polymer (DPP-DTT) mixed with PC70BM (see figure) showed



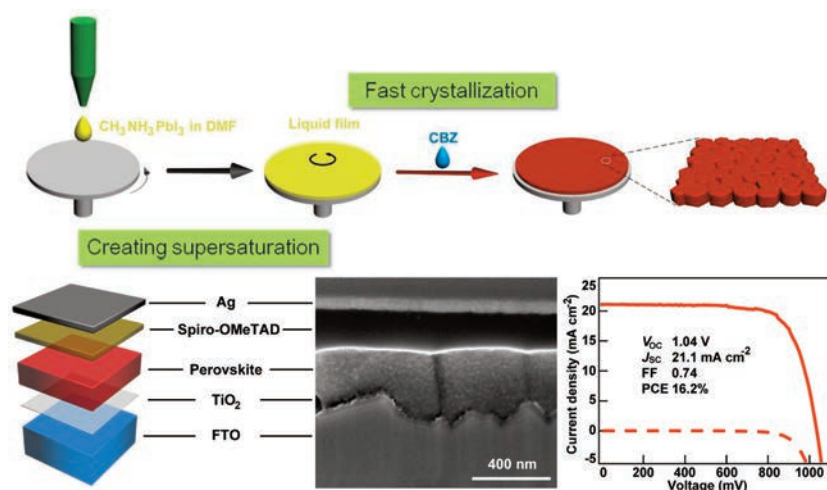
two distinct spectrally flat regions in the internal quantum efficiency (IQE), consistent with the two channels operating with different efficiencies. Hot

excitons or other exotic processes are not in play, with differences in efficiency being due to the energetics and exciton dynamics.

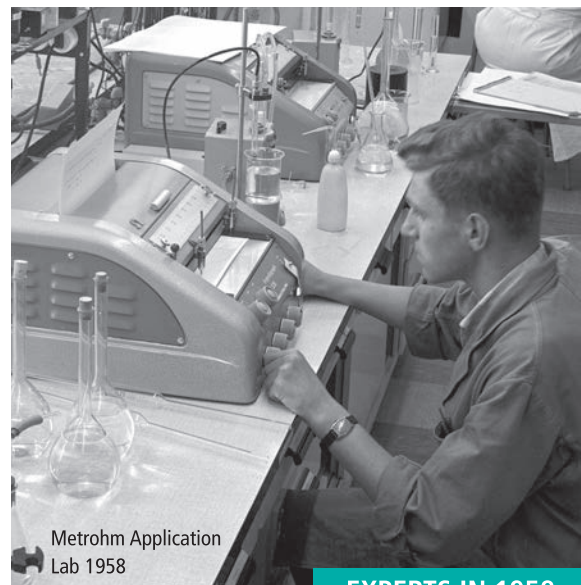
Times have changed...

New frontier in solar energy conversion

Thin-film photovoltaics (PVs) based on alkylammonium lead iodide perovskite light absorbers have recently emerged as a promising low-cost solar-energy-harvesting technology. To date, the perovskite layer in these efficient solar cells has generally been fabricated by either vapour deposition or a two-step sequential deposition process. A team from Monash University, headed by Professors Leone Spiccia, Yi-Bing Cheng and Udo Bach, has now demonstrated that uniform $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films can be deposited by using an easily scalable one-step procedure, which involves spin-coating of a DMF solution of $\text{CH}_3\text{NH}_3\text{PbI}_3$, followed immediately by exposure to chlorobenzene to induce rapid crystallisation (Xiao M., Huang F., Huang W., Dkhissi Y., Zhu Y., Etheridge J., Gray-Weale A., Bach U., Cheng Y.-B., Spiccia L. *Angew. Chem., Int. Ed.* 2014, **53**, 9898–903). The resulting perovskite films consist of large crystalline grains with sizes up to microns. Planar heterojunction solar cells constructed with these films afforded a maximum power conversion efficiency of 16.2% and an average efficiency of $13.9 \pm 0.7\%$ under standard AM 1.5 conditions. This simple low-temperature solution process is fully compatible with the construction of tandem devices applying existing photovoltaic technologies, such as silicon PVs and polymer solar cells. In addition to aiding the development of perovskite-based PVs, it will also bring new possibilities to perovskite-based hybrid optoelectronic devices, such as field effect transistors and light-emitting diodes.



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



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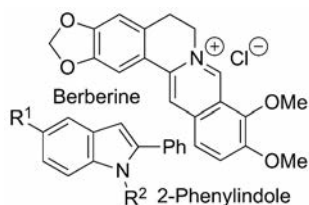
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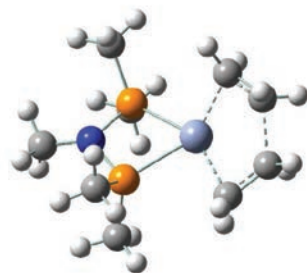
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Aust J Chem

Our colleagues in Japan have long had the custom to publish accounts of their work in *Bull. Chem. Soc. Japan* whenever they get an award from the Chemical Society of Japan. Taking a leaf out of their book, *Aust. J. Chem.* reached agreement with the RACI to publish accounts from recipients of research-related RACI medals and awards. The current October and November issues contain papers from some of the 2012 and 2013 RACI award winners.

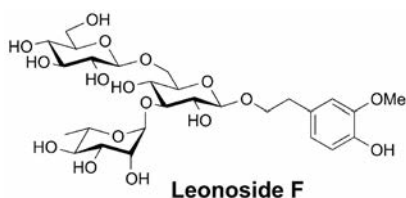


Michael Kelso and co-workers (University of Wollongong) compared the antibacterial activity of berberine together with synthetic NorA multidrug resistance pump inhibitors (2-phenylindoles) versus hybrid compounds, where these two molecules are covalently linked. The conclusion, reported in the October issue, is that the activity of the hybrid molecules is not just the sum of the two parts: the mechanism(s) of antibacterial action of the hybrids must be different from the mechanisms at play when berberine is co-administered with 2-phenylindoles as separate compounds. Dr Kelso was the recipient of the 2013 Biota Award for Medicinal Chemistry.



N, blue; P, orange; Cr, pale blue.

David McGuinness and co-workers (University of Tasmania) describe a theoretical model for the industrially important conversion of ethylene to higher alpha-olefins, using homogeneous Cr-PNP catalysis (PNP = Me₂P-NMe-PMe₂). DFT calculations suggest a Cr^I-Cr^{III} mechanism involving spin surface crossing from sextet to quartet states. The Cr complex shown with a PNP ligand and two ethylene molecules is a likely intermediate in the first step, the dimerisation of ethylene. Dr McGuinness was the recipient of the 2013 Organometallic Chemistry Award.



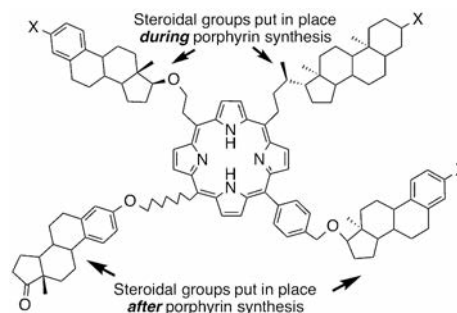
Keith A. Stubbs and coworkers (University of Western Australia) report on the synthesis of carbohydrate-based natural products from the herb *Leonurus japonicus* as well as a biological evaluation of these compounds as anti-oxidants. This genus contains numerous species that can be found throughout Europe and Asia, as well as in some regions of the Americas and Africa, where they also feature in traditional medicine. Three carbohydrates, including leonoside F pictured, were synthesised

and shown to have the capacity to reduce oxidative stress. Dr Stubbs was the recipient of the 2012 Rennie Memorial Medal and the 2013 Athel Beckwith Lectureship.

Junming Ho was the winner of 2012 Cornforth Medal for best PhD thesis (at the ANU, supervised by Michelle Coote). In the October issue, he reports a review on computational prediction of pK_a values as an alternative to experimental measurement. Reliable prediction of pK_a is important in many areas of science, including chemical synthesis, structural biology, and the development of drugs and functional materials, and this is achievable for many species ranging from small monoprotic acids to larger and conformationally flexible polyprotic acids. This paper is freely available on the RACI website as the October *Aust. J. Chem.* paper.

Max Crossley and co-workers (University of Sydney) describe syntheses of steroid-porphyrin conjugates from the natural steroids estradiol, estrone and lithocholic acid in the November issue. Four different construction motifs are explored by using two different strategies for forming the required alkylidenepyrrole-steroid linkages, i.e. pre- or post-porphyrin synthesis. It was found that the best method involves late introduction of the steroid component by means of a nucleophilic substitution reaction. This paper is freely available on the RACI website as the November *AJC* paper. Professor Crossley was the recipient of the 2013 Leighton Memorial Medal.

Leone Spiccia (Monash) was a recipient of both the Burrows Medal (2013) and the H.G. Smith Memorial Award (2012). An article, 'Fluorescent analogues of NAMI-A: synthesis, characterisation, fluorescent properties, and preliminary biological studies in human lung cancer cells', with S. Antony, J.C. Morris, T. Bell, T. Brown and Hugh H. Harris as co-authors is available 'Online Early' on the *Aust. J. Chem.* website and will be published in the December issue.



Aust. J. Chem. looks forward to a series of exciting contributions from the 2014 RACI National Award winners.

The November issue also contains a series of nine papers on molecular magnetism resulting from a Southampton-Australia-New Zealand Workshop held in Sydney in February. This Research Front is guest-edited by Suzanne Neville, University of Sydney.

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

The perfect roast reaction



Forget caffeine – following your favourite barista around town is all about the chemicals in the flavours and aromas of a great coffee.



BY **COLIN A. SCHOLES**

Coffee is one of the world's favourite beverages because of caffeine, an alkaloid that so many of us find addictive. But we don't choose our coffee on strength alone.

As any coffee devotee knows, bean type has long been associated with coffee quality. The best beans, cultivated in the right location, soil conditions and climate, come at premium prices. However, it is the roasting process that really sets up the organic chemistry to produce so much of the flavour and aroma.

During the high-temperature roasting (greater than 140°C), a complex series of reactions occurs within the beans, largely between the amino groups of amino acids and the carbonyl groups of carbohydrates. The hundreds of compounds produced then undergo further chemistry or break down under the high temperature and oxidation conditions of the roast. The result is hundreds more organic compounds, all of which elicit taste and smell responses.



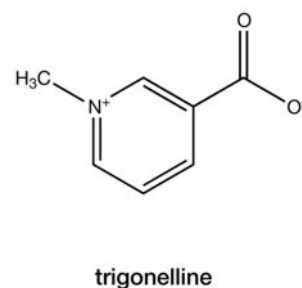
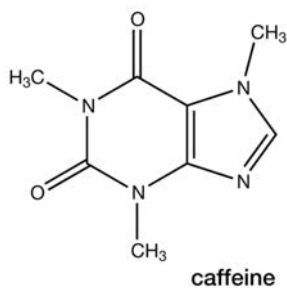
Collectively known as the Maillard reaction, these reactions describe the food chemistry of many high-temperature food processes. For example, the Maillard reaction causes crust formation during bread baking and gives baked potatoes their delicious crispy brown coating. Many of the organic groups formed during the roasting Maillard reaction can be associated with certain flavours.

Furans are responsible for the taste of sweet caramel, while pyridines register as nutty, and diacetyl butanedione gives us butterscotch flavour.

To date, around 500 flavour compounds have been identified in coffee, of which around 60 have important roles in taste. This is significantly different from other foods, such as apricots and strawberries, which have only 20–30 flavour compounds. The brown colour of coffee is the result of the formation of melanoidins during the Maillard reaction.

The higher the temperature and the longer the roasting process, the more extensive the Maillard reaction and the more the beans' organic chemistry is altered. This is why high-quality beans are only lightly roasted, to limit the extent of the Maillard reaction and retain the original flavours. Poorer quality beans undergo longer roasts, more commonly known as darker roasts, which convert much of the bean's original organic chemistry through the Maillard reaction. This makes it more difficult to distinguish the origins of the bean, and, importantly, can be used to hide the poorer quality of the bean.

One of the most common myths of roasting is that it alters the caffeine content of the bean. However, caffeine is a stable alkaloid and has a higher sublimation temperature than that reached during roasting. The other major alkaloid, trigonelline, which protects the bean from insects and fungal attack, is less stable and undergoes degradation during roasting. The products supply coffee's



Caffeine and trigonelline, coffee's two main alkaloids. Both have insecticidal and fungicidal properties.

earthy caramel aromas as pyridines and your daily requirement (in just over a cup) of vitamin B3 (nicotinic acid).

The bitter taste of coffee is due to a combination of these alkaloids and organic acids, chlorogenic acid being the most prevalent. During roasting, some of the chlorogenic acid degrades into quinic and caffeic acids, which are responsible for the bolder flavours of good coffee. Citric acid is also present in the bean and will survive the roasting. Too much citric acid will linger as a sour taste in the mouth, and is often an indicator of

To date, around 500 flavour compounds have been identified in coffee, of which around 60 have important roles in taste.

poorer quality beans. The triglycerides, fatty acids and other lipids in the bean are relatively unaffected by the roasting process, but they have an important role to play in the taste of a good brew, especially in espressos.

A whole art of coffee preparation is devoted to achieving the correct

coffee grounds size for the type of bean and coffee beverage. The coffee beans are ground to increase the surface area of the beans exposed to the water and to ensure faster transfer for the leaching of the organic compounds during extraction of the organic compounds into the coffee.

Hot water is the most common solvent for extraction: the high temperature ensures a high extraction rate as well as high solubility. For most coffee brewing, water temperatures around 90°C are needed to ensure the organic compounds leach into the water fast enough to get a freshly brewed coffee in your hands in minutes. Compounds that are exceptions to this rule are the bitter acids, which have a stronger affinity for the coffee grounds. Near-boiling water is needed to overcome their hydrophobic association and leach them into the water. If these organic compounds are extracted into the water, the change to a highly polar environment and high temperature leads to their further breakdown,



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producing further flavours. The smaller and more volatile of these compounds will rapidly vaporise and leave the brew in the steam. These volatiles are registered by our noses as the freshly brewed smell. However, these volatiles are quickly lost, and this is why reheated coffee never regains its original flavour, and coffee left brewing in the pot always has a poorer taste.

The cold brew process gets around the loss in volatile organics. Cold water is poured through the coffee grounds and they are left to steep for more than eight hours. Hot water is added later to create the finished drink. Using cold water minimises volatile organic losses and limits the breakdown of other organic compounds. The cold temperature also limits the solubility of the bitter acids, and they are retained in the ground bean. For this reason, cold-brew coffee is said to have a smoother taste and fewer bold flavours.

Espressos take the extraction process further and apply the hot water to the finely ground beans at pressures of 8–18 atmospheres. The



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The crema on an espresso contains emulsified triglycerides, fatty acids and lipids.

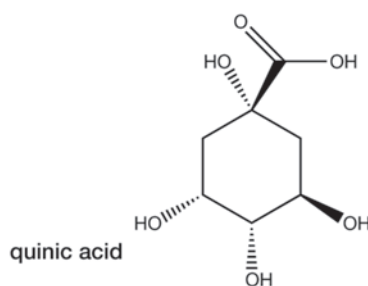
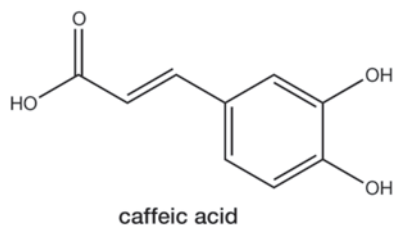
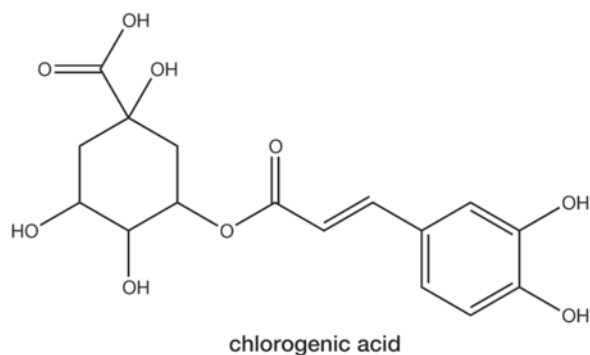
high pressure ensures a higher solubility of organic compounds in the hot water, and therefore a more concentrated brew. The high-pressure shock of the process breaks down the ground coffee beans, some of which become suspended in the coffee solution. This produces the concentrated hit that is an espresso, and the sharp taste. Interestingly, the actual amount of caffeine and other organic compounds within one

espresso is almost always less than a regular coffee, because the volume of water used is significantly less.

One of the side products of espresso brewing is that the triglycerides, fatty acids and lipids become emulsified and enter the coffee. This is generally in the form of the espresso crema – the tawny coloured liquid that initially comes out during espresso formation and settles on top of the darker espresso brew. Residual carbon dioxide in the coffee beans, left over from the roasting process, dissolves in the hot water at the high pressure and emulsifies the fatty acids and lipids. This forms a colloidal suspension of fatty acids, lipids and carbon dioxide. The fatty acid emulsification is strongly dependent on the fat content of the original coffee bean and the time period between roasting and brewing (residual carbon dioxide slowly escapes from the bean with time), as well as the barista's skill. This addition of fatty acids and lipids is part of the reason an espresso is the basis of many different coffee beverages, such as café latte and café mocha.

Next time you visit your local café, try a different brew and compare the chemistry for yourself.

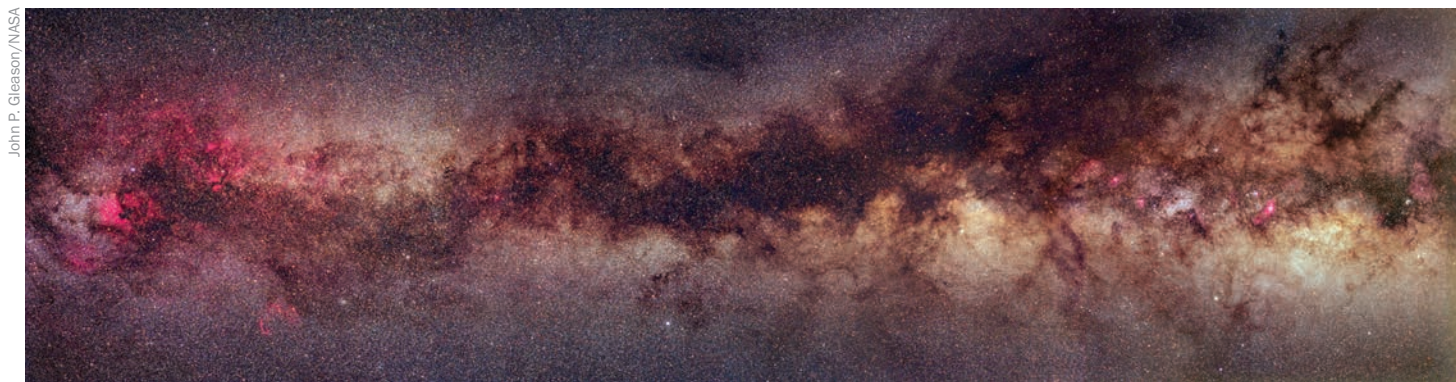
Colin Scholes FRACI CChem is at the University of Melbourne.



Chlorogenic acid degrades into quinic and caffeic acids during roasting.



Galactic chemistry and the GALAH survey



John P. Gleason/NASA

Our galaxy, the Milky Way, stretches across the southern sky. Here we can see the bright regions of the inner galactic stellar disk, obscured in patches by the dark nearby dust clouds.

For astronomers interested in the formation and evolution of galaxies, chemistry usually means measuring spectroscopically the abundances of elements relative to hydrogen in the stars and in the gas of galaxies. Although a few of the lightest elements (He, D, Li, Be, B) were produced in the Big Bang itself, most of the heavier elements are produced on different timescales by nuclear processes in different kinds of stars, so we can use element abundances to work out what happened as the galaxies were built up. We derive the element abundances in stars by using stellar spectroscopy to measure the strengths of the absorption lines in the spectra of starlight.

Stars form and die: each generation of stars enriches the interstellar gas in

heavier elements such as iron, and the abundance ratio of heavy elements relative to hydrogen gradually rises. In disk galaxies like the Milky Way, most of the stellar mass lies in a thin, flat disk in which star formation started about 10 gigayears ago and has been going on steadily ever since. We find that the inner regions of thin disks are usually more enriched than the outer regions. This happens because the galaxies start forming from the inside, so the chemical evolution is more advanced in the inner regions.

To quantify this abundance gradient, we can compare the abundance of iron in the inner and outer galaxy with the abundance at the Sun, which lies at an intermediate radius. In the inner galaxy, the abundance of iron relative to hydrogen is about twice that of the Sun, and in

BY **KEN FREEMAN**

A new multi-object spectrometer means we no longer have to quantify galaxies one star at a time.

the outer galaxy it is only about one-third of the solar value. We use a logarithmic bracket notation to denote the element abundances relative to the Sun. The solar abundance of iron relative to hydrogen is denoted as $[Fe/H] = 0$, and an abundance of one-tenth solar has $[Fe/H] = -1$.

In addition to the dominant thin disk, almost all disk galaxies have a second more diffuse disk component known as the thick disk. It contains about 10% of the mass of the thin disk and, as its name suggests, it is thicker than the thin disk. Its important characteristic is that the star formation in the thick disk started earlier (about 12 gigayears ago) and ended quite abruptly only a gigayear or so later. The thick disk appears to be an inevitable step in the process of building up disk galaxies, but at this time we do not understand the details of what went on early in the life of a disk galaxy: why did its star formation end so quickly?

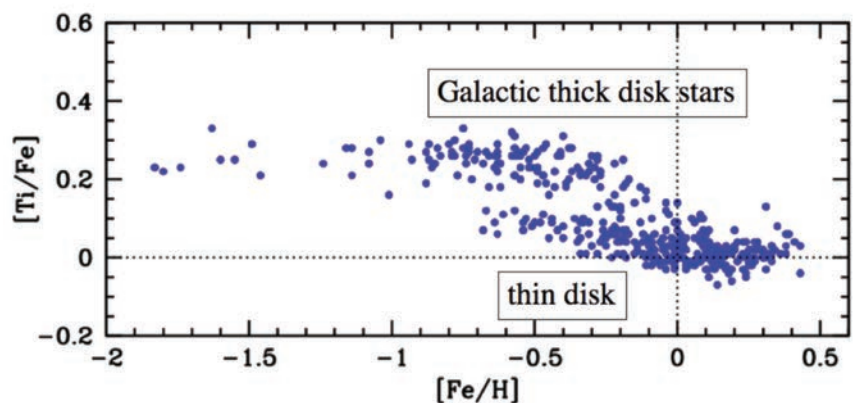
The short period of star formation for the thick disk has chemical consequences that we can observe. Massive stars have short lives (around 10 million years): when they die as supernovae, their nuclear-processed material is returned to the interstellar gas from which the next generation of stars will form. The ejecta from massive stars are rich in the alpha-elements (Mg, Si, Ca, Ti).

In contrast, the heavier elements in the iron-peak come primarily from the supernova deaths of less massive

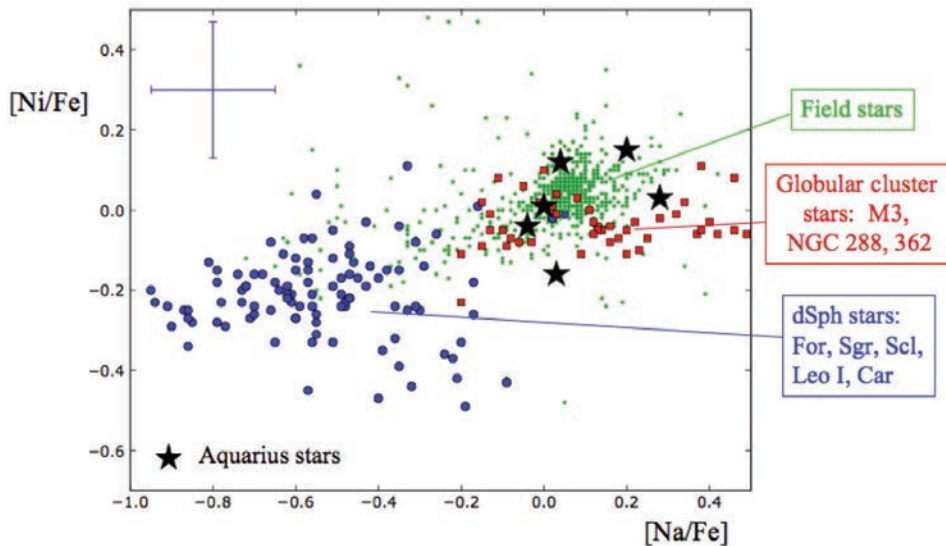
stars, which take longer to evolve and die. So the relative abundances of alpha-elements and iron-peak elements is a measure of the duration of star formation. In the thick disk, it appears that the star formation was over before these low-mass supernovae had time to explode and enrich the interstellar gas with their iron and other iron-peak elements. The thick disk stars are therefore much richer in alpha elements relative to iron than the stars of the thin disk, in which the star formation has been going on steadily for many gigayears (see diagram).

In this way, the chemistry of the thick disk gives us an important clue about how disk galaxies are built up, even though we cannot fully interpret it yet. Most of what we know about the formation of galaxies comes from

... the chemistry of the thick disk gives us an important clue about how disk galaxies are built up, even though we cannot fully interpret it yet.



The distribution of nearby stars in the $[Ti/Fe]$ - $[Fe/H]$ plane. The thick and thin disks of our galaxy overlap in $[Fe/H]$ but the thick disk stars are relatively enriched in the alpha element Ti, because the thin disk had a short history of star formation and chemical evolution. The Sun lies at the intersection of the dotted lines (Bensby T. et al. *Astron. Astrophys.* 2014, vol. 562, p. 71).



The Na-Ni distribution for globular cluster stars, dwarf spheroidal galaxy (dSph) stars (faint dwarf galaxies containing mostly old stars), field stars and stars of the recently discovered Aquarius star stream (black star symbols: Wylie de Boer E. et al. *Astrophys. J.* 2012, vol. 755, p. 35). Stars of the dwarf galaxy are well separated from the other kinds of stars. The stars of the Aquarius stream do not appear to be the debris of an accreted dwarf galaxy. M3, NGC288, NGC362 are the names of globular clusters. Forn (Fornax), Sgr (Sagittarius), Scl (Sculptor) and Car (Carina) are dwarf spheroidal galaxies.

computer simulations, in which gravity, star formation and chemical evolution are all included. Much of the detailed physics of these processes is still uncertain. Although the simulations are starting to produce galaxies that look like the ones we observe, we urgently need observations to constrain the simulations of the assembly of galaxies. We would like to know how the build-up of galactic disks occurred – was it primarily long ago, shortly after the Big Bang, or did it take place steadily or in bursts over the past 10 gigayears?

Stellar chemistry can help. Stars mostly form in clusters of typically a thousand to a million stars. These clusters are loosely bound gravitationally; they usually disrupt after about 20 million years as the cluster loses mass via the evolution of its massive stars. After the cluster disrupts, the stars of the cluster quietly diffuse right around the galaxy and become part of the galactic thin disk. A few clusters do survive. In these surviving clusters, we find that the stars are chemically identical over all of the

elements heavier than magnesium, at least to the level of accuracy with which their abundances can be measured (about 10%). The gas from which the clusters formed must have been very well homogenised.

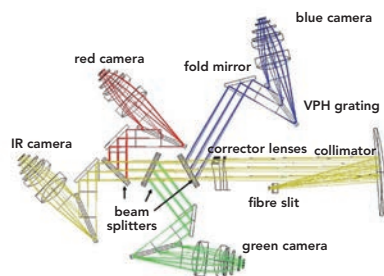
This gives us a way to reconstruct the star formation history of the galaxy. We measure the abundances of about 30 elements in each of about a million stars in the galaxy, and look for families of stars of identical composition. These stars are very likely to have been born together in a common star cluster that disrupted and dispersed. In this way, we can chemically reconstruct disrupted clusters, measure their ages, and so build up the star formation history of the galaxy. This process is called chemical tagging.

Until recently, abundances of stars had to be measured one star at a time. Measuring detailed abundances of 30 elements in a million stars was totally out of reach. Over the past few years, we have built a multi-object spectrometer (HERMES) fed by optical fibres on the Anglo Australian Telescope near Coonabarabran in

New South Wales. With HERMES, we can make these measurements for 400 stars at a time. Determining element abundances for a million stars is still a very large project, but that is what we need to do chemical tagging, and it has become possible. The project is known as GALAH (Galactic Archaeology with HERMES) and involves about 50 astronomers, mostly Australian. The instrument is now working and has already measured more than 60 000 stars. The project will take about five years to complete.

We can think of a chemical space (C-space) of abundances of the elements: e.g. Na, Mg, Al, Ca, Mn, Fe, Cu, Zr, Ba, Eu ... With the HERMES instrument, abundances for up to about 30 elements will be measurable. Not all of these elements vary independently from star to star; many vary together from star to star in near-lockstep. The dimensionality or number of independent dimensions of this chemical space is 8 to 9 (Ting Y.-S. et al. *MNRAS* 2012, vol. 421, p. 1231). In the C-space, the stars of a dispersed

We would like to know how the build-up of galactic disks occurred – was it primarily long ago, shortly after the Big Bang, or did it take place steadily or in bursts over the past 10 gigayears?



The light from each of the 400 stars is transferred from the focal plane of the telescope to the fibre slit. The light is then collimated, and is sent off to the four cameras (blue, green, red and IR) by the dichroic beamsplitters. CCD cameras image the 400 spectra in each band. The CCD images are then passed to the data reduction pipeline, which extracts the spectra for each star and passes them on to the chemical analysis pipeline.

cluster will lie in a tight clump.

Star formation from interstellar gas is the main route to building up the disk of a galaxy, but numerical simulations of galaxy formation indicate that the infall of small already-formed galaxies into larger galaxies is also a significant contributor. While the outcome of numerical simulations of galaxy formation from the expanding universe work well on scales larger than galaxies, on galactic scales they become progressively more uncertain because the physics becomes progressively more uncertain. We need good observational measures of how much infalling galaxies have

actually contributed. Again, element abundances can help to recognise the debris of small galaxies from among the stars that formed within the galaxy itself. For example, the relation between [Na/Fe] and [Ni/Fe] in surviving small galaxies is observed to be different from the relation for the more common stars of the disk (see diagram). The million-star GALAH survey of element abundances will be an excellent source of data for finding debris of accreted galaxies.

Ken Freeman is Duffield Professor, Research School of Astronomy & Astrophysics at the Australian National University, and wrote this article on behalf of the HERMES/GALAH team. Visit www.mso.anu.edu.au/galah/home.html.

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Dung Tr Phung

Chlorpyrifos

Getting prepared for spraying a rice crop with chlorpyrifos in Vietnam

A global health problem

BY **DES CONNELL**

One of the world's most widely used insecticides, chlorpyrifos poses health problems for agricultural workers where regulation is lacking.

The world breathed a sigh of relief in the 1980s when DDT (dichlorodiphenyltrichloroethane or 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane) was banned in most countries. Australia banned its use in 1985. The Earth was rid of a dangerous environmental chemical heavily used in agriculture, but few gave any thought to its replacements. The world's agricultural chemical manufacturers had a host of candidates available, with many

already registered and in use. The organophosphate pesticides were strong candidates and one of these, chlorpyrifos, was available in Australia in the 1970s. Its use has ramped up since DDT was banned and it is now one of the most widely used insecticides in Australia and on the planet.

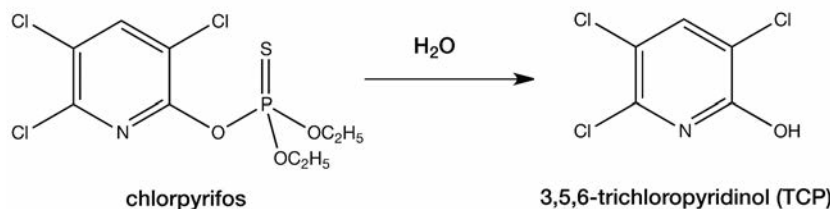
Chlorpyrifos use in Australia has been restricted, but research by the School of Environment at Griffith University in Vietnam and worldwide

has shown that chlorpyrifos harms the health of most farmers from the many developing countries that use it. Even in countries where use is restricted, there remain concerns about adverse neurological effects on children. It clearly poses a problem for public health of global dimensions (Marasingh J., Yu Q., Connell D. *Toxics* 2014, doi: 10.3390/toxics2020092).

Chlorpyrifos and DDT

Chlorpyrifos is a broad-spectrum insecticide used in Australia for crop protection and protection of buildings against termite attack. It is used extensively overseas in developing countries to protect rice crops against insect attack. It acts by interfering with the enzyme acetylcholinesterase in the nervous system and causes paralysis of the muscles and ultimately death. WHO considers chlorpyrifos to be moderately toxic with an LD₅₀ in experimental animals of 32–1000 milligrams per kilogram of body weight. This toxicity to mammals, particularly humans, was one of the main reasons for its limited use in the past and the preference for DDT, which has relatively low toxicity.

DDT was banned principally because it forms residues in many foods, in humans and in wildlife. It is very toxic to fish and other aquatic organisms and bioaccumulates in the eggs of the top predatory birds. This had an adverse effect on populations of eagles in many parts of the world, a trend reversed by the DDT ban. Chlorpyrifos is non-persistent in the environment, does not form residues or bioaccumulate. However, it is very toxic to most forms of life.



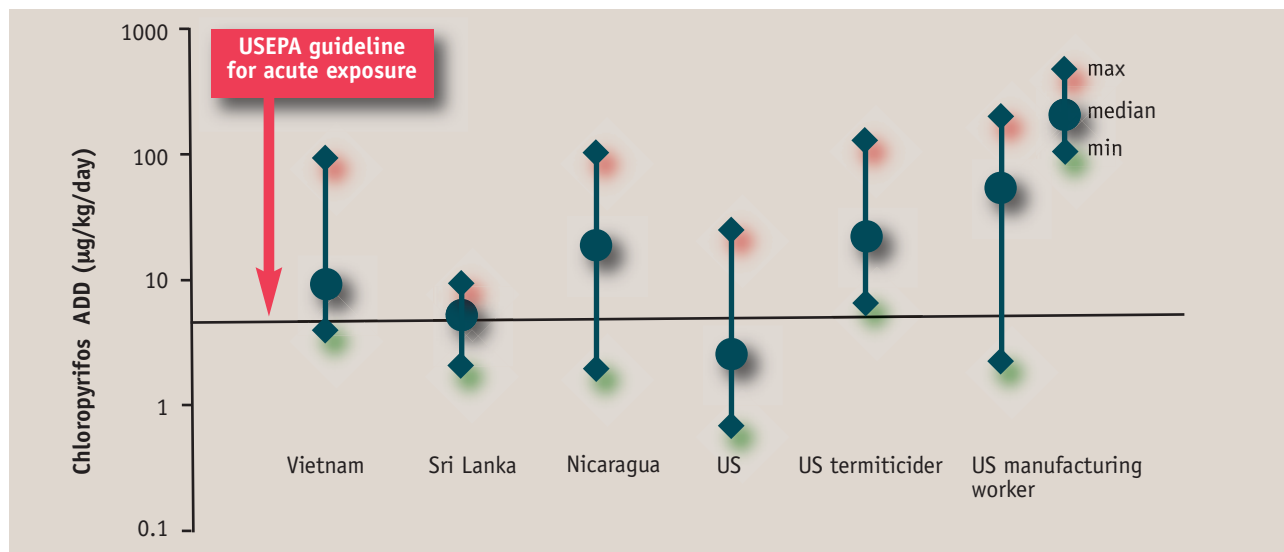
Chlorpyrifos and its biodegradation product TCP. Analysing urine samples for the TCP metabolite is used to determine exposure to chlorpyrifos.

In Australia and other developed countries, many restrictions control where chlorpyrifos can be used, particularly in the home and garden. But some relatively small occupational groups, such as manufacturing workers and pesticide applicators, can be exposed to high levels. Non-target animals and plants can also be exposed, with consequent adverse effects.

Chlorpyrifos in developing countries

The pattern of global usage has changed since the DDT ban. Developing countries are now major users of pesticides, including chlorpyrifos, and usage is increasing

rapidly. In Vietnam, the use of chlorpyrifos, and other pesticides, increased from 14 000 tonnes in 1990 to 50 000 tonnes in 2008. This has not been accompanied by enhanced regulation and control. WHO has reported that pesticide poisonings are occurring more frequently on a global scale and at a more serious level. WHO estimates that three million poisonings occur each year; this includes 220 000 deaths, most of which (99%) occur in developing countries. For each acute poisoning case in the US, about 600 acute poisoning cases occur among agricultural workers in Vietnam. There is widespread concern in the US that even trace residues of chlorpyrifos are having a detrimental



Chlorpyrifos exposure, as ADD (absorbed daily dose), of farmers and other workers in different countries compared to USEPA guideline for acute exposure

effect on human mental processes. Recently, a large team of experts from North and South America carried out an extensive review of the published research. They concluded that low-level exposure leads to neurotoxicological disorders in children, such as behavioural problems, working memory deficits, abnormal reflexes and many others (Muñoz-Quezada B.B. et al., *NeuroToxicology* 2013, doi 10.1016/j.neuro.2013.09.003)

One of the major problems with chlorpyrifos in developing countries is how it is applied. The common method of application employs a backpack reservoir with a hand-operated pump and the spraying nozzles on a pipe facing forward. The operators, both men and women, are engulfed in a mist of pesticide for the spraying event. By contrast, in developed countries the pesticide is often applied by tractor-mounted boom sprayers, the operator avoiding exposure in the cabin of the tractor.

Research in Vietnam and globally

Our research team has been involved with the human health risk assessment of a range of chemicals in the

... exposure to chlorpyrifos after a spraying event increased by a factor of about 100 from the background. Exposure at this level represents a major health hazard to the median farmer in Vietnam – even more critical considering that the spraying is repeated several times each year – and for the farmers’ working lives.

environment, in particular benzene, chlorobenzenes and chlorpyrifos. A global analysis of published data on chlorpyrifos revealed the hazard quotients (HQ) for occupationally exposed populations to be high in some situations. A median individual farmer in Vietnam had exposures up to 3.9 times the USEPA guideline (HQ 3.9), whereas the 5% most exposed among the manufacturing workers from the US had 42 times this value. Hazard quotients greater than unity usually represent a significant hazard to health. A comparison of the exposure to chlorpyrifos in different occupations in several countries has

indicated exposure occurs in many countries throughout the globe.

We collected samples of the urine of farmers in Vietnam before and after a spraying event. These samples were analysed for the TCP metabolite and back calculated to the original exposure to chlorpyrifos. This data on the exposure of the applicators was plotted as cumulative probability distributions showing the wide range of exposures that occurred. Surprisingly, the range was about 100-fold from the lowest to the highest with both the pre- and post-event exposures. It also demonstrated that exposure to chlorpyrifos after a

spraying event increased by a factor of about 100 from the background. Exposure at this level represents a major health hazard to the median farmer in Vietnam – even more critical considering that the spraying is repeated several times each year – and for the farmers' working lives (Phung D.T. et al. *J. Exp. Sci. Env. Epidem.* 2012, doi: 10.1038/jes.2012.32; Phung D.T. et al. *Risk Anal.* 2013, doi: 10.1111/risa.12023).

A highly exposed group constitutes the 5% most exposed at the cumulative probability level of 95%. We concluded that about 30% of the farming population suffered from pesticide poisoning, which agrees with epidemiological surveys.

We also evaluated the effectiveness of protective clothing because the extreme discomfort of personal protective clothing in tropical climates can mean it is not practical to use. The use of long-sleeved shirts reduced the exposure level significantly.

Education and alternatives

Quite clearly, chlorpyrifos is a major global health problem. Our work in Vietnam has shown that there are ways to reduce exposure in the field in developing countries with minimal impact on the farming operation. But it has also indicated that the regulation and control of chlorpyrifos and other



Dung Tri Phung

Using the backpack sprayer with the hand-operated pump and spraying wand with a rice crop in Vietnam

pesticides requires urgent action by individual countries, as well as a global basis (Phung D.T. et al. *Bull. World Health Organ.* 2012, doi: 10.2471/BLT.11.096578).

At the very heart of this problem is the training and education of farmers and all those using chlorpyrifos. Also, the world's pesticide research institutes need to design and test pesticides that don't have the human toxicity properties of chlorpyrifos, but do have desirable environmental properties such as non-persistence.

Research should be directed towards the use of alternative, non-chemical, methods of insect control. Hopefully, in many situations pesticide use can be reduced or avoided. Such measures will help to reduce the human cost of this chemical.

Des Connell FRACI CChem is Emeritus Professor at the Griffith School of the Environment, Griffith University, Brisbane. His research has been on the behaviour and effects of organic chemicals in the environment for which he was awarded a DSc and made a Member of the Order of Australia. In recent years, he has focused on the evaluation of the health risk of chemicals in the environment.

chemistry in Australia

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iStockphoto/Onur Döngel

A photograph of a water treatment facility, showing a large concrete structure with multiple channels of water cascading down. The water is in motion, creating a blurred effect. The background shows a clear sky and a building.

Special treatment: Australia's pioneering wastewater plant

BY **BRONWYN KENT**

The centenary of activated sludge inspired Bronwyn Kent to research the Glenelg Wastewater Treatment Plant, the oldest of its type in Australia.

In April this year, the centenary of the creation of the activated sludge process was celebrated at a conference in Manchester, UK. One of Adelaide's most popular and affluent seaside suburbs is the home of the Glenelg Wastewater Treatment Plant, Australia's first activated sludge plant.

In 1928, after much research and healthy debate, and faced with a growing population, the South Australian Government embarked on the design and construction of the Glenelg Wastewater Treatment Plant. The process was successfully commissioned in December 1932. Since then, other major additions have been made to the plant, with extensions in the 1940s, 1950s, 1970s and 2000s. Through these upgrades, the plant, serving a connected population of more than 200 000, remains committed to the activated sludge process and is a plant capable of a high level of wastewater treatment, continuing to reduce the nutrient load

discharged to the sea and enabling the recycling of effluent for dual reticulation and irrigation purposes.

In 1928, the Public Works Committee in South Australia began hearing reports from the Engineering and Water Supply Department on the re-organisation of the sewerage system of Adelaide and suburbs and, importantly, the need for an up-to-date sewage treatment works. A new and advanced treatment works was required at Glenelg for several reasons: population and industry in Adelaide were growing, local residents of affluent suburbs were demanding a high degree of treatment and discharge to the sea was increasingly seen as viable.

The department set about hiring a consultant specifically experienced in activated sludge treatment, A. Gordon Gutteridge (see box). Gutteridge was assisted in the design of the Glenelg Wastewater Treatment Plant by the Assistant Engineer for Sewerage,

Henry Hodgson (see box). Hodgson would soon become a leading expert in activated sludge treatment.

Glenelg beach was fashionable in the 1920s, and remains Adelaide's premier beach destination. Therefore, a high level of treatment and the absence of odour were essential in the plant design.

The treatment process incorporated a main pumping station, which pumped raw sewage under the Patawalonga River (on the eastern boundary of the plant) to the new treatment plant (situated on sand dunes, beach front). From here the sewage passed through a primary sedimentation tank prior to treatment via the activated sludge process, which consisted of mixing tanks, aeration tanks and secondary sedimentation tanks. Effluent was disposed of via absorption beds into the sand dunes. The sludge stream was treated in a digester with the sludge sent to drying beds before

removal from site and subsequent land disposal. This treatment stream was to be known as 'A Plant'.

By December 1932, the Engineering and Water Supply Department had the nation's first activated sludge plant fully operational and functioning well, capable of treating 10 megalitres per day annual average flow for a connected population of approximately 40 000.

Plant extensions

The Glenelg catchment expanded at an unexpectedly high rate. The connected population for the original works was achieved by the second year of operation and by 1939 the plant was attempting to treat a connected population 50% above the design capacity. For the next upgrade to the plant, the government decided that external assistance from consultants was not required and the department set about ensuring the extensive training of the Assistant Engineer for Sewerage, Hodgson, who through his work at Glenelg and on other sewage works in the state had shown considerable ability.

The much-needed extension to the Glenelg plant was delayed while awaiting the return of Hodgson from his US fellowship study tour (see box).

The Public Works Committee determined that Hodgson's design for

Glenelg would not require external review – he was now considered the most experienced designer in Australia on sewage treatment. The extension was approved and construction could begin.

By 1941, the department had a successfully commissioned, extended plant with a winery waste treatment stream, capable of treating 20 megalitres per day for a connected population of 92 000.

The design population was reached within 10 years, creating the need for another large extension. By this stage, Hodgson now held the title of Engineer for Water and Sewage Treatment. Construction began in 1956.

By 1962, the department had successfully commissioned the B Plant extension, creating a plant capable of treating 40 megalitres per day (AAF) for a connected population of 175 000.

In 1960, a scheme supplying chlorinated effluent to nearby playing fields was approved. This scheme proved to be highly successful and profitable, leading to further recycled water schemes. In 1961, 1963 and 1970, significant expansions occurred to the recycled water network to include several local golf courses, sporting ovals, a primary school, local council and the Adelaide Airport. The Glenelg Wastewater Treatment Plant and the Engineering and Water Supply

Department had become leaders and innovators in recycled water schemes in Australia.

By 1969, the plant was again receiving flows above the design capacity. But this next extension was easy. In 1966, Henry Hodgson had retired from the department as the Assistant Director of Engineering Services; however, his design employed in the construction of the successful B Plant extension could essentially be copied.

By 1975, the Glenelg Activated Sludge Plant was capable of treating 60 megalitres per day annual average flow for a connected population of 250 000.

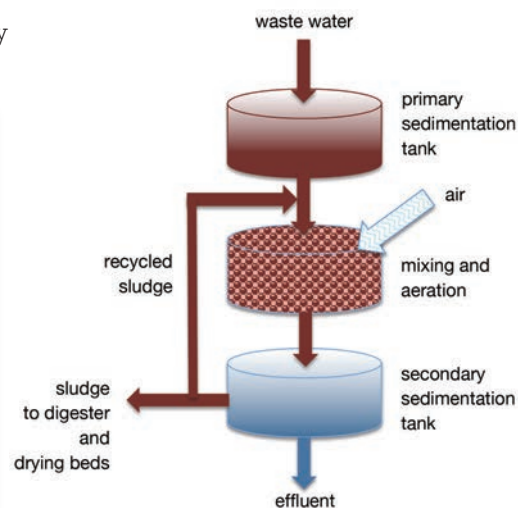
The EPA began a series of licence changes in the late 1990s, imposing on SA Water (now corporatised) the need for an Environmental Improvement Program at Glenelg. The aim of this was to reduce the total nitrogen discharge to the sea to ≤ 10 milligrams per litre, and reduce the impact of effluent discharge on seagrasses. No increase in capacity was required; instead the activated sludge process was changed to incorporate biological nutrient removal. Construction began in 2000 with commissioning in 2002.

The success of the recycled water plant was so great and customer

Gutteridge, GHD and Glenelg

Gorden Gutteridge studied engineering at the University of Melbourne and later completed a Masters at Harvard University. In 1928, following his work as Director of the Commonwealth Division of Public Health, he formed a private practice specialising in the design of water and wastewater schemes. In 1939, Gutteridge merged his practice with Gerald Haskins and Geoffrey Davey to form GHD, a large, international engineering consultancy.

In his role as Director of Public Health Engineering, Gutteridge was known for his 'zeal, knowledge, learning, industry, discretion and ability' (Arneil 1988). He insisted on high standards, and quality of workmanship was an obsession. His work on the Glenelg plant was so successful that he won commissions for other schemes in Victoria and Tasmania. GHD quickly became one of the largest consultancies in its field in Australia. Gutteridge was an impressive character, whose influence would forever define the work culture at Glenelg.

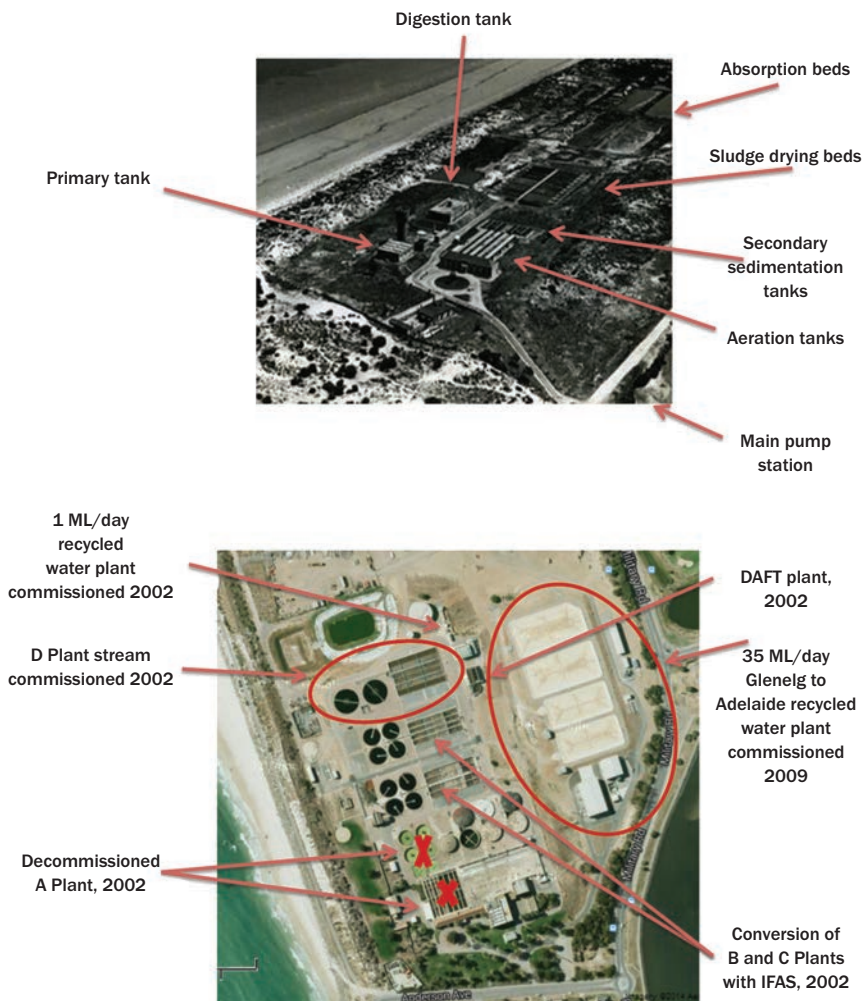


Simple schematic of the activated sludge process – a process that uses air and microorganisms to break down sewage into carbon dioxide, water and other compounds

Hodgson and his Harvard study

Henry Hodgson (1901–92) received a Bachelor of Civil Engineering from the University of Melbourne in 1923 and was appointed to the Engineering and Water Supply Department in South Australia in 1924. In 1935, Hodgson received the Commonwealth Fund Fellowship, New York, which involved a 15-month study tour in the US, studying at Harvard University. This fund still exists today and focuses on promotion of health-based research and the fostering of relationships between the US and the British Empire.

In addition to his study, Hodgson toured activated sludge plants in the US, Germany, Holland and Great Britain. He visited more than 150 sewage treatment works. On his return to South Australia, Hodgson wrote and had printed a book called *Sewage and trade wastes treatment*, providing exquisite detail of his travels. This was published in 1938, within 12 months of his return from overseas, and was very quickly recognised as a comprehensive assessment of sewage treatment practices around the world and later used as a university textbook in the US.



Glenelg Wastewater Treatment Plant: top – A Plant, 1933; bottom – the plant in 2009.

demand so high that in 2009 a new 35 megalitres per day recycled water plant was commissioned at Glenelg, providing effluent for dual reticulation and irrigation purposes for the existing customers as well as new customers reaching from the western to the eastern suburbs of Adelaide, including the central business district. This plant incorporates ultrafiltration membrane filtration followed by UV disinfection and chlorination.

Gutteridge and Hodgson are the heroes of this story, but Hodgson

clearly stands out. He was involved with the plant from its conception in 1928 through to 1966 when he retired from the department after 42 years of service. Hodgson was described throughout his career as an innovator, a teacher, a modern engineer and an expert in his field. He was also a visionary: not only did he put into place strategic plans for water and wastewater systems in South Australia, he was responsible for the formation of the Australian Water Association in 1961. He was its federal president in

1964 and in 1973 he was the first person to receive honorary life membership to the AWA. The work of Henry Hodgson has stood the test of time, and you can't get much better than that. We in South Australia couldn't be more proud of this plant and its history, and I like to think that Henry Hodgson would be pretty proud today too.

Bronwyn Kent (Bronwyn.Kent@sawater.com.au) is at SA Water Corporation, South Australia. A list of references is available from the author.

2014 RACI National Award winners

Applied Research Award



Professor David Lewis FRACI CChem joined Flinders University in 2009 to become Professor of Materials Science and the founding Director of the Flinders Centre for NanoScale Science and Technology. This followed a 21-year career in industrial research at IBM in the US and research management at SOLA Optical/Carl Zeiss in Australia.

During his career, David became internationally recognised for work in microwave processing of polymers, and had key roles in the development of the first 'copper wire chips', multichip modules for mainframe computers, Transitions Velocity photochromic lenses and a range of high-index ophthalmic lens materials and coatings. With a focus on translational research and assisting companies to become more competitive, David created NanoConnect, a mechanism to allow companies to explore the potential of nanotechnology on their businesses since joining Flinders.

David has delivered over 20 plenary and invited papers at international meetings, edited two conference proceedings, authored or co-authored over 50 papers and has 50 granted patent families; he has been recognised by professional bodies for technical and professional leadership. He has also been active in professional societies, such as the RACI, being a former Chair of the Polymer Division and SA Branch President as well as taking on a number of roles internationally.

Citation: Contributions to Chemistry and the Profession



Dr Brian J. Smith FRACI CChem is a computational chemist and molecular modeller with extensive experience in protein X-ray crystallography and structural biology. His research is directed towards understanding biochemical processes, drug discovery and the development of new treatments for diseases of global importance. He has served on the Victoria Branch committee for more than 10 years, and was the President of the Victoria Branch 2011–12. He has co-authored more than 130 scientific publications.

Brian graduated from the University of Melbourne with a PhD in 1987, after which he took up a postdoctoral position at the Australian National University. Returning to Melbourne in 1991, he held a research scientist position at the Biomolecular Research Institute, and later moved to the Walter & Eliza Hall Institute of Medical Research. In 2011, he was appointed the inaugural LIMS Principal Research Fellow at La Trobe University.

Dr Anthony O'Mullane MRACI CChem graduated from University College Cork, Ireland, in 1997 and completed a PhD at the same university in 2001 in the field of gold electrocatalysis under the supervision of Professor Declan Burke. He undertook postdoctoral fellowships at Technische Universität Darmstadt, Germany, University of Warwick, UK, and then in Australia at Monash University with Professor Alan Bond. In 2008, he worked briefly as a research scientist at CSIRO before taking a position at RMIT University where he was then awarded a Vice Chancellor Senior Fellowship. In 2012, he was awarded an ARC Future Fellowship and in 2013 continued this fellowship and started a senior lectureship at Queensland University of Technology.



Anthony's research interests are the electrochemical synthesis and characterisation of nanostructured materials; electrocatalysis; catalysis; organic semiconductors; metal oxides; Li batteries; and in particular the application of electrochemical methods to various aspects of physical, chemical and biological science. He combines innovative (but simple) synthetic methods with state-of-the-art characterisation to develop new insights into both old and new electroactive materials. In these areas he has published one book chapter, 97 articles and 15 conference papers.

Anthony has also made strong contributions to his discipline as RACI ambassador for RMIT during his time there and as the secretary (2010–13) and now Chair of the Electrochemistry Division of the RACI.

Cornforth Medal



Dr Ganna (Anya) Gryn'ova MRACI (Student) graduated with a Master's degree in chemistry *summa cum laude* from Dnipropetrovsk National University in Ukraine. She then moved to Australia to pursue her interest in applying computational chemistry to study reaction mechanisms and predict physical and chemical properties of the molecules. In 2013, she completed a PhD at the Australian National University under the supervision of

Professor Michelle Coote. Her thesis, entitled 'Understanding and Manipulating the Reactivity of Nitroxides and Other Stable Free Radicals', is highly multidisciplinary and contributes to a better understanding of the role of free radicals in the degradation of industrial materials and biomolecules, as well to fundamental aspects of free radical chemistry and the nature of the polar effects.

Ganna's PhD research led to, among other contributions, clarifying a realistic mechanism of materials protection by hindered amine light stabilisers, designing a redox mediator that doubled the light conversion efficiency of a dye-sensitised solar cell; and uncovering previously unappreciated, surprisingly large through-space electrostatic effects on delocalised free radicals. The latter discovery has been reported in the *Nature Chemistry* and resulted in a patent application. During her PhD, Ganna presented her research at numerous Australian and international conferences, published 14 research papers including seven first-author papers in high-profile international journals such as JACS and received a number of awards, including the Postgraduate Student Researcher Award from the Australian Research Council Centre of Excellence for Free Radical Chemistry and Biotechnology. Currently, Ganna is employing the findings of her PhD to design new organic molecules for molecular electronics applications in the Ecole Polytechnique Fédérale de Lausanne in Switzerland.

Fensham Medal: Outstanding Contribution to Chemical Education



Professor Simon Pyke FRACI CChem has over 20 years' experience in higher education at the University of Adelaide where he is currently Associate Dean (Learning & Quality) in the Faculty of Sciences. Simon is highly regarded as a teacher and has been recognised with numerous awards including the D.R. Stranks Medal for Excellence in Chemistry Education, an ALTC Citation for Outstanding Contribution to Student Learning and the

University of Adelaide's Stephen Cole the Elder Award for Excellence in Teaching (he is the only person in the history of this award to have received it twice).

His interests in science educational research encompass curriculum design, construction and assessment (with particular focus on threshold learning outcomes); facilitating development of skills (discipline related and generic); and student engagement through classroom practice. He has been a member of numerous CAUT/ALTC/OLT-funded project teams and has recently led a working party of ChemNet, the OLT-funded national Chemistry network, focused on development and implementation of threshold learning outcomes in Chemistry. He is also an active contributor to senior secondary education in South Australia through a long-standing relationship with the SACE Board.

H.G. Smith Memorial Award

Professor Martin Banwell FRACI CChem was born and educated in New Zealand.

In 1979, he completed his PhD in organic chemistry at the Victoria University of Wellington where he worked under the supervision of Brian Halton. After a postdoctoral period with Leo Paquette at the Ohio State University, he took up a senior teaching fellowship at the University of Adelaide in South Australia. In 1982, he moved to a lectureship at the University of Auckland in New Zealand and then to an equivalent position at the University of Melbourne in 1986. He was promoted to a readership in Organic Chemistry at the same institution in 1993. In 1995, he moved to the Research School of Chemistry (RSC) at the Australian National University and, at that time, held the position of senior fellow. In 1999, he was appointed Professor of Chemistry and served as Director of the RSC from the beginning of 2008 until mid-2013.

Martin's research interests are in synthetic organic chemistry, particularly the development of new methodologies and their application to the total synthesis of biologically active natural products. He is the author or co-author of some 300 journal articles in this broad area. A particular emphasis has been the exploitation of strained organic compounds and the products of whole-cell biotransformations for such purposes. In recognition of his work, Martin has received a number of awards, including the Rennie and Birch Medals of the RACI. In 2003, he received the Royal Society of Chemistry (UK) Award in Synthetic Organic Chemistry, and he was elected to the Fellowship of the Australian Academy of Science in the following year.



Le Fèvre Memorial Prize – Australian Academy of Science



Associate Professor Richard Payne MRACI CChem graduated from the University of Canterbury, New Zealand, in 2002. In 2003, he was awarded a Gates Scholarship to undertake his PhD at the University of Cambridge. After 18 months as a Lindemann Fellow at The Scripps Research Institute (La Jolla), he began his independent career (in January 2008) as a lecturer in organic chemistry and chemical biology at the University of Sydney.

Richard's research focuses on utilising the power of synthetic organic chemistry to interrogate biological systems and address problems of medical significance. As a result of his research endeavours, he has been the recipient of several prestigious awards including the RACI Biota Medal in Medicinal Chemistry (2008), a NSW Young Tall Poppy Science Award (2010), the Rennie Memorial Medal (2012), the Athel Beckwith Lectureship (2013), the Tregear Award for Peptide Science (2013) and an ARC Future Fellowship (2013).

Leighton Memorial Medal



Professor Robert O. Watts FAA, FTSE, FRACI CChem, was Vice President Technology & Chief Scientist for BHP Billiton, where he was responsible for technology development throughout the BHP Billiton Group. He managed teams to develop and transfer research findings to industry, including establishing feasibility trials and taking results through to commercialisation. Bob joined BHP in 1997 and was responsible for ensuring technology standards across the company,

including new capital projects and interaction with universities, CSIRO and other external R&D providers.

During a research career spanning some 40 years Bob acquired extensive experience in computational chemistry, modelling of complex molecular systems, experimental atomic and molecular physics, R&D in an industrial setting, problem solving in the resource industry, and management issues in complex commercial settings. Before joining BHP, he had extensive experience in research and teaching roles in universities in Canada, the US and Australia.

Over the years, Bob has served on many review and advisory bodies in the US and Australia, including the Australian Research Council. He has served the RACI in several capacities, including chair of the Physical Chemistry Division in the early 1980s, and as Vice-President then President of the national body from 2007 to 2010.

Bob's contributions to research and industry have been recognised through his election to the Australian Academy of Science, the Academy of Technological Sciences and Engineering, the RACI and as a Fellow of the American Physical Society.

Pearson Education/RACI Chemistry Educator of the Year Award

Dr Daniel Southam MRACI CChem completed his bachelors and PhD degrees in chemistry at the University of Tasmania. It was there that a passion for education was sparked, both from opportunities offered in Chemistry during his degrees and while tutoring at a residential college. While completing a postdoc at Curtin University, he was offered the opportunity to 'do a bit of teaching'. Surrounded by colleagues who value and support teaching, he has been able to build a portfolio based on innovative pedagogical practice and research into its efficacy. He is now Senior Lecturer (Teaching Focused) and Director of First Year Studies in the Department of Chemistry.



Daniel has an interest in the dynamic relationship between science education research and its application to practice, especially in large first year classes. Daniel is a passionate advocate of active learning in large classes, where he crafts engaging social environments that support student success. His broad aim is to improve students' perceptions and to develop capacity for real change in the depth of their understanding and enjoyment of science. To achieve these aims, his research also includes exploring issues of educational measurement in different sociocultural contexts, and in interdisciplines such as forensic science and nanotechnology. He has received over \$1 million in teaching- and learning-related grants to explore the efficacy of such environments.

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		PERTH 08 9302 1911 rowewa@rowe.com.au
		SYDNEY 02 9603 1205 rowesw@rowe.com.au

Rennie Memorial Medal



Dr Deanna D'Allesandro MRACI CChem received her BSc (Hons) in 2001 and her PhD in Chemistry from James Cook University in 2006 under the supervision of Emeritus Professor Richard Keene. She held a brief postdoctoral position at the University of Sydney before venturing to the US to undertake a postdoctoral position with Professor Jeff Long at the University of California, Berkeley from 2007 to 2009 as a Dow Chemical Company Fellow of the American–Australian Association and a Royal

Commission for the Exhibition of 1851 Research Fellow. Deanna returned to Australia in 2010 as a University of Sydney postdoctoral research fellow and L'Oréal for Women in Science Fellow in the School of Chemistry.

In 2011, she received an Australian Research Council QEII Fellowship, which allowed her to start building her own research group exploring electronic and optical properties of inorganic materials, along with their applications in energy-related fields.

RACI Post Graduate Student Travel Bursary

The RACI Post Graduate Student Travel Bursary was introduced to assist students to attend an overseas conference or research facility. The following students have won a Travel Bursary: Briana Davie, Georgina Sauzier, Bradley Stringer, Carol Hua, Deborah Sneddon and Michelle Gazdik.



Briana Davie



Georgina Sauzier



Bradley Stringer



Carol Hua



Deborah Sneddon



Michelle Gazdik

RACI membership milestones

The RACI congratulates the following members for achieving their 50 years of membership. Congratulations also to members who have achieved 40- and 25-year membership milestones (see www.raci.org.au/raci-news/membership-milestones-414 for details).

NSW

David St Clair Black
Graeme Julian Burgess
John Kingsford Haken
Robert William Jones
Donald Harold Napper

Qld

Raymond Walter Yerbury
George Alexander
Brotherton
Mary Leona Carseldine
Paul Wie Tat Oh
Peter George Wright

SA

Constantin Parouchais
Tzvetanka Parouchais

Vic.

David Howard Strong
Anthony Trevor Hickson
John Lawson
Robert John Leydon
Bryan Clarence Loft
Harry Mantell
Ian Maxwell Marshall
Patrick William McIlvena
Norman Alexander
McWhinney
William Stark
Peter Richards Terry

WA

Neville Victor Blesing



New Fellows



Associate Professor Bayden Wood is an Australian Research Council Future Fellow working at the Centre for Biospectroscopy located in the School of Chemistry, Monash University. He completed his PhD in 1999 under the supervision of Professor Don McNaughton, pioneering new ways to analyse cells and tissues using infrared modalities. His research now focuses on applying vibrational spectroscopic techniques to solve a range of biomedical and biological problems, including malaria

diagnosis and treatment, cancer diagnosis and testing novel drugs for cancer treatment, assessing oocyte competence for in vitro fertilisation (IVF), stem cell research, heart disease, liver disease, phytoplankton studies, aquatic wetland studies and fundamental studies into how light interacts with cells and tissues.

Wood is one of the founding members of the Centre for Biospectroscopy, which was established in 2002 after the inaugural Austral-Asian Biospectroscopy Conference held at Suranaree University of Technology in Korat, Thailand, which attracted over 180 international scientists and introduced biospectroscopy into South-East Asia, placing the Centre for Biospectroscopy on the world stage.

Wood's career highlights include developing a new diagnostic tool for malaria using a simple infrared-based technique. The paper published in *Analytical Chemistry* was awarded the American Chemical Societies Editor's Choice in 2014 and received widespread media coverage, including television and radio. This has led to a clinical pilot study to trial the technology in Thailand in December 2014. As a Humboldt Fellow working in Germany at the Institute for Analytical Sciences in Dortmund with Professor Volker Deckert in 2008, he applied tip-enhanced Raman spectroscopy, a near-field technique capable of achieving a spatial resolution of 10 nm, to analyse biomolecules in single malaria-infected cells and investigate the oxidation from the surface of haemoglobin crystals.

He has received a number of awards, including he 2011 Kowalski Prize for best applied paper in *Journal of Chemometrics* for 2009–2010 and was the 2009 winner of Monash University Science Faculty Early Career Research Award. He has over 100 publications, including 10 book chapters with an *h*-index of 30. Wood teaches in analytical chemistry and has recently developed a biospectroscopy course for undergraduate students at Monash University.

Dr Chris Fellows is a polymer chemist and a senior lecturer at the University of New England. Dr Fellows attended Pimlico State High School in Townsville, North Queensland. He majored in chemistry and biochemistry at James Cook University and obtained a BSc(Hons I) and PhD in the mechanism of alternating radical copolymerisation at the same institution under the supervision of Associate Professor Ernie Senogles, graduating in 1998. After a brief period working on the development and testing of flocculants in Chemical Engineering at the University of Sydney, he worked as Scientific Projects and Education Officer with Professor Bob Gilbert at the University of Sydney's Polymer Centre/Key Centre for Polymer Colloids. In 2000, he was appointed as a half-time fixed-term lecturer in hydrocolloids at the University of Sydney, and in 2004 he obtained a permanent academic position as a lecturer in chemistry at the University of New England, where he was promoted to senior lecturer in 2008. Dr Fellows has had a longstanding involvement with the RACI's Polymer Division, serving as Treasurer of the Division from 2002 to 2009.

As well as the fundamental kinetics and mechanisms of radical polymerisation, Fellows' research is primarily in applications of polymers in processes where they modify behaviour at interfaces – flocculation, modification of crystal growth, transport through membranes – and in structure/property relations of carbohydrate foods. Fellows has published 65 peer-reviewed journal articles in journals ranging from *Dental Materials* to *Cereal Chemistry* to *Macromolecular Theory and Simulations*.

Fellows lives in a state of continuous total amazement at the comprehensibility of the universe and is a passionate proponent of the value of a scientific education. Engraved on his heart are these words attributed to Max Planck: 'Experiments are the only means of knowledge at our disposal. Everything else is poetry, imagination.' He is not, however, dismissive of poetry and imagination and writes fiction together with his wife, Amanda, under the name A.C. Fellows. They have two children, Caillan and Elena, who outshine them as the sun outshines the fixed stars.

Fellows is a contrarian, a theist, and was born in the shadow of the Santa Catalina Mountains in Tohono O'odham country.





Dr Neale Jackson obtained both his BSc (Hons – Chemical Sciences) and PhD in Inorganic Chemistry from Leeds University, his thesis title being ‘The Chemistry of Binary non-Aqueous Solvents Containing Carbon Halides with Transition Metals’. While at Leeds University, the late Professor Norman Greenwood was one of his most significant mentors. On leaving university, Jackson undertook positions with a number of organisations, including

Cussons (UK) Ltd as Product Development Manager and Laboratory Health and Safety Coordinator. In 1991, he moved to Australia after accepting a position with CSIRO Division of Forest Products as a research scientist, where he researched timber preservatives. He then joined Gibson Chemicals as a Product Development Manager and Health and Safety Coordinator.

After years in industry, Jackson transitioned to an academic setting, first at Swinburne University of Technology where he lectured for five years and then in the School of Applied Sciences, RMIT University, where he has worked as the Program Leader – BSc Applied Sciences (Multi Major) and as a senior lecturer in occupational health & safety for the past 16 years.

As a chemist, Jackson became involved in health and safety in a number of roles, this experience becoming a pathway to becoming a lecturer in OHS and in the development of the very successful three-day, Safety in Laboratories (AS/NZS 2243 and AS/NZS 2982). He has delivered the course across Australia and overseas, including China and India.

More recently, Jackson has been involved with the development of the Chemical Safety Laboratory (SNET) virtual laboratory safety CD as a collaborative project between the Chemistry Schools of Melbourne, Monash and RMIT Universities. SNET today forms part of the teaching resources for undergraduates in RMIT’s Degree in Applied Sciences.

He is an active researcher into safe work practices for working with engineered nanomaterials, sponsored by SafeWork Australia. More recently Jackson has worked with Associate Professor Helmut Hügel in the area of Chinese herbal medicines and their effectiveness as dietary supplements and potential medications. He has 23 peer-reviewed publications and has had four research grants.

Aside from his career, Jackson and his partner Lisa enjoy a range of activities, including stamp collecting, photography and sailing.

Dr Nial Wheate completed both his BSc and PhD (2002) through the Australian Defence Force Academy campus of University of New South Wales while serving as an officer in the Royal Australian Navy. He completed another three years of military service before he was appointed a senior fellow at the University of Western Sydney, followed by a lectureship at the University of Strathclyde in Scotland. In 2012, Nial returned to Australia to take up a senior lecturer position in the Faculty of Pharmacy at the University of Sydney. In 2013, he was appointed Head of Cancer Research within the faculty. Wheate has a strong service commitment both to the RACI, as a member of the NSW Pharmaceutical Sciences Group, and in other charitable causes, including as a founding committee member of the Ellie a’Beckett Bowel Cancer Research Trust.



Wheate’s research interests are in the field of cancer and he has established an international reputation in the field of platinum anticancer drug design and drug delivery. He is best known for his work in examining the interactions between platinum drugs and DNA and as the first person to demonstrate the medical applications of the macrocycle family of molecules called cucurbiturils. Over his career, he has published 65 journal articles, two book chapters and two international patents. Previously he was an associate editor of the *Australian Journal of Chemistry* and is currently an editor of the *Source Journal of Pharmaceutical Sciences*.

Wheate believes strongly in the importance of science communication and has written numerous articles for *Chemistry in Australia*, *Australasian Science* and the news analysis and commentary on-line newspaper *The Conversation*. Recently he was appointed a member of the community council of *The Conversation*, a body of academics and lay readers who oversee commentary standards of the newspaper.

In his spare time Wheate is heavily involved in volunteering activities. Since 2012 he has been a member of the NSW State Emergency Service and in 2014 started as a St John’s Ambulance volunteer in the Glebe division. He also enjoys reading and has recently taken up salsa dancing.

Con and Ceci: 50-year members with an extraordinary story



Sometime late in 1963, a married couple joined RACI together. They were recent migrants from Eastern Europe, escaping the oppression of a Communist system and hoping to start a new life. When their 50-year membership certificates arrived, the chance for a story could not be passed.

Constantin Parouchais (Con) was born in 1934 and completed his early and secondary education in Varna, Bulgaria. That secondary education involved two years in a high

school and three years in the Technical College of Industrial Chemistry. He successfully completed matriculation and separate special university entrance examinations to enter the University of Sofia, Bulgaria, in 1953, to study chemical engineering. That degree course took six years to complete. The first five curriculum years comprised 12 chemistry subjects, 22 engineering subjects, two foreign languages and four subjects of a political nature; the final year was devoted to postgraduate work culminating in a thesis and dissertation before a State Commission consisting of university lecturers and external technical experts. On the face of it, this seems to be fairly normal for the times.

Meanwhile, also in Eastern Europe, Tzvetanka (Ceci) led a much less stable life. Her father was an Eastern Orthodox priest who was posted to Pecs, Hungary, to establish a church. The town of Pecs, fifth largest in Hungary, boasted a large congregation of Bulgarian expatriates, students, itinerants and several Slavic minorities. He was busy; additional to his pastoral care he was advising on legal and consular matters, so, to facilitate that work he undertook and graduated in law and sociology studies at Pecs University. During World War II he helped persecuted Jews in their attempts at avoiding concentration camps: his work eventually put him in a dangerous political position and he fled West using his diplomatic passport. His wife and two young daughters then followed, using the ruins of a heavily bombed railway system to gradually find their way across wartorn Europe. They rejoined and the priest, his traumatised wife, an older daughter and little seven-year-old Ceci joined the throngs frantically fleeing the advance of the armed forces of the USSR.

After much danger, misery and hunger, they reached the Altötting district of Bavaria, Western Germany, where they later

celebrated the capitulation of the Duetsche Wermacht on 8 August 1945. The repatriation of refugees from the devastation was a lengthy process, during which Ceci's mother pined for her homeland.

Disregarding warnings of an uncertain future and her ability to manage life with a small child in a country with a now well-established Communist regime, she decided to return and took ten-year-old Ceci. The father and older sister did not go, and they eventually chose



Australia for their home. Ceci and her mother returned to Sofia, Bulgaria, in the spring of 1946 and were immediately isolated to a holding camp for processing and interrogation by Internal Security personnel. Because of their connection with a high-ranking priest and envoy who was a former member of the diplomatic community serving pre-Communist governments, there was intense interest in them. Her mother was subjected to long hours of interrogation over weeks, and upon release was stripped of her permanent citizenship of Sofia and classified as an 'unreliable element and potential enemy of the State'. This denied her the right to apply for permanent residence or employment in Bulgarian towns and forced her into a life of permanent exile in the country. Her daughter, young Ceci, shared this status, and it stayed with her until she left the country in 1963.

Ceci's education had been severely fragmented by the war – she had attended German schools using the Gothic alphabet, and she was multilingual. Despite this and fighting a curriculum, cultural and language catch-up, she completed the remaining grades to Year 7 in a village school of Northern Bulgaria. The local Communist apparatchicks warned her to be modest in her goals, to never aspire to a higher education and to resign herself to a life in the fields of the local cooperative. To escape this, young Ceci left for Sofia, where an aunt took her in and arranged attendance at an elite high school for girls.

Barely a month into her first year at this school, Ceci was summoned to the Headquarters of State Security in Sofia. This unusual request was quite distressing; it involved a lost school day for no apparent reason, so her uncle accompanied her. He was turned away at the door, and she was met and interrogated by two strangers, one in the uniform of lieutenant, and the other plain-clothed (but later addressed as 'Colonel'). They were

seeking information of her family and her father's work during the war, but she was unable to enlighten them. Her lack of knowledge frustrated them and after 12 hours of shouting and abuse, they released the frightened 13 year old at 1.00 am.

This treatment firmed her resolve to succeed, and she performed at straight 'A' level throughout her school years, including her matriculation examinations. This performance granted her a medal from the Ministry of Education, circumventing the need for a political reference to enter university and giving her a choice of study discipline. Her lifetime political classification would have otherwise endangered any chance of university entrance, but her well-deserved medal cleared the way.

She chose the discipline of 'Technology of Liquid and Solid Fuels' at the faculty of Chemical Engineering. Her university life was not easy – she struggled through first year studies with no financial support – but after good results, she was granted a small stipend and some aid for basic accommodation. Along the road, she had regular security interrogations and warnings that she was under constant observation but she somehow avoided being included in the lists designed to remove potential enemies of the State from students' ranks.

Despite the hardship, she graduated at the same time as Con.

Ceci's first job as a graduate was that of shift manager at an antiquated explosives factory remote from Sofia. This position had been unfilled and reasons soon became apparent. The factories used mixtures of TNT and nitrates of ammonia, potassium and sodium, along with powdered aluminium and 'ferro-siliconTM' to produce bombs and cartridges of varying sizes and potency. Unsafe equipment, antiquated technology and shocking conditions resulted in many ill workers and constant breakdowns in operations, and the shift manager was responsible to the State for these. During her time there, she was under the constant scrutiny of State Security and after two years the position became untenable and she resigned.

Her aunt assisted her to find her work as a chemist in the Film Processing Laboratories of the Bulgarian Cinecentre. This was very challenging but rewarding, but her background lack of permanent citizenship of Sofia, essential to holding a permanent position, ended it.

Meanwhile, she had married Con and they managed to become sponsored by her older sister for a visit to Australia. Neither could speak English, and an interview at the University of Adelaide was facilitated by Ceci's sister, who attended as interpreter. The outcome was good, the qualifications were acknowledged and they found employment, albeit of 'temporary' state until their Australian citizenship could be established.

They joined RACI as Junior Graduate Members, eventually becoming full members (Associate in those days) in 1967.

Con eventually settled in to work in the South Australian Government Department of Chemistry starting at first in the Cereals and Explosives Sections, later joining the Food and Drugs Section to specialise in pesticides analysis. In his first five years, he published in pesticides residues analyses, one of

which became a recommended procedure in the US Food & Drugs Administration Manual for Pesticides Residues. He successfully completed wide-ranging surveys of pesticide residue levels in food supplies and the environment and the formation and establishment of the Pesticides Residues Section. He progressed to become Assistant Senior-Analyst in the Agricultural Chemicals Section (including Plant & Soil Nutrients and Minor Constituents Sections) of the Agricultural Chemistry Branch, Chemistry Division of the SA Department of Services and Supply, where he continued his good work.


He was also involved in the design, specification and instrumental set-up of the laboratories in the Forensic Science Centre.

From 1983 to 1993 Con held the position of Head of the Trace Elements Laboratory of the Chemistry Division – SA Department of Services and Supply. Con proposed this service and it rationalised all trace element and metal analyses within the department. It operated successfully as a stand-alone business unit.

Meanwhile, Ceci was suffering the social and economic restrictions of the sexist sixties, but became a mother and established herself as a good professional chemist. She held positions from Analyst through to Head of Blood Alcohol, Illicit Drugs and Horse/Dog Doping Laboratory, Head of Food & General Laboratory, then Head of Pesticides Residues Laboratory of the Chemistry Division of the SA Department of Services and Supply, and, eventually, 1986–1994, became Senior Forensic Scientist in the State Forensic Science Division of the SA Department of Services. She published in the fields of forensic science and environmental pollution, and presented at numerous conferences related to drug analysis, control of the use of drugs in horses, analytical chemistry, forensic science and mass spectrometry.

Con and Ceci retired and travel extensively, often regaling the local Retired Chemists Group with tales of far-away lands. Ceci's mother died under suspicious circumstances in a traffic accident in 1968. During a visit to her homeland in 2006, she was unsuccessful in establishing the details of this incident and was warned to stop trying.

John Mason FRACI CChem, with thanks to Con and Ceci Parouchais for sharing their story.



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'Fifty shades of litmus?'

Chemistry in the marketplace 40 years on

The five editions of *Chemistry in the marketplace* provide an imperfect record of the changing social interests and concerns relating to chemistry. Its contents tried to respond to feedback from a variety of sources over many years.

In the 1970s, product labelling was non-existent and product or safety information from industry or government was like pulling hen's teeth. Our words of wisdom generally came from older-style textbooks such as Noller's *Organic chemistry* and references such as Kirk-Othmer *Encyclopedia of chemical technology*, and H. Bennett's *The chemical formulary* series.

Today, it is about infotainment, and slipping in material important for a chemical education needs to be more subdued. Besides, there is so much good straight chemistry in the internet.

The school and university chemistry syllabuses have moved from the practical to the theoretical, from the colourful H₂S qualitative analysis and borax beads, to s, p and d orbitals and curly arrows. However, it is the descriptive and applicable chemistry that answers community questions.

The public understanding of science becomes the scientists' understanding of the public. While Science weeks have been an outstanding success, named lectures preach to the converted and there is no public lecture aimed specifically and public concerns. Perhaps the internet has replaced this but it is not monitored for quality and balance.

In the 21st century, the most dramatic change has been the internet and the search algorithms developed by Google and others. A result revealed by a non-representative survey of the less-affluent greater western Sydney local libraries is the disappearance of science books in general and Dewey 540 (chemistry and allied sciences) in particular. In one of the larger municipalities, the only Dewey 540 book was *The idiots' guide to chemistry*. Popular science, Dewey 500, does better.

Talking of old, the Lifeline book fairs throw up what libraries throw out, and I nostalgically picked up Alex Boden's 1940s school text *An introduction to modern chemistry*. Library turnover can be slow; modern is a dangerous word to use in a title!

And as for old, the section 'Chemical Attractions', at Sydney's Powerhouse Museum (which replaced the original Museum of Science and Technology) was launched on St Valentine's Day 1996. This chemistry section (partly sponsored by the RACI) hasn't changed one iota in almost 20 years. The exhibits are dated, and there are no visitors in sight, in spite of the crowds of schoolchildren elsewhere. Some exhibits are not working (in particular the highlight – the chocolate chemistry-cum-dispensing machine).

Chemical information from government sources can be just as dated. For example, *The National Chemical Gateway* (https://apps5a.ris.environment.gov.au/pubgate/cig_public/!CIGPUBLIC.pStart) was last updated on the day it was launched – 10 February 2004.

Magazines are the great survivors of the internet media massacre. Articles appear that make chemists wish they had never adopted the word 'organic', which is now used to clobber us at every opportunity. What can be our response?

During a sabbatical in Europe in 1991 I toured with a lecture called 'Chemistry for Tourists'. It struck me that what I wanted as a tourist was for someone else to have done all the hard work, used their experience to sift through the totality, and extract a sample of what might be of most use and interest. The choice had to appeal to me, as well as to many other people of diverse interests and backgrounds. So the aim for the later editions was to be a 'Tourist Guide to Chemistry'. I'm taking you through a foreign country pointing out and explaining landmarks I hope will interest you; giving the cultural setting, telling a few funny stories, helping you with the shopping, and explaining that the natives (the chemical industry) are now quite friendly. Then I'll leave you to explore further. I will also warn you against new age snake oil salespeople who will try to strip your wallets with pseudo science.'

Chemistry in the Marketplace 5th edition 1998

So, we need to throw another non-organic chemical on the Bunsen.

Ben Selinger FRACI CChem (benselinger39@gmail.com)



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A very large grain of salt

When eating, I am often guilty of a slightly heavy-handed use of salt. This activity ionically attracts unsolicited advice from friends, family and strangers – the core of which is that salt is ‘bad’ for me. When quizzed for details, my educator usually makes vague reference to blood pressure and heart disease. My blood pressure and markers for heart health are much better than average for my age, and my life-long disdain for popular opinions on health matters remains.

I have always argued back to the salty nay-sayers that my body contains around half a kilogram of salts and that the few milligrams I am about to ingest hardly merits consideration. I also note that without salt in our diet we don’t survive very long. Indeed, migration patterns of ancient humans usually followed coastal regions where salt was readily available and only extended inland when either salt deposits were discovered or trading allowed reliable supply from coastal regions. That is, salt is a necessary input into our diet without which we cannot live.

Before the advent of technology, humans got their salt through ingestion of seafood or the use of dried ‘rock’ salt found in naturally available deposits. By dry weight, sea salt is usually (it varies in coastal regions, near rivers for example) 55.03% chloride, 30.59% sodium, 7.68% sulfate, 3.68% magnesium, 1.18% calcium, 1.11% potassium and trace levels of bicarbonate, bromide, borate, strontium and others. Due to the sequential precipitation in evaporating salt water bodies that form rock salt deposits, sodium chloride levels in rock salts are typically 90–98%, the remainder being the usual sea salt minerals but in lower relative quantities.

But of course, humans being humans, we started playing with these compositions as soon as we had the nous to do so. Driven by supply issues, and later on by food aesthetics as well as productivity and profit motives, we have over a few thousand years managed to reduce food salt to (almost) pure sodium chloride plus a bunch of unnatural additives; more on this later.

In ancient times, humans either mined rock salt or extracted salt from sea water by filling a ceramic pot with sea water (which is only around 2.5% total salts) and boiling it until it was dry. This netted a greyish, somewhat hygroscopic salt with the full gamut of trace minerals. The rest of the history of salt production can be summarised by three major innovations.

Firstly, humans started using concentration ponds to precipitate and dry salt water, either brine from mines or sea water, whereupon careful removal of the layers of dried salt precipitates resulted in various grades, including the preferred sodium chloride-rich evaporate (halite) for table salt use.

Later on, concentration ponds were used in series so that unwanted and less soluble salts were first crystallised in one pond and then the pure sodium chloride brine was pumped into its own pond to allow precipitation of a more pure salt produced by a higher yielding process. Modern salt works have very complex interdependent pond systems, so this is an oversimplification of what they are really up to. Chemical additives



Salt stock pile at Dampier, Western Australia.

iStockphoto/JohnCarnemolla

are often added at each stage to help precipitate or float unwanted impurities.

For over a hundred years, salt production facilities have been using a process in which the concentrated sodium chloride brine from the pond system is thermally evaporated under near-vacuum conditions in a series of tanks. The resulting slurry is dried by centrifuge and a fluid bed drier, and contains very pure sodium chloride cubic crystals of near-uniform and controllable dimensions – the perfect table salt. Salt production facilities, by extracting and purifying all the salts separately, can sell various salt types and grades for different consumer and industrial applications.

Common table salt is so ubiquitous that is viewed by health authorities as a useful carrier for a number of food additives, including iodide, fluoride and folic acid. These are variably added to salt to help combat common health issues associated with the deficiency of these chemicals in the average diet. The addition of iodide also requires the addition of a stabiliser, such as sodium thiosulfate, sodium bicarbonate, basic phosphates or dextrin (yes, there may be sugar in your salt) to prevent oxidation of the iodide to iodine.

Sodium chloride crystals are cubic and their flat surfaces are susceptible to fusing together, especially in the presence of water. Anticaking agents are added at around 0.5% by weight to prevent this issue and can include desiccants such as sodium alumina silicates, calcium silicates, calcium carbonates, calcium phosphates and magnesium carbonates. These desiccants are added as very fine powders (relative to the sodium chloride crystals) so they also act to physically inhibit the interactions of sodium chloride crystals. Sometimes salt precipitation is manipulated by using ferrocyanide salts to produce non-cubic salt crystals that are less prone to caking.

Of late I have noticed the emergence of ‘sea salt’ as a healthy alternative to ‘table salt’. Some salt is even labelled as

'organic'! This is another example where common terminology can confuse the chemically trained. All the salt that we consume originates from the sea and yet some is confusingly and proudly labelled as 'sea salt'. What we normally don't know as consumers is how a particular 'sea salt' has been processed. It could be from some natural deposit or from a brine pond system, and in both cases it might contain more sodium chloride than we imagine. The odd thing is that sea salts are usually much less processed than table salt and yet cost much more, a reflection of the efficiencies of industrial scale production and also of a little price gouging of health-conscious consumers by niche operators and retailers.

Does our level of salt consumption actually matter? Not according to *Scientific American* (8 July 2011 and 26 September 2012). In these two articles, the author does a very good job of deconstructing the arguments and evidence that have been used to drive the ubiquitous public health messages related to the risks of high salt consumption. If true, this has frightening ramifications for the faith people might place in our so-called health authorities. In 2013, the US Centers for Disease Control and Prevention retracted their previous advice to Americans that they keep sodium consumption to less than 2300 milligrams a day because a new study found no evidence to support this previous advice.

Other commentators have taken a different approach and suggested that natural sea salt, with its wonderful balance of

salts and minerals, can be consumed with abandon but that 'industrial' table salt is in fact the real culprit that drives health issues. The evidence supporting this argument is very tenuous but nevertheless appealing to many. The most likely reality is that an over-reliance on pure sodium chloride might result in a deficiency of certain minerals if these are not otherwise present in a diet. In addition, a diet that is rich in industrial table salt is also possibly correlated to processed and fast foods, which have other negative health consequences.

For me it is simply a case of consuming carefully chosen and (to me) much tastier 'sea salt' – the grey version with salt in the same proportions to salt in the sea and not the more pure rock salt. This way I dodge all the xenobiotic additives in industrial salt (which may or may not do harm) and get all the trace elements (which I may or may not need). I tend to use salt up to a quantitative level that is limited by my body's reactions (yuk, too salty!). With routine trips to my doctor, I also intermittently monitor the key heart-health indicators, which one does anyway. However, the more processed or pre-prepared food I eat, the more industrial table salt that I unwittingly ingest. If this matters enough to me, or if I ever develop suspicious health issues, I will know what do.



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Summer is a good time for informal education

Students look forward to summer because usually it means a break from formal and non-formal education. Formal education refers to education in formal educational institutions, such as preschools, primary, secondary and tertiary educational institutions, and other registered training organisations. Non-formal education refers to organised educational activity outside the established formal system that is intended to deliver a defined set of learning objectives to an identifiable group of learners (see October issue, p. 33). Informal education refers to all learning outside the formal and non-formal educational system, and is often associated with life-long learning as it can include reading non-fiction books and scholarly articles, viewing documentaries and other informal professional development.

iStockphoto/Luckyraccoon



Informal education can also include travel to other countries and climates. Social constructivist theory maintains that learning occurs in social settings; conversely, most learners are limited by their cultural experiences. For example, Australian students have little first-hand experience of sublimation, but this is commonly observed in very cold climates when frost, ice or snow apparently ‘disappears’ as it sublimates to water vapour, without passing through the liquid state.

Food spoils more quickly in summer than in winter because higher temperatures increase the rate of (bio)chemical reactions. This Arrhenius behaviour is also why bacterial and insect activity is increased in summer.

Ice is often used to cool food and drinks. The presence of condensation on containers of iced drinks illustrates transfer of heat energy from warmer objects to cooler objects. As temperatures exceed 30°C and approach or exceed normal body temperatures, the ability of mammalian bodies to lose heat to the environment becomes ineffective because there is less temperature difference between the body and the environment: hyperthermia.

The warmer weather provides incentive to make cold foods such as ice cream, an activity which in turn is full of learning opportunities. Salt–ice slush is an example of the colligative property of freezing point depression. The rate of cooling affects the size of the solid particles in ice cream, which affects the texture and taste. Rapid cooling gives smaller ice particles, and a smoother, creamier taste. This is analogous to the geochemical formation of igneous rocks, in which more rapid cooling produces rocks with smaller grains, while slower cooling produces larger grains.

A favourite summertime activity is to go to the movies, especially in air-conditioned cinemas on a hot day or night. Watching movies are a form of virtual travel, and many educators make use of movies to illustrate chemistry concepts.

Some movie producers want a sense of authenticity and work hard to get the details right, even though those details might be incidental to the main plot. For example, in *Centurion*, Roman soldiers fail in a rescue attempt, and are taunted by the Picts for stupidity – they would have succeeded if they had only realised that metal become brittle in the cold. Another favourite example comes from *The Lord of the Rings: The Two Towers*, when Bilbo, Samwise and Gollum are crossing the Dead Marshes and see lights that appear to float over the marshes. These will-o-the-wisps have been known for centuries, and were the subject of a debate between George Washington and his officers. Washington and Thomas Paine, ‘the Father of the American Revolution’, believed that the lights were due to a flammable gas released from the marsh, while Washington’s officers believed that the lights were due to a flammable liquid on the surface of the marsh. On Guy Fawkes Night, 5 November 1783, the Washington–Paine experiment showed that when mud at the bottom of a river was disturbed, bubbles of flammable gas rose to the surface of the water. (Unknown to Washington and Paine, Alessandro Volta had performed a similar experiment in 1776.)

A problem with informal education is that it is often unguided. Students may find it difficult to discern the difference between scientific reality and an artistic distortion of reality in novels and movies. Educators have an important role here. If we only teach facts and concepts, learners will be dependent on a teacher. If, however, we foster students’ curiosity and ability to exercise judgement, they will be able to learn for themselves, not just during the summer, but also in every season of every year.



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The festive season and Icewine

The festive season is celebrated in many different climates around the world. In Australia, viticulturists and winemakers contemplate what the heat load may do to the development of grapes for the following harvest, while their counterparts in some northern hemisphere countries gear up for the production of Icewine. Icewine (Eiswein) is an intriguing curio, being made from frozen grapes; hence the name. Variations on the traditional style can be found in many other wine-producing countries, including Australia (bit.ly/1nyNnL7).

Dr Marc Bradshaw, a former doctoral student of mine, has now established a highly successful career in cool-to-cold-climate winemaking in the Niagara region in Ontario, Canada. It was Marc who introduced me to Icewine. Winemaking practice in Ontario is controlled by the Vintners Quality Alliance (VQA Ontario). For Icewine, there is a requirement that the grapes be harvested as low as -9°C . Many winemakers actually prefer -12°C or lower. Freezing the water in the grape berry results in an increase in the sugar concentration by 'removal' of the water. This harvest temperature requirement necessitates a few rather complex and physically demanding practices, including grape picking at night time and when the vines are under snow. The image illustrates workers hand-harvesting grapes at night under floodlights. I understand that it is a major challenge to cut frozen bunches using secateurs while wearing protective gloves. The image also shows the netting used to cover the vines up to harvest. The nets catch grapes that fall off the bunch under the weight of snow as well as protecting against bird attack and from coyotes prowling the vineyards, seeking the sweet grapes to satiate their hunger.

After harvest, the frozen berries are pressed at up to about 6 atmospheres. This is where some good physical chemistry comes into play. The harvest and pressing conditions are below the triple point for water, so operations are performed when most water is in its solid state. Some obviously remains in the sugar solution. The Clapeyron equation for the solid-liquid line indicates that for every increase in 1 atmosphere pressure, the freezing point of water will decrease by 0.0074°C . A 6 atmosphere increase during pressing will lower the melting point by 0.044°C , a negligible change ensuring that there will be little melting of the frozen water although some will melt due to friction and local 'mechanical' heat.

Pressing results in 150–170 litres per tonne of grapes, much lower than the 700 litres in regular wine production. Inoculation of the pressed juice that may be at 350 gram/litre sugar or more induces considerable osmotic stress in the yeast. Dr Debra Inglis at Brock University, Ontario (bit.ly/1DCz3p5), has shown that the impact of this osmotic stress is the production of acetic acid and maybe also ethyl acetate, both quality defects. Fermentation usually takes 6–8 weeks. If longer, stress in both the yeast and winemaker can occur.

The fermentation is stopped when the sugar concentration is between 100 gram/litre (regulation) up to about 170 gram/litre (market preference) with an alcohol concentration between

10 and 12%. The sweetness from the sugar and alcohol is to some extent balanced by the relatively high acidity of the finished wine. Aroma descriptors include apricot, raisin and honey, with lusciousness and viscosity describing the palate. A sparkling Icewine, made by the tank fermentation process to trap the carbon dioxide, has the added dimension of bubbles, which tend to reduce the sensation of sweetness.

Icewine can be made from Riesling and Chardonnay as well as Vidal (a hybrid variety). Red varieties include Cabernet Franc (winemaker preferred) and Shiraz. Tasting a red Icewine is an experience to behold, not one that holds much joy for me, but clearly it does for others. Pillitteri's Shiraz Icewine, put together by Marc Bradshaw, was named in the top ten at the 2008 Syrah du Monde competition (bit.ly/1tdDHGJ).



Marc Bradshaw

Donald Ziraldo (bit.ly/ZNxSE9) has led the charge for international marketing of Niagara Icewine. The major markets are in Asia, especially China and Japan. Presentation of the wine in bottle is one of the keys to market success. Generally, the wine is available in 375 millilitre bottles, although some 50 millilitre bottles can be found. Donald's book, *Icewine – extreme winemaking*, co-authored with Karl Kaiser, gives more detail on production practices, a flavour wheel, and recipes for matching Icewine and food.

Finding Niagara Icewine in Australia is a challenge. Inniskillin and Ziraldo wines can be found at around \$100 per 375 millilitre bottle. Or you may care to try something from Australia. Andrew Hood initiated Icewine making in Tasmania by using cryo-extraction. Here, the harvested grapes are frozen in tanks and then pressed and the juice fermented as described above. A quick Google search will identify several local wines made by this cryo-extraction approach: Frogmore Creek is one that can be purchased for around \$20 for a half-bottle. You might wish to decide whether the cryo-extraction method is the 'real thing' or not.



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.

Let's not waste our e-waste

Waste. Most people will associate this word with something they want to get rid of, something without value. But electronic waste, or so-called e-waste, still contains vast amounts of scarce metals and valuable elements.

E-waste is the most rapidly growing type of waste all over the world, as the first generations of mobile phones and computers are reaching the recyclers. In 2012, 14.2 kilograms of e-waste was discarded on average by every person on Earth (www.step-initiative.org/index.php/WorldMap.html). The potential of this type of waste as a sustainable resource for scarce elements is enormous because e-waste is already a concentrate of gold, palladium, silver, rare earths etc. For example, a mobile phone contains about 305 milligrams of silver and 30 milligrams of gold which is 40–50 times more concentrated than in the ores from primary mining (www.oeko.de/oekodoc/1375/2012-010-en.pdf; K. Binnemans et al. *J. Clean. Prod.* 2013, vol. 51, pp. 1–22).

In addition, the recycling of e-waste also regenerates the required metals in the ratios needed to manufacture these devices again. The amount of useless side products is therefore reduced to a minimum compared to ordinary mining.

Closed loop production

The biggest bottleneck at this moment is the efficient collection of this type of waste. Surveys show that every American consumer holds two unused cell phones on average at home, because 60% cannot be bothered to turn in their old devices – even though the recycling value of modern smartphones can easily reach \$100 (www.prweb.com/releases/2013/2/prweb10432797.htm). It is estimated that US consumers are sitting on \$33.8 billion in used mobile phones. More effective marketing and financial incentives could motivate people to bring their unused electronic equipment to collection points.

Several encouraging examples exist, such as shops offering discounts for a new mobile phone when an old one is handed in.

Fluorescent lights and batteries have an advantage compared to other electronic equipment because they contain toxic elements that have to be dealt with accordingly, to avoid them ending up in the wrong places. Governments therefore put in place efficient collection methods and urged the public to bring in their used batteries and energy-saving lightbulbs, using advertising campaigns to raise public awareness about this issue.



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These strategies were initially put in place to deal with the toxic elements they contained, but very soon different companies started to develop recycling schemes to retrieve the valuable elements from this new type of feedstock. Several successful examples exist such as the recycling of computer circuits, rechargeable batteries, mobile phones, high-end magnets and energy-saving light bulbs by chemical companies such as Umicore and Solvay (K. Binnemans et al. op cit.) These companies have developed a profitable business around this idea of urban mining, where waste is no longer considered a problem but a solution!

With over \$21 billion worth of gold and silver used in electronic gadgets every year, and only 15–20% of that being recycled, it is not surprising that green tech was the most rapidly growing industry of 2013 (<http://thediplomat.com/2013/11/the-potential-of-urbanmining>).

The rapidly growing amount of e-waste is therefore receiving increasing attention as the feedstock of the future. The European Commission and the United Nations have identified the recycling of e-waste as a top priority for the development of a sustainable high-tech industry and the safeguarding of scarce resources (http://ec.europa.eu/enterprise/policies/sustainablebusiness/sustainable-industry/forums/index_en.htm; www.unep.org/pdf/Recycling_From_e-waste_to_resources.pdf). Reusing the valuable elements trapped inside these devices is the key to a 'closed loop' sustainable manufacturing of the electronic gadgets we are all so keen on.

The burden on the environment often associated with primary mining would become too large if the upcoming economies started consuming high-tech products as we do. But in a closed-loop system, very few of these rare elements are lost and a completely new innovative industry can even emerge to try and retrieve them as efficiently as possible – transforming piles of mobile phones into fresh new bars of gold, silver, palladium, cobalt and all the other elements needed to manufacture these amazing devices that connect us to the world. The way we think about waste is changing rapidly!



David Dupont is a PhD student in chemistry at the University of Leuven, Belgium. His research focuses on the recycling of rare earths and valuable metals. YourFormula.eu is an online platform and multimedia magazine, powered by Cefic (The European Chemical Industry Council), where young chemistry enthusiasts blog about chemistry's role in a sustainable world.

First published at www.yourformula.eu and reproduced in *Chemistry International*, 2014, vol. 36(4), pp. 10–11.

Dr Stewart trims the joint

Alfred W. Stewart (1880–1947) was a physical chemist who held a chemistry chair at Queens University in Belfast (1919–44) where he managed to combine chemical research with the writing of 27 crime fiction novels under the *nom de plume* J.J. Connington. By then, he was well into reviewing chemical literature, beginning in 1908 with *Advances in Organic Chemistry*, followed the next year by *Advances in Physical and Inorganic Chemistry*. Both series ran to nine editions, but his biographer, George Kauffman, felt that in the end it was clear that he was not keeping up with developing ideas in chemistry. For example, I found him questioning the validity of the Debye–Hückel theory of strong electrolytes long after it had passed into the chemical lexicon.

I have a number of Stewart's *Advances* volumes on my shelves, the earliest being the third edition (1919) of *Recent Advances in Physical and Inorganic Chemistry*. Sir William Ramsay had contributed an introduction, which must have been prepared for an earlier volume since Ramsay died in 1916. It makes interesting reading.

Ramsay began by proposing that scientific problems should rank among the great questions facing society, such as the divine right of kings and the question of women's suffrage. The first of his scientific examples was quite high-flown – an 'all-absorbing theme which (sic) exercised the minds of men of science as regards the true nature of phlogiston'. He also wrote of a contemporary problem, 'the present contest regarding the structure of the cobaltamines' and went on to claim that problems in science are more easily solved than those in politics, since (a) experiments could be devised to decide knotty questions, and (b) it is not in the interests of scientists to conceal the truth. Curiously, I found no mention of the cobaltamines in this edition of *Advances*, but on the third-last page, in a short section on stereochemistry, I found 'the tetrahedron was used ... by Werner in his explanation of the isomerism of complex salts'. I learned about them from J.S. Anderson's brilliant third-year lectures at the University of Melbourne.

Ramsay assured readers that Stewart, in his *Recent Advances in Physical and Inorganic Chemistry*, was dealing with 'subjects which (sic) are at present prominent in the minds of chemists'. Although Stewart had presented rival theories in cases where there was contention, he had 'not scrupled to express his own opinion where he holds a decided view'. Ramsay reflected that although the present problems represented the current state of knowledge, they were likely to be succeeded by others that would engross chemists. It was also possible, he wrote, that the old problems would be re-examined from time to time, with knowledge gained by incessant experiment, enabling or causing revisions to be made.

Ramsay drew attention to the enormous mass of chemical literature, which was making it impossible for the chemist to do more than take a quick look at the titles of the papers, although it was recognised that every paper 'represents much patient and careful work' by other researchers and it was sad to think that it could be so easily passed over by a busy reader. Looking more broadly, Ramsay wrote that there were many people not actively engaged in scientific research but nonetheless possessed of some chemical knowledge and with 'neither the leisure nor inclination to sit down and read the *Transactions of the Chemical Society* or the *Zeitschrift für Anorganische Chemie*'. Dr Stewart's work will be a boon to them, he said, because it provides readable and up-to-date accounts of the main lines of chemical development in ways that are not to be found in a typical textbook. Thanks to him people now have the opportunity of 'having their chemical food prepared for the table instead of trying to assimilate indigestible masses of what is often very crude material. Dr. Stewart may be likened to a skilful cook, who has trimmed his joint, rejecting all innutritious and redundant excrescences, and has served it up to table in a palatable form'.

Ramsay elaborated on his distinction between important and unimportant research. 'Nothing is so sad', he wrote, 'as to see much time and labour spent, with patience and devotion, in the investigation of some matter which possesses no real importance. It may be retorted that every true statement is of importance, but this is not so. It is only statements which hold forth some prospect of contributing to an organic whole which can be held valuable. There may, perhaps, be a little more merit in ascertaining to hundredth of a degree the boiling point of sulphur than of measuring the area of the wings of some particular butterfly; but the difference is barely appreciable. One is as likely to prove useless as the other.' Stewart's *Advances* was the ideal place for 'those imbued with the spirit of investigation to make a happy choice of a subject of research. Should this hope be realised, Dr. Stewart will have done a most useful work'.

And to close the year on a personal note, I should like to thank the readers who paid me compliments on my 30+ years of Letters. I get great pleasure from researching and writing them and from the correspondence that is often generated. Just keep reading!



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.

events

11th Australasian Aluminium Smelting Technology Conference

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

RACI National Congress

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

Advanced Materials & Nanotechnology (AMN7)

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

35th Australasian Polymer Symposium

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

IUPAC 2015

48th General Assembly 6–13 August 2015,
45th World Chemistry Congress 9–14 August 2015,
Busan, Korea
www.iupac2015.org

Pacificchem 2015

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

RACI events are shown in blue.

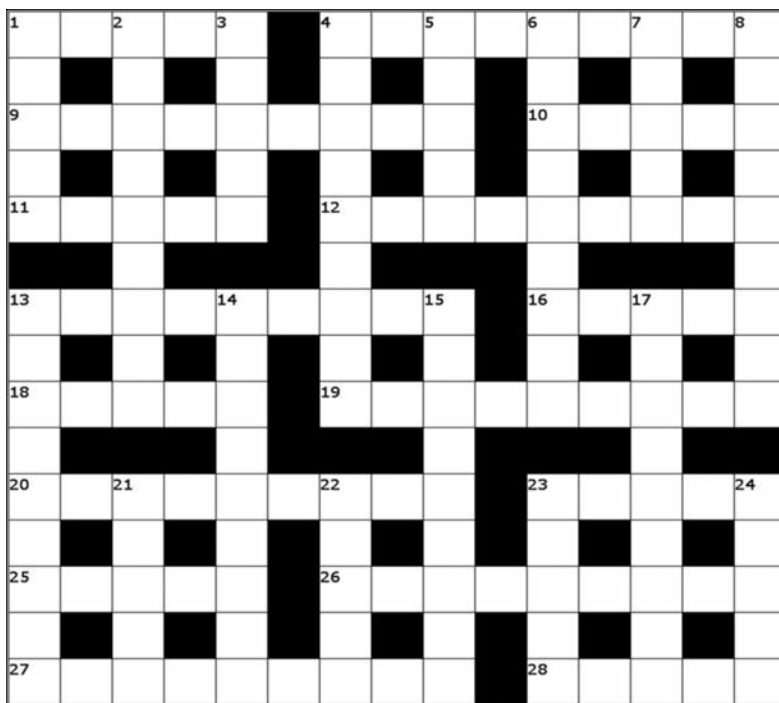
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Coming up

- Medicinal chemistry explained
- Chlorophyll, carotenoids and other autumnal pigments
- Transporting sodium cyanide
- Molecular deuteration in optoelectronics

cryptic chemistry



Across

- 1 Ultra fast laser spectroscopy comes back with inclusion of ionic compounds. (5)
- 4 React acetal? Nod when the story is told. (9)
- 9 Perhaps a thermostat makes rules. (9)
- 10 Presents man at NASA over inclusion. (5)
- 11 Resin sales talk. (5)
- 12 Similar helipad daredevil centres little animal. (9)
- 13 Started new dietitian. (9)
- 16 3365353 character-encoding scheme. (1.1.1.1.1.1.)
- 18 Called for phosphorus getting on. (5)
- 19 Undecided in the grid adjustment. (9)
- 20 Contamination: actively confine it. (9)
- 23 Punts for thrills. (5)
- 25 A profit repeated. (5)
- 26 Locating and using it at interchange. (9)
- 27 Centred py complex needs to be decoded. (9)
- 28 New Age is protection. (5)

Down

- 1 Undress band. (5)
- 2 Spooner's evening fish flashes. (9)
- 3 Fairy is shapely without vowels changing. (5)
- 4 Tried unkempt matted pet. (9)
- 5 Put your name down to go back to a Victorian seaside town. (5)
- 6 Dry out drunken diet cases. (9)
- 7 Perhaps past being stressed. (5)
- 8 Yeast, for example is going to hold ethylenediamine. (9)
- 13 Tip maleic reaction to show involvement. (9)
- 14 It's an obscenity! Cyanide centre drops rate when mixed. (9)
- 15 Set off diethyltryptamine on a spread for drying. (9)
- 17 Spooner's lower face stick conclusive. (9)
- 21 98876 in old money. (5)
- 22 A picture in a picture in firm. (5)
- 23 Cuddly animal under vehicle according to Spooner. (5)
- 24 Wise guys' mixture of gases. (5)

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



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