

chemistry

April 2015

in Australia

**Autumn pigments:
when chlorophyll takes
a back seat**

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April 2015



cover story

A spectrum of seasonal change

Colin Scholes appreciates the light and energy of colour in autumn leaves.

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18 Underwater insights from wrecks of war

The devastation of a World War II naval operation marked the beginning of an in-situ corrosion experiment.

22 Fundamentals of the fourth state

Tiny particles do extraordinary things at incredible temperatures, discovers Dave Sammut as he looks on the sunny side.

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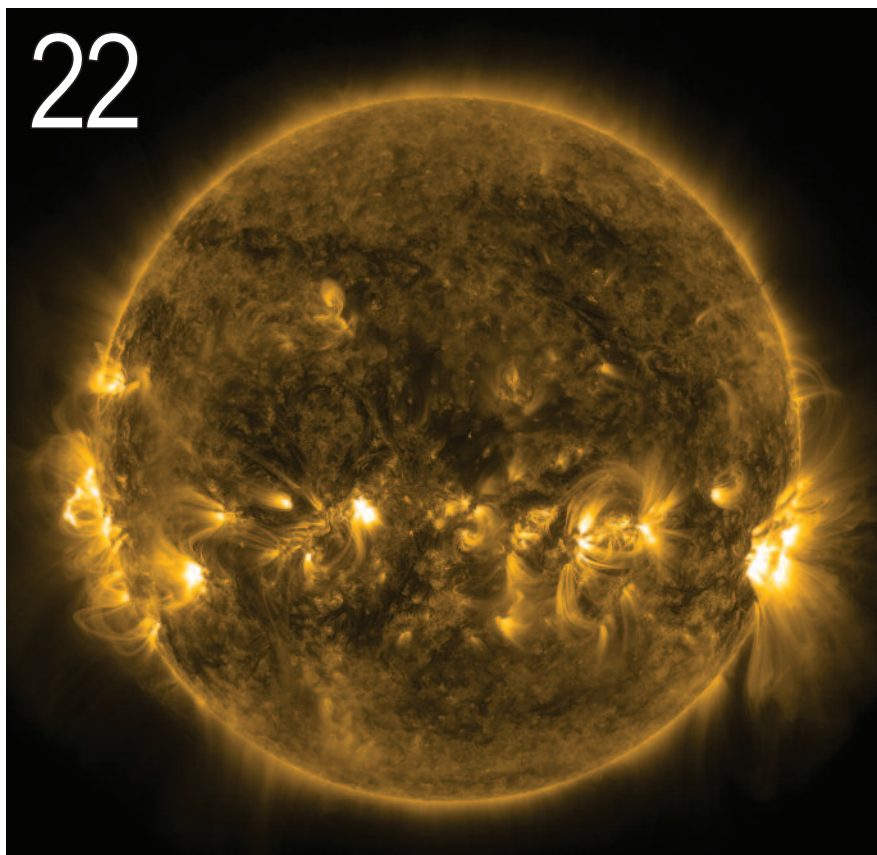
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Appreciating colour

Inadvertently this month, I've chosen stories featuring colour. In his cover story, Colin Scholes explains how leaf pigments such as carotenoids and anthocyanins produce the vibrant hues of autumn (p. 14). Reading Ian Macleod's article on marine corrosion (p. 18), I visualised rich red, orange and teal in the 'range of iron corrosion products that contain mixtures of oxides, hydroxides and chlorides as well as iron carbonates'. Exploring the fourth state of plasma, Dave Sammut evokes images of the white-hot centre of a freshly formed star, ejecting matter that cools through orange and purple out to blue (p. 22).

Charlotte Jirousek, associate professor of textiles and apparel at Cornell University until her death last year, wrote on her website about art, design and visual thinking (bit.ly/1BYIP4a):

The word *color* is the general term which applies to the whole subject – red, orange, yellow, green, blue, violet, black and white and all possible combinations thereof. *Hue* is the correct word to use to refer to just the pure spectrum colors. Any given color can be described in terms of its value [relative darkness or lightness] and hue. In addition, the various physical phenomena and psychological effects combine to affect our perceptions of a color.

She recommended Pantone's interactive test of ability to distinguish gradations of hue (bit.ly/1AmBtJY), and I couldn't resist. For those who aren't familiar with it, the Pantone Matching System is a standardised colour reproduction system whose options dwarf the selection of swatches available at your local paint retailer.

Pantone's interactive colour challenge is a version of the Farnsworth-Munsell (F-M) 100 hue test. Devised by US naval commander Dean Farnsworth in 1943 for wartime sailors, its common clinical use is to measure chromatic discrimination and identify certain deficiencies in colour vision. Albert Henry Munsell was a lecturer in colour composition and artistic anatomy at the then Massachusetts Normal Art School in Boston. Widely regarded as the basis of colour notation – a way of accurately identifying every possible colour – his model was based on hue, value and chroma (intensity). The early principles of his system were published in *A color notation* in 1905.

Initially a commercial printer set up in the 1950s, Pantone hired Lawrence Herbert, newly graduated with a Bachelor of



Arts in chemistry and biology. Herbert worked wonders streamlining Pantone's pigments and ink production and within a decade was running his division. Like Munsell, he realised that an accurate colour system must take into account human perception. Later, he bought the tech assets and Pantone as we know it today was born.

According to Pantone, their colour standards are 'often used for design inspiration, brand color development and communicating color ... Munsell colors are scientific absolutes which need to be interpreted according to the reproduction medium, substrates or end use'. Pantone's 2015 colour of the year is marsala, Pantone 18-1438 – or 5R 4/6, as Munsell calls it. If you want to convert accurately between colour systems yourself, you'll need a spectrophotometer. Personally, I find Pantone 2058 more my cup (well mug, actually) of tea.

I was pleased with my hue test score of 8. I suspect Charlotte may have done rather well, too.



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Dangers of 'chemical free'

I couldn't agree more with the President's editorial in the December 2014/January 2015 issue. Just as an example, I recently took the manufacturers of a product to task – they claimed their yoghurt product was 'free from chemicals, pesticides and preservatives'.

I drew it to their attention that in the first instance, this is not possible, particularly when one of the ingredients is 'water' (which, itself, is a chemical); terminology such as 'chemical free' preys upon the misconceptions held by the public, and their scientific illiteracy that synthetic substances ('chemicals') are dangerous or 'evil', while 'natural' or 'organic' substances are harmless. It is a nonsense and analogous to other companies who word things as 'free from nasty chemicals' ... who exactly decides what is 'nasty' and just 'how' nasty is 'nasty'?

My polite advice to the manufacturers was that they rethink their product label wording or, otherwise, claim the \$2.3 million dollar bounty available from the Royal Society of Chemistry for a product that the RSC considers to be 100% chemical free. It is ironic that many things nature makes (that are 'organic' and 'natural') can be far more potent than anything humans have ever made, especially in terms of toxicity.

Chris Embery MRACI 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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New OMNISEC for efficient sample separation and high sensitivity analysis

Malvern has produced a market-leading gel permeation chromatography (GPC)/size exclusion chromatography (SEC) solution by coupling efficient sample separation with fully optimised, multidetector analysis.

This completely new GPC/SEC platform from Malvern Instruments delivers high performance, ease of use and productivity demanded in the development of novel natural and synthetic polymers, pharmaceutical products, foods and other macromolecules.

OMNISEC REVEAL includes the following four detectors: refractive index (RI), UV/vis photodiode array (UV-PDA), low angle/right angle light scattering (RALS/LALS) and viscometer. Its light-scattering detector is the most sensitive on the market, meaning it can accurately measure molecular weights as low as 200 Da. Excellent temperature control across the complete module further boosts the accuracy of all measurements.

OMNISEC RESOLVE consists of a sample degasser, pump, autosampler and column oven, each optimised for precise, high-resolution separations. Key features include a low-volume, high-efficiency degasser design that enables rapid switch-over from one sample type to another. The new temperature-controlled autosampler eliminates injection waste, minimising the sample required for routine measurement, and in combination with the column oven maintains all samples under closely controlled conditions throughout the analysis. This is especially important when dealing with materials such as proteins, which can be temperature sensitive.

For further details, contact ATA Scientific Pty Ltd, ph. (02) 9541 3500, email enquiries@atascientific.com.au or visit www.atascientific.com.au.



Grip on iron-60 half-life vital for galactic history



Some beamlines serving various particle detection stations at the Department of Nuclear Physics, Australian National University. The ANU facility works like a big and extremely sensitive sorting machine, allowing single-atom counting of specific isotopes.

Scientists have settled a long-running debate on one of the fundamental time measures for galactic history – the half-life of a radioactive isotope of iron.

The new, accurate figure for the iron-60 half-life will bring clarity to many details of how the heavy elements were formed during the evolution of the galaxy.

The team found that the half-life of iron-60 is 2.6 million years, resolving the large discrepancy between two previous measurements that found values of 1.5 million and 2.62 million years.

'The iron-60 half-life is integral to theories about supernovae and the early solar system,' said Dr Anton Wallner, from the Australian National University

Research School of Physics and Engineering.

'Because iron-60 is formed predominantly in supernovae, its presence on Earth is thought to indicate that there were nearby supernovae in the last 10 million years. These may have had an effect on Earth's climate or even triggered the birth of the solar system more than four billion years ago.'

Most iron-60 is formed in massive stars, which explode at the end of their lives in a supernova event, spreading the radioactive element through space.

Today, iron-60 can be observed directly in our Milky Way through characteristic radiation emitted during its radioactive decay, indicating where

recent supernovae have created new elements.

The slow decay of iron-60 makes it difficult to measure the decay time precisely. The team used a unique mass spectrometer system at the Heavy Ion Accelerator Facility at ANU, which is more sensitive than previous experiments.

The team of scientists from Australia, Switzerland and Austria used artificially produced iron-60 extracted from nuclear waste.

The research (<http://dx.doi.org/10.1103/PhysRevLett.114.041101>) is an editor's highlight in *Physical Review Letters*.

AUSTRALIAN NATIONAL UNIVERSITY

Global ammonia capacity on the rise

Global ammonia capacity will increase from 204.2 million tons per year (mmt) in 2013 to 249.4 mmt by 2018, driven primarily by capacity additions in China, Iran, Nigeria and the US, according to research and consulting firm GlobalData.

The company's latest report, *Global ammonia outlook – production capacity set to continue strong growth led by United States and Iran*, states that Asia-Pacific will remain the largest region in terms of both ammonia capacity and demand, accounting for almost half the world's capacity with 120.7 mmt by 2018.

China's significant influence on Asia-Pacific's ammonia supply is apparent from the country's capacity of 70.6 mmt in 2013, accounting for almost two-thirds of the region's total capacity, according to GlobalData.

The major end-use sectors of ammonia, such as urea and other nitrogenous fertilisers, have promising growth in the region. With huge feedstock reserves and strong demand, China has a favourable landscape as opposed to countries that have either demand or capacity, but not both.

While coal is less cost effective than natural gas, its availability makes it the preferred choice for Chinese manufacturers.

GlobalData's report also states that the Middle East and Africa will continue its impressive growth of the past decade, which saw Egypt, Iran, Qatar and Saudi Arabia increasing their ammonia capacities using natural gas.

The Middle East and Africa's ammonia capacity will rise from 27.8 mmt in 2013 to 44.1 mmt by 2018, led by Iran and Nigeria, with planned additions of 5.8 and 4.6 mmt, respectively. Most of the region's capacity will target export markets in Asia, such as China and India.

Additionally, GlobalData observes that North America's ammonia industry will receive a small boost, having suffered in the past from high natural gas prices and declining demand from the major end-use sectors.

However, shale gas is now affecting the industry, with North American capacity expansion to be completely driven by the US, from 20.1 mmt in 2013 to 26.8 mmt by 2020. GLOBALDATA

Penta-graphene discovered

Researchers have discovered a new structural variant of carbon called 'penta-graphene' – a very thin sheet of pure carbon that has a unique structure inspired by a pentagonal pattern of tiles found paving the streets of Cairo.

The scientists are from Virginia Commonwealth University, US, Peking University, the Chinese Academy of Science, Shanghai, and Tohoku University in Sendai, Japan, and their paper will appear in *Proceedings of the National Academy of Sciences*.

Penta-graphene is a single layer of carbon pentagons that appears to be dynamically, thermally and mechanically stable.

'The three last important forms of carbon that have been discovered were fullerene, the nanotube and graphene. Each one of them has unique structure. Penta-graphene will belong in that category,' said the paper's senior author, VCU's Professor Puru Jena.

Qian Wang, a professor at Peking University and an adjunct professor at VCU, was dining in a restaurant in Beijing with her husband when she noticed artwork on the wall depicting pentagon tiles from the streets of Cairo.

'I told my husband, "Come, see! This is a pattern composed only of pentagons." I took a picture and sent it to one of my students, and said, "I think we can make this. It might be stable. But you must check it carefully." He did, and it turned out that this structure is so beautiful yet also very simple.'

Most forms of carbon are made of hexagonal building blocks, sometimes interspersed with pentagons. Penta-graphene would be a unique two-dimensional carbon allotrope composed exclusively of pentagons.

The researchers simulated the synthesis of penta-graphene by computer modelling. The results suggest that the material might outperform graphene in certain applications, as it would be mechanically stable, possess very high strength, and be capable of withstanding temperatures of up to 1000 K.

Penta-graphene has several interesting and unusual properties, Jena said. For example, penta-graphene is a semiconductor, whereas graphene is a conductor of electricity.

'When you take graphene and roll it up, you make what is called a carbon nanotube, which can be metallic or semiconducting,' Jena said. 'Penta-graphene, when you roll it up, will also make a nanotube, but it is always semiconducting.'

The way the material stretches is also highly unusual, the researchers said.

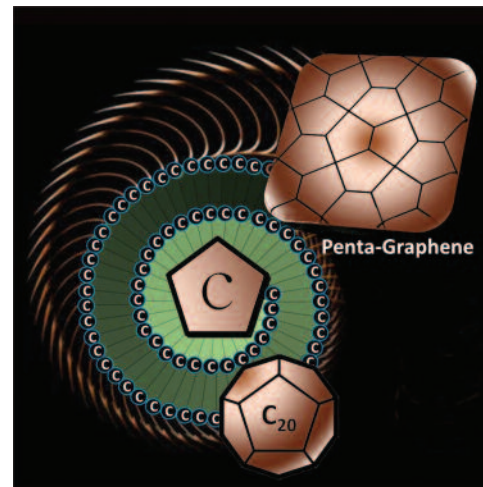
'If you stretch graphene, it will expand along the direction it is stretched, but contract along the perpendicular direction,' Wang said. 'However, if you stretch penta-graphene, it will expand in both directions.'

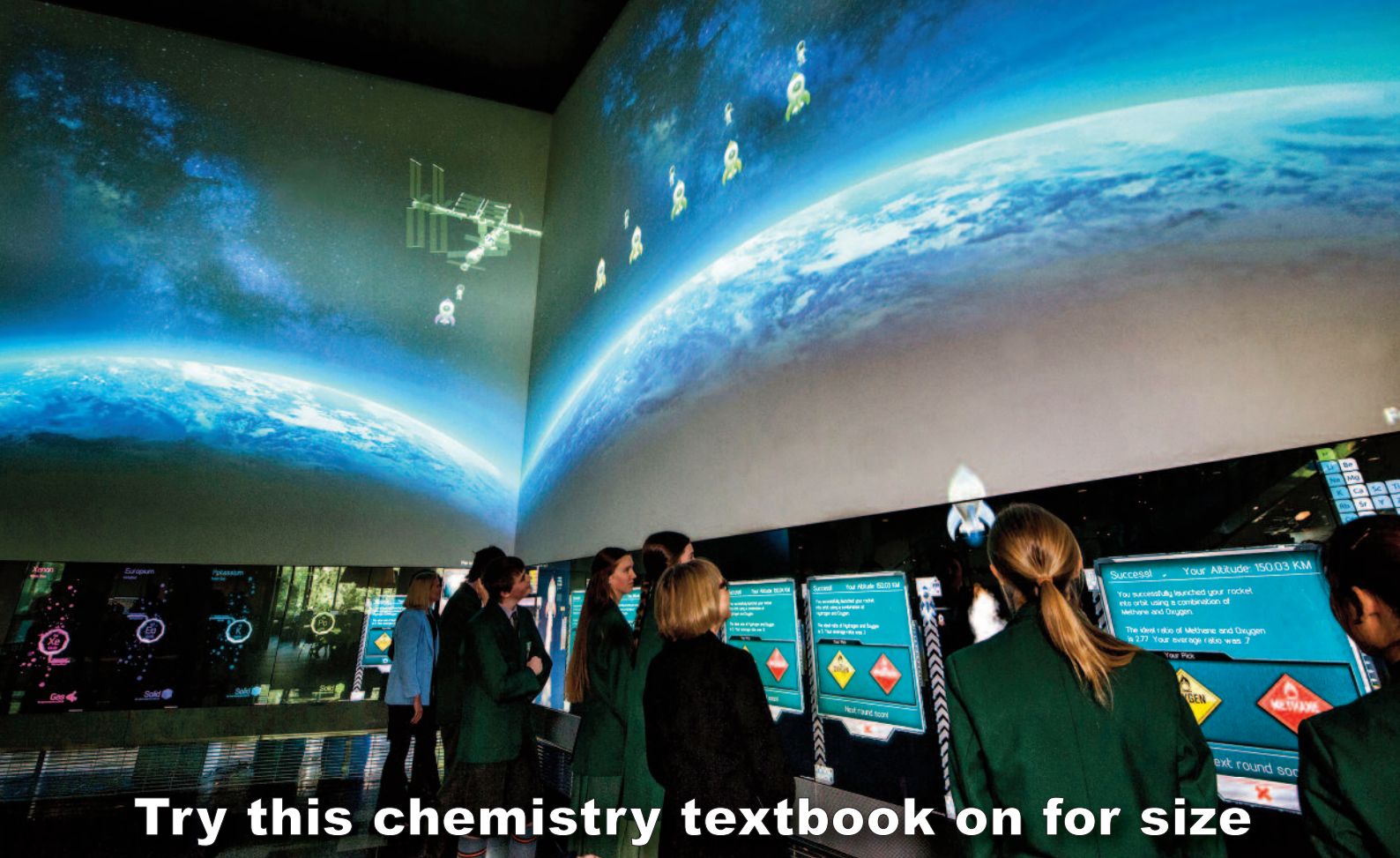
The material's mechanical strength may hold especially interesting applications for technology, the researchers said. Penta-graphene's properties suggest that it may have applications in electronics, biomedicine, nanotechnology and more.

The next step, Jena said, is for scientists to synthesise penta-graphene.

'Once you make it, it [will be] very stable. So the question becomes, how do you make it? In this paper, we have some ideas. Right now, the project is theoretical. It's based on computer modelling, but we believe in this prediction quite strongly. And once you make it, it will open up an entirely new branch of carbon science. Two-dimensional carbon made completely of pentagons has never been known.'

BY BRIAN MCNEILL, VIRGINIA COMMONWEALTH UNIVERSITY





Try this chemistry textbook on for size

Queensland University of Technology (QUT) has created the world's largest interactive chemistry textbook. Developed in partnership with hundreds of students, teachers, academics and scientists, Chem World (www.thecube.qut.edu.au/project/chem-world) links directly to the new Australian curriculum for chemistry.

The two-storey interactive display at The Cube, a digital interactive learning and display space, allows students to conduct virtual chemistry experiments too dangerous or difficult to run in a classroom, including launching rockets into orbit and creating colourful fireworks.

'Chemistry is fascinating but it involves concepts that are quite difficult to comprehend,' said QUT's STEM teacher-in-residence Anne Brant, who co-conceived and championed the project.

'Students often have trouble moving from the physical side of chemistry into the abstract concepts that underpin the things they can see and touch.

'Because Chem World is highly visual, it can explain the abstract more easily than your traditional textbook – it's an intuitive, informative experience with a library of knowledge accessible at a finger's touch.'

Chem World includes an interactive periodic table with crowd-sourced content moderated by professional chemists, and artworks created by students.

Chem World also contains three interactive experiments, where users can:

- produce spectacular virtual firework displays to learn why some chemical elements produce colour and discover the 'fingerprints' of elements

- compete with others to launch rockets into space, in order to explore how fuels produce energy and compare different fuel types
- see how water behaves on a molecular level and what happens when substances are added, in order to learn about solubility and what makes some things dissolve in water when others do not.

The interactive display was built by game developers in The Cube's studio team.

Co-creator and studio manager Sean Druitt said his team had spent 18 months engaging with the community and six months coding the software to bring it to life.

'If things like this were around when I was young, I probably would have become a scientist rather than a games developer,' Druitt said.

Brisbane schools are already planning to incorporate Chem World into their lesson plans.

'Students today have grown up in a digital world and they relate far more to technologies like this than the hard-copy textbooks older generations are used to,' Kelvin Grove State College Head of Science Karen Gosney said.

'As educators, we will rely more and more on digital tools like this to enhance the learning experience for students.'

It will remain part of The Cube's permanent library installations, sharing the main display space with the Virtual Reef.

QUEENSLAND UNIVERSITY OF TECHNOLOGY

10 years of *Chemistry – An Asian Journal*

This issue marks the beginning of Volume 10 of *Chemistry – An Asian Journal*, and round birthdays are always a good reason to celebrate!

Of course, round birthdays are also a time for reflection, for looking back on what has happened in the past. We have invited our most prolific authors, whose work is featured in this issue, to do just that – to look back on the past 10 years and share what has changed for them professionally and personally since *Chemistry – An Asian Journal* was founded. You can find their responses on ChemistryViews.

Looking back at the journal's history, a lot has changed as well. In 2006, the journal published just 94 articles – 88 Full Papers and six Focus Reviews. In 2009, *Chemistry – An Asian Journal* began accepting Communications, and in 2014 the journal published 132 Communications, 305 Full Papers and 36 Focus Reviews, for a total of 473 articles. Never before has *Chemistry – An Asian Journal* published more articles in a single year!

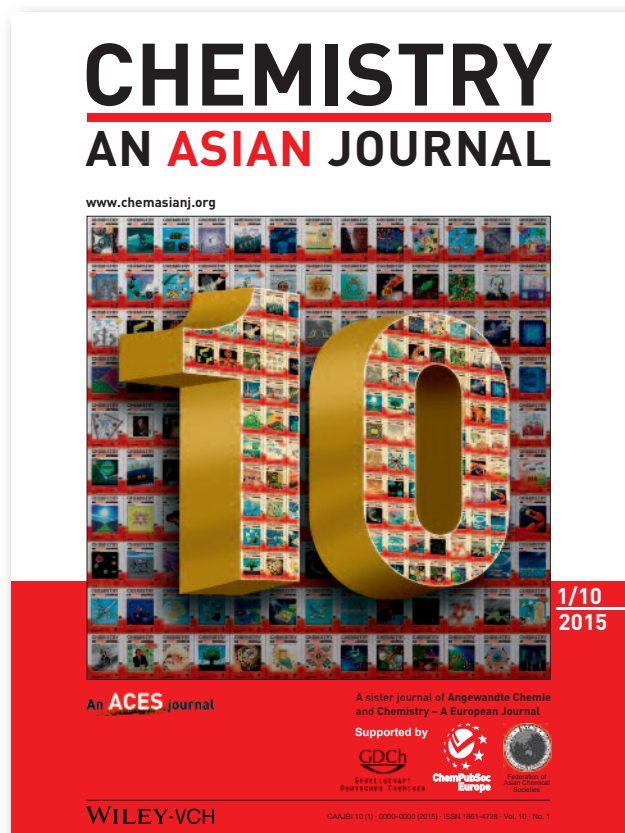
The shift in geographic origin of the papers has been even more dramatic. In 2006, only nine papers from China were published, with more than six times as many coming from the rest of Asia and nearly twice as many from Europe. Since then, chemistry in China particularly has expanded at a furious pace, and last year nearly half of all contributions had corresponding authors in China. Of course, this development is mirrored by other parts of Asia as well, while there has been much more modest growth in the established communities in Europe and North America.

What else has changed over the past decade? The speed of research, driven by an increased number of active scientists and the resulting competition, has increased tremendously. To keep pace and make our authors' excellent results available as soon as possible, *Chemistry – An Asian Journal* now publishes accepted articles online within hours, before editing, typesetting and proofing. Mobile computing is another way to keep up with the literature, and the *Chemistry – An Asian Journal* app helps you do just that!

Speaking of connections, no one wants to celebrate alone, and so too with *Chemistry – An Asian Journal*. We're glad to be able to celebrate our readers and authors, referees and board members, without whom there would really be nothing to celebrate.

Who else are we celebrating with? The partners of the Asian Chemical Editorial Society (ACES), the 13 chemical societies throughout Asia and the Pacific region that co-own the journal, are certainly part of the party.

It was through their initiative that the journal was founded in the first place. As it's grown, they have continued to benefit from their connection to each other, to the publisher Wiley-VCH and to the journal. If you work in one of the countries represented by an ACES partner, your local chemical society receives royalties when you publish in *Chemistry – An Asian*




Journal. So join the celebration and support your local community at the same time!

Friends, relatives and neighbours shouldn't miss out on any birthday celebration. In this case, we savour the moment with our sister journals, *Angewandte Chemie* and *Chemistry – A European Journal*, with whom we collaborate closely, as well as with the rest of the journals of the ChemPubSoc Europe family. Last but not least are the ACES sister journals, the *Asian Journal of Organic Chemistry* and *ChemNanoMat*, the latest addition to the family.

Theresa Kueckmann, Editor *Chemistry – An Asian Journal*

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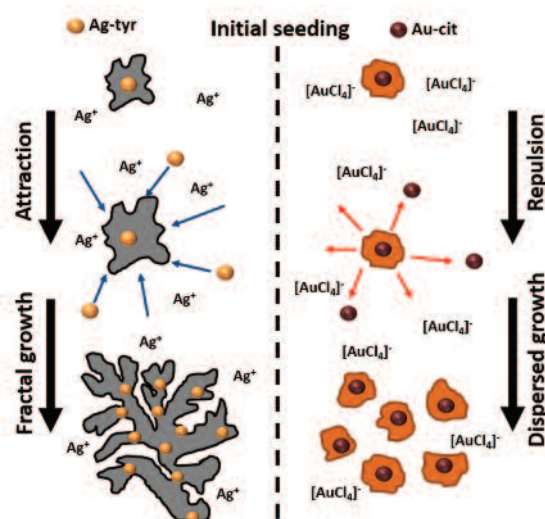
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Growing nanoparticles on electrodes

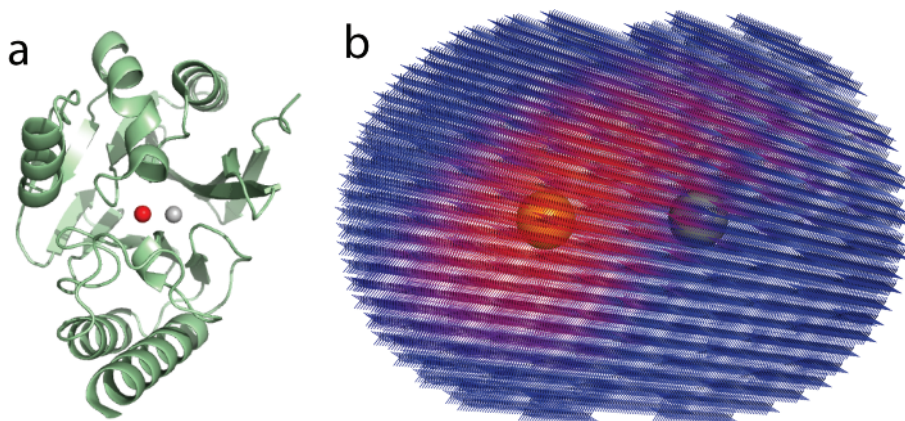
In recent years, electrochemical research has moved in an interesting direction in which collisions between colloidal nanoparticles and an inert electrode have been used to characterise metal nanoparticles. This avoids the inherent ensemble effect of dropcasted particles and allows access to single nanoparticle electrochemistry. However, the concept of using nanoparticle collisions to direct the growth of materials on the surface of an electrode has yet to be explored. Researchers at the Queensland University of Technology, in collaboration with RMIT University, have now demonstrated that nanoparticle collisions at a glassy carbon electrode, during the electrodeposition of Ag and Au, enables hierarchical Ag dendritic nanostructures, as well as isolated Au metal nanoparticles, to be formed (Pearson A., O'Mullane A.P., *Chem. Commun.* 2015, doi: 10.1039/c4cc09614b). The morphology is highly dependent on the electrostatic interaction between the surface charge on the nanoparticle and metal salt in solution and leads to structures with interesting electrocatalytic properties, as well as providing insights into the behaviour of nanomaterials in highly charged media.



A new way of locating Fe^{III} in proteins by NMR

High-spin Fe^{III} has a d₅ electron configuration, like Mn^{II}, and thus seems unlikely to produce pseudocontact shifts (PCS) in NMR spectra. But, as Australian National University PhD student Tom Carruthers has shown for the first time, it does (Carruthers T.J., Carr P.D., Loh C.-T., Jackson C.J., Otting G. *Angew. Chem. Int. Ed.* 2014, **53**, 14269–72)! The PCSs are very small but

detectable, if a diamagnetic reference sample is prepared with Ga^{III}. The PCSs allowed identification of the Fe^{III} site in the 25 kDa dinuclear metallo-β-lactamase (MβL) IMP-1, and agreed with anomalous X-ray scattering results obtained in the same project from a single crystal. IMP-1 is the first MβL shown to form an [FeZn] active site under natural conditions.

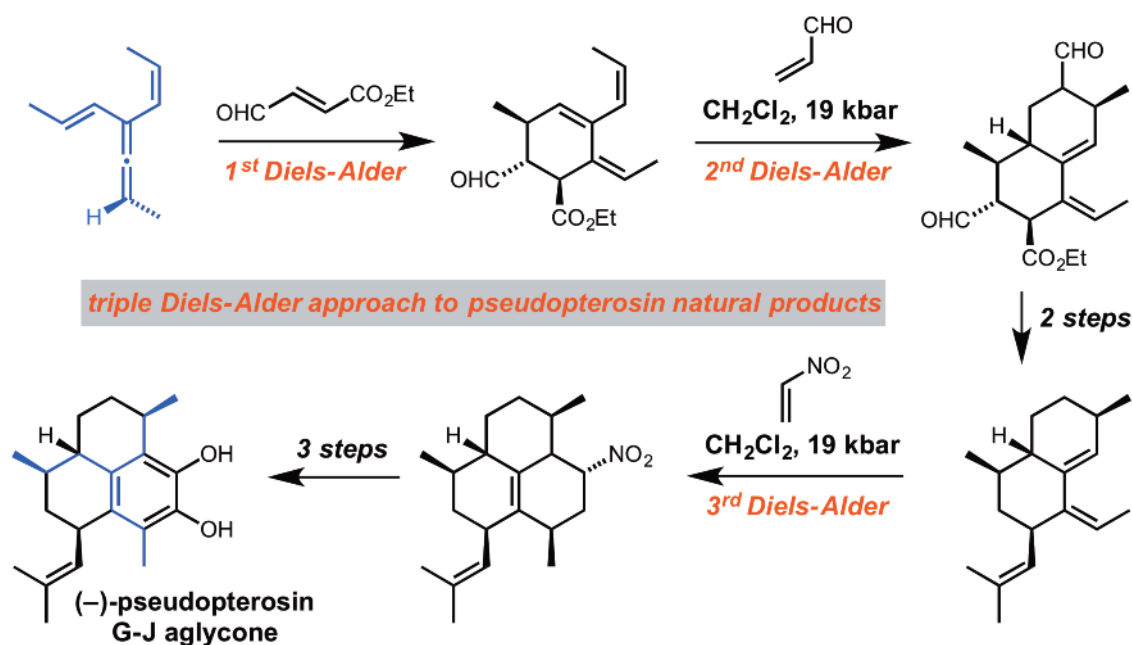


PCSs identify the Fe^{III} site in IMP-1. (a) Protein structure with the two metal ions as red and grey spheres. (b) A grid search highlights the Fe^{III} site as the site that best explains the experimental PCSs.

Allene and mean pseudopterosin synthesis

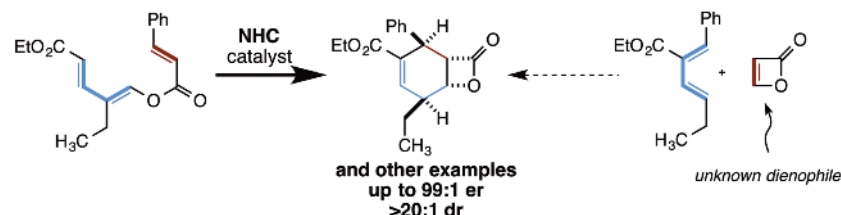
The pseudopterosins are a family of amphilectane diterpene natural products produced in minute quantities by a rare species of coral off the coast of the Bahamas. Bearing synthetically challenging tricyclic frameworks and exhibiting a range of biological activities (anticancer, antimalarial and anti-inflammatory properties), the pseudopterosins have inspired a large body of synthetic work. An Australian team has now prepared the pseudopterosins in an unconventional manner, starting with a chiral cross-conjugated hydrocarbon and

resulting in a significantly shorter synthesis (Newton C.G., Drew S.L., Lawrence A.L., Willis A.C., Paddon-Row M.N., Sherburn M.S. *Nat. Chem.* 2015, **7**, 82–6). Guided by computational studies by Professor Mike Paddon-Row, Scientia Professor Emeritus of Chemistry at the University of New South Wales, the Australian National University's Professor Mick Sherburn and PhD students Chris Newton and Sam Drew used a sequence of three Diels–Alder reactions to construct pseudopterosin G–J aglycone in only 10 steps.



Enantioenriched cyclohexenes by *N*-heterocyclic carbene catalysis

(4 + 2) Annulations, often considered synonymous with Diels–Alder reactions, are integral to the synthesis of many complex cyclic structures. A program of study within the Lupton group at Monash University is focused on the development of novel all-carbon (4 + 2) annulations. This research has recently culminated in a highly enantio-, diastereo- and chemo-selective cycloisomerisation of trienyl esters to yield cyclohexenyl β -lactones, materials inaccessible by the Diels–Alder reaction. Central to realising this transformation was the application of stabilised dienols which, under Curtin–

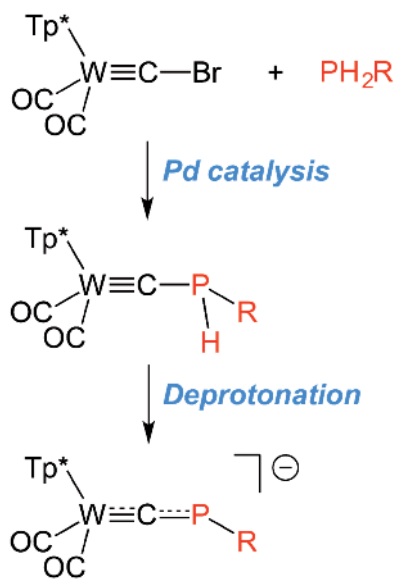


Hammett control, react in a highly enantioselective (up to 99:1 er) and diastereoselective (up to >20:1 dr) stepwise annulation catalysed by electron-rich triazolylidene *N*-heterocyclic carbenes (Candish L., Levens A., Lupton

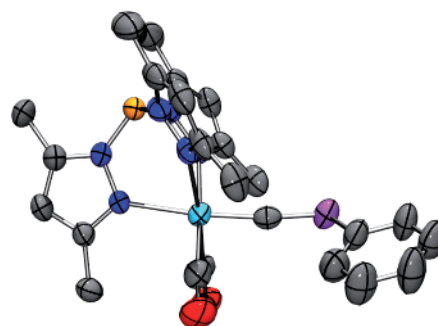
D.W. J. Am. Chem. Soc. 2014, **136**, 14397–400). The generality of the reaction is considerable, allowing 15 cyclohexenyl β -lactones, each bearing 4-contiguous stereocentres, to be prepared with excellent selectivity.

The first terminal phosphaisocyanides

For almost 160 years, isocyanides ($\text{C}\equiv\text{N}-\text{R}$) have been commonly encountered either as free molecules or as ligands that are isoelectronic with the more familiar CO. In contrast, their heavier group 15 phosphorus analogues $\text{C}\equiv\text{P}-\text{R}$ have been long sought but, until now, remained unknown because of a lack of viable synthetic strategies and a propensity to rearrange to phosphalkynes $\text{P}\equiv\text{C}-\text{R}$. Researchers at the Australian National University have recently developed a new synthetic method that has enabled preparation of the first examples of terminal phosphaisocyanide complexes (Colebatch A.L., Hill A.F. *J. Am. Chem. Soc.* 2014, **136**, 17442–5). Palladium-catalysed phosphination of the bromocarbyne complex $[\text{W}(\equiv\text{CBr})(\text{CO})_2(\text{Tp}^*)]$ ($\text{Tp}^* =$



hydrotris(3,5-dimethylpyrazolyl)borate) with primary phosphines affords the first examples of terminal secondary phosphinocarbyne complexes

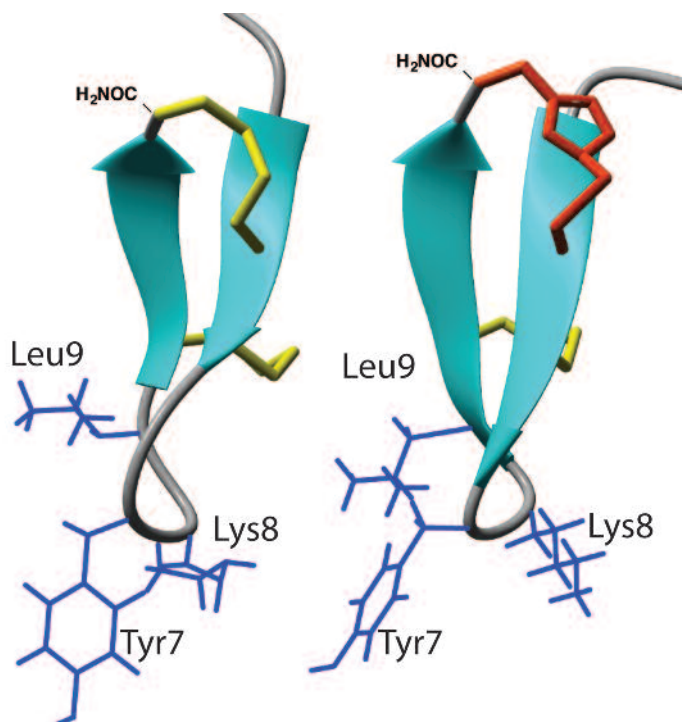


$[\text{W}(\equiv\text{C-PH(R)R})(\text{CO})_2(\text{Tp}^*)]$. These species can be deprotonated using potassium hydride to yield phosphaisocyanide salts $\text{K}[\text{W}(\text{CPR})(\text{CO})_2(\text{Tp}^*)]$. Both spectroscopic and crystallographic data indicate that there is significant charge localisation at both the tungsten and phosphorus centres, as evidenced by the elongated W–C bond and contracted C–P bond in comparison to the precursor $[\text{W}(\equiv\text{C-PH(R)R})(\text{CO})_2(\text{Tp}^*)]$.

Click go the conotoxins

An Australian team has addressed the complications of both disulfide bond folding and scrambling in the synthesis of small cysteine-rich peptides called χ -conotoxins, which target noradrenaline transporters and have shown considerable promise in treating chronic neuropathic pain. Though small, these peptides present folding challenges and are often susceptible to S–S scrambling in the presence of thiols. The University of Queensland's Professor Paul Alewood and Dr Andreas Brust have now overcome these issues by replacing a single disulfide bond with a 1,2,3-triazole, using simple 'click' chemistry to give a structurally and functionally equivalent peptide mimetic (Gori A., Wang C.-I.A., Harvey P.J., Rosengren K.J., Bhola R.F., Gelmi M.L., Longhi R., Christie M.J., Lewis R.J., Alewood P.F., Brust A. *Angew. Chem. Int. Ed.* 2015, **54**, 1361–4). This chemical approach is broadly applicable and should lead to new drug candidates with improved stability.

Ribbon representation of the lowest energy structure of 1,2,3-triazole analogue (right) and parent peptide MrlA (left). The cyan arrows represent the β -hairpin between residues 3 and 12, disulfide bonds are shown in yellow, and the triazole bridge is shown in orange.



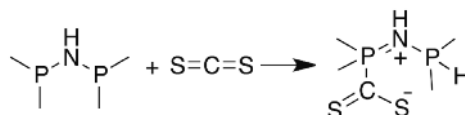
Compiled by **Matthew Piggott** MRACI CChem (matthew.piggott@uwa.edu.au). This section showcases the very best research carried out primarily in Australia. RACI members whose recent work has been published in high impact journals (e.g. *Nature*, *J. Am. Chem. Soc.*, *Angew. Chem. Int. Ed.*) are encouraged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

Aust J Chem

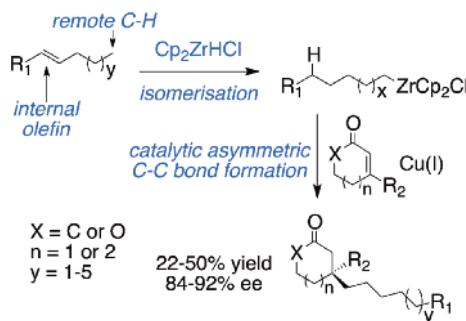
The March issue contains a series of papers in memory of Professor Richard Francis Langer, who died on 3 February 2014 in Nova Scotia. Richard Langer was a Canadian chemist, who chose *Aust. J. Chem.* as one of his favourite journals, in which he published a very substantial number of papers on organic, organometallic and theoretical chemistry in recent years.

The collection of papers is organised by his former student Stephanie MacQuarrie (Cape Breton University, Canada), who reports on the stabilisation and improved catalysis of the enzyme phenylalanine ammonium lyase. A former student, Christopher Graves from Albright College, and co-workers synthesised and characterised several aluminum-amidate complexes and further demonstrated that the complexes were pre-catalysts for both the MPV reduction of carbonyls and the Oppenauer oxidation of alcohols.

Diane A. Dickie (University of New Mexico) and her colleagues describe a synthesis of the brick-red, air- and moisture-sensitive, zwitterionic adducts of CS₂ and bis(dialkylphosphino)amines. These zwitterions are characterised by X-ray crystallography.

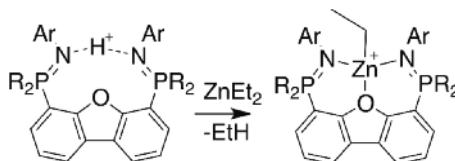


Catalytic asymmetric C–C bond-forming cyclisation of the terminal CH function of an internal olefin through a chain-walking isomerisation mechanism is reported by Stephen P. Fletcher et al. (Oxford). Hydrometallation of internal olefins with the Schwartz reagent gives the least hindered alkyl-zirconocene after thermal isomerisation. This was then used in copper-catalysed asymmetric conjugate additions to a variety of cyclic α,β -unsaturated species, which were achieved with modest yields of 22–50% but with high enantioselectivity (84–92% ee).

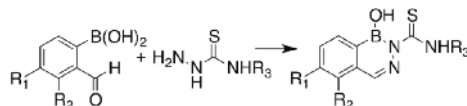


Stacey Wetmore and co-workers report on the characterisation and analysis of the interactions between the side chains of Ser and Cys and DNA or protein π -rings.

Paul Hayes et al. (University of Lethbridge, Canada) describe the synthesis and characterisation of several sterically hindered bis(phosphinimine) dibenzofuran ligands followed by zinc metallation.



Steve Westcott et al. report the synthesis, characterisation and antifungal activity of new fluoro- and methoxy-substituted benzodiazaborines.



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

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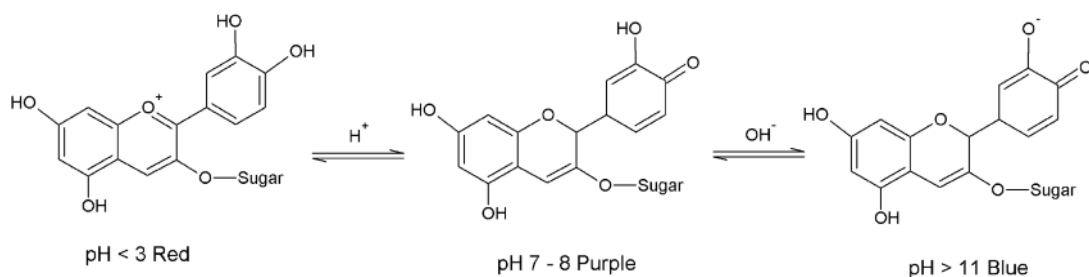
A spectrum of seasonal change

Colin Scholes
appreciates the light
and energy of colour
in autumn leaves.

The changing colour of tree leaves is one of the surest signs in nature that autumn has arrived and winter is on the way. What most people don't realise is the interesting organic chemistry and spectroscopy going on within those leaves to provide autumn's visual display.

As most of us know, the green colour of leaves is caused by chlorophyll, and in particular chlorophyll a. Chlorophyll converts light into chemical energy through photosynthesis, and strongly absorbs light in the blue and red regions of the electromagnetic spectrum. Hence, the amount of red and blue light being reflected is diminished, and we perceive tree leaves as being green. Chlorophyll is not a stable compound – sunlight causes decomposition over time – and so trees are continually breaking down and synthesising new chlorophyll to maintain desired levels within the leaves.

During autumn, deciduous trees respond to decreasing sunlight and cooler temperatures by curtailing their chlorophyll production. This process, senescence, comes about for two reasons. In temperate regions, decreasing sunlight means the chlorophyll in a leaf is generating less energy and there comes a point for



Anthocyanin states as a function of pH.

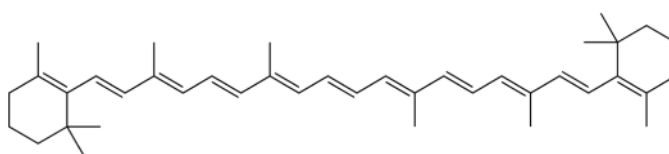
many deciduous trees, especially those that are broad leaf, where maintaining the leaf requires more energy than the leaf produces. Also, in many temperate regions the ground freezes during winter, cutting off the tree's water source. By shedding leaves, trees are able to minimise their water loss, enabling them to survive until spring.

The gradual loss of chlorophyll during autumn allows other leaf pigments to begin to be observed; the major groups are carotenoids, flavonoids and anthocyanins. The first two compounds are always present within leaves, but their colour is masked by chlorophyll and so we only perceive them as autumn progresses (see box p. 17). All of these pigments have large amounts of conjugation (alternating double and single bonds) within their molecular structure, which allows them to absorb wavelengths in the visible spectrum, and hence provide leaves with colour.

α -Carotene, a major carotenoid present in most leaves, absorbs light in the blue and green region. So light reflected from α -carotene is perceived as yellow. This compound accounts for much of the yellow foliage generated during autumn. Carotene in leaves is an accessory absorber, with light energy absorbed by carotene transferred to chlorophyll for photosynthesis. Carotene is much more stable than chlorophyll, and so it persists within the leaf as chlorophyll disappears – hence the gradual change from green to yellow. β -Carotene, another carotenoid common in certain trees, is



Brilliant golden yellows of an Aspen autumn.



β -Carotene structure, showing the conjugation.

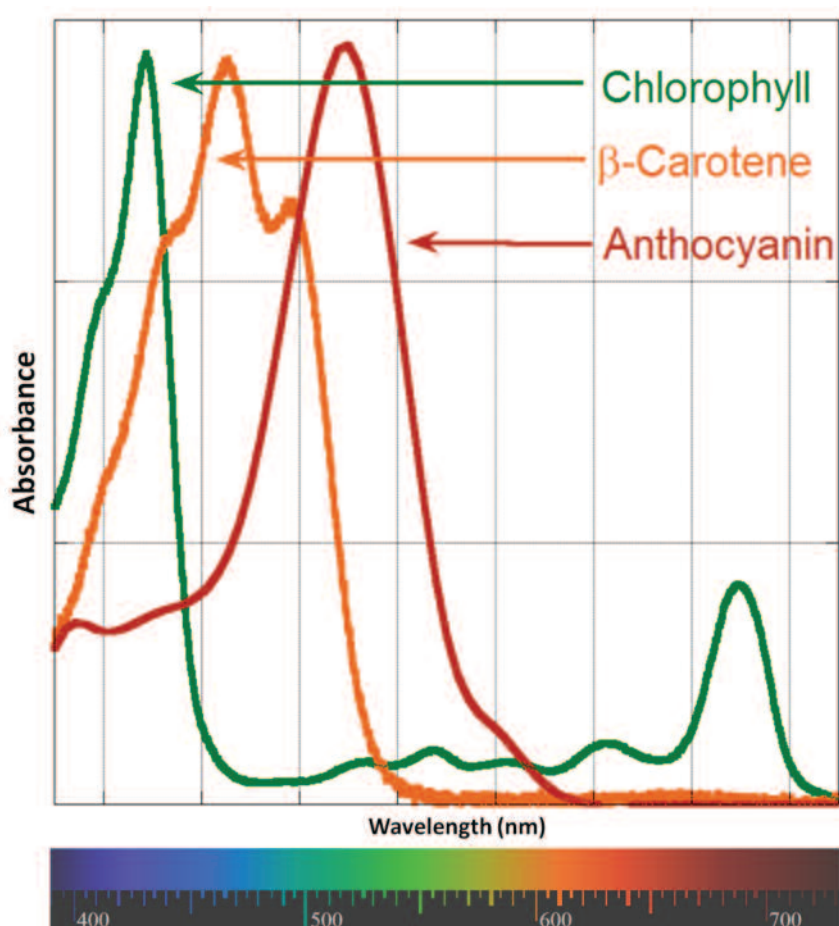
responsible for the orange colour of autumn. It is one of the most stable carotenoids and so it persists far longer in the dying leaf than other carotenoids. It is for this reason that the autumn leaves of some trees progress from green to yellow through to orange, as chlorophyll degrades and leaves β -carotene behind.

Other common carotenoids in autumn leaves are lycopene and xanthophylls. The combination of these gives the golden colour of Aspen, Colorado's, autumn leaves.

Flavonoids within plants have a variety of functions: in leaves they

reduce damage from UV light, acting as a sunscreen, and are the most important pigments in flowers and fruits. Flavonoids are based on a conjugated diphenylpropene moiety, which causes them to absorb light in the visible spectrum, and hence be coloured. The two most common





Absorbance spectra of chlorophyll, β -carotene and anthocyanin.

The two most common flavonoids in leaves are flavone and flavol, which absorb in the blue-green region of the visible spectrum and thus provide a yellow colour to autumn leaves.

flavonoids in leaves are flavone and flavol, which absorb in the blue-green region of the visible spectrum and thus provide a yellow colour to autumn leaves.

The third class of pigment, anthocyanins, is a derivative of flavonoids and is not present within leaves all year round. Anthocyanins absorb light in the blue-green region, and leaves with significant amounts of anthocyanins are perceived as being different shades of red, purple and even blue. This is because the chemistry of anthocyanins is much more complex than for other flavonoids and carotenoids, due to the presence of the sugar bonded to a diphenylpropene moiety. Hence, the amount of carbohydrates present alters the absorption spectrum and corresponding colour of anthocyanin.

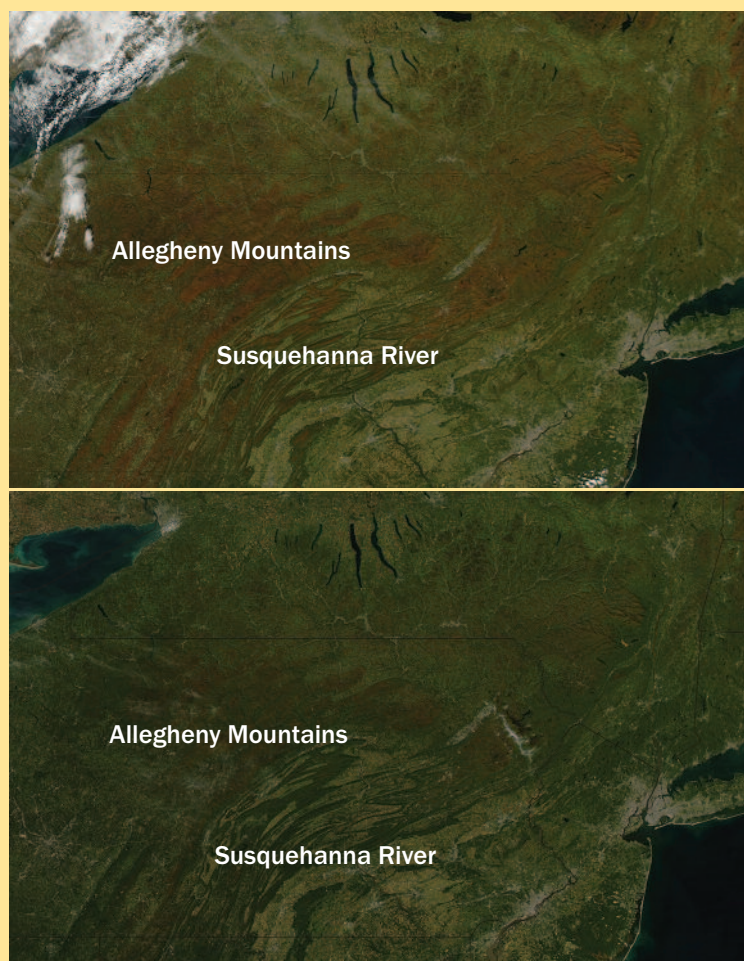
Equally important in terms of colour, anthocyanins are amphoteric, meaning they have acid-base characteristics, which has a strong impact on their absorption spectra and hence colour. In highly acidic environments, anthocyanins produce bright red colours, while in more basic environments the colour shifts to magenta, purple and, at very high pH, blue.

The acidity in the leaves is strongly associated with soil acidity. This is why the one species of tree will produce leaves of the same colour hue in similar locations, but different colour hue in another location. The best example of this is maples. This vivid colour range of anthocyanins is also responsible for the red in apple skins, the purples of grapes and the blue in blueberries, as they are also present in fruit skins.

Anthocyanins are generally only produced within a leaf towards the end of its life. As the plant blocks the flow of water and nutrients through the leaf's stem, the sugars being produced within the leaf become trapped and their concentration increases. As a result, the anthocyanin flavonoid precursor and sugar react. This reaction requires light to initiate as is evident by the most vivid displays of autumn leaves usually only being obtained after a series of sunny days. The production of anthocyanins are believed to have a role in colour masking the yellows of carotenoids and flavonoids in some plants, because insects such as aphids are known to be drawn to leaves with yellow hues.



Capturing colour change from space



Autumn burst upon the northern Allegheny Mountains in Pennsylvania in mid-October 2010. Within a span of just five days, the forests went from green, with a slight hint of autumn colour, to vivid orange.

The Moderate Resolution Imaging Spectroradiometer (MODIS) on NASA's Aqua satellite captured the transformation in this pair of images. The top image is from 13 October, while the lower image is from 8 October.

The annual display of autumn colour peaked during the week of 12 October, making it the optimum time for leaf viewing in northern Pennsylvania, according to the Pennsylvania Bureau of Forestry. Southern regions were just approaching peak colour. The area depicted is primarily mountains and highlands of northern Pennsylvania.

Autumn colour typically peaks in mid-October as leaves gradually lose chlorophyll during the lengthening autumn nights. Chlorophyll colours leaves green, so as the concentration of the pigment fades, so too does the leaves' green colour. Other pigments – carotenoids (yellow, orange and brown) and anthocyanins (red and purple) – can then show their colours.

NASA images courtesy Jeff Schmaltz, MODIS Rapid Response Team at NASA GSFC. Caption by Holli Riebeek. References available at <http://1.usa.gov/1yx9EsJ>.

The browner tones of some deciduous tree leaves are due to high levels of tannins, which are complex stable macromolecules with a range of properties, including pesticidal. Oak autumn leaves are an example of the combination of tannins and anthocyanins producing the distinct brown to red pallet.

The large size and stability of tannins means their chemical breakdown and decomposition is very slow; therefore, they are the last colour pigment to remain in a leaf. Most leaves rapidly lose their vivid colours within a few days of falling and become brown because of the presence of residual tannins. A range of other minor pigment compounds specific to each tree species also contribute to the colour hue observed during autumn, and the rate of chemical degradation influences the leaf's colour change.

So as autumn continues, enjoy the chemistry that goes into making the spectacular colour display.

Colin A. Scholes FRACI CChem is a lecturer in the Department of Chemical and Biomolecular Engineering at the University of Melbourne.

Underwater insights from wrecks of war

The devastation of a World War II naval operation marked the beginning of an in-situ corrosion experiment.

BY IAN MACLEOD

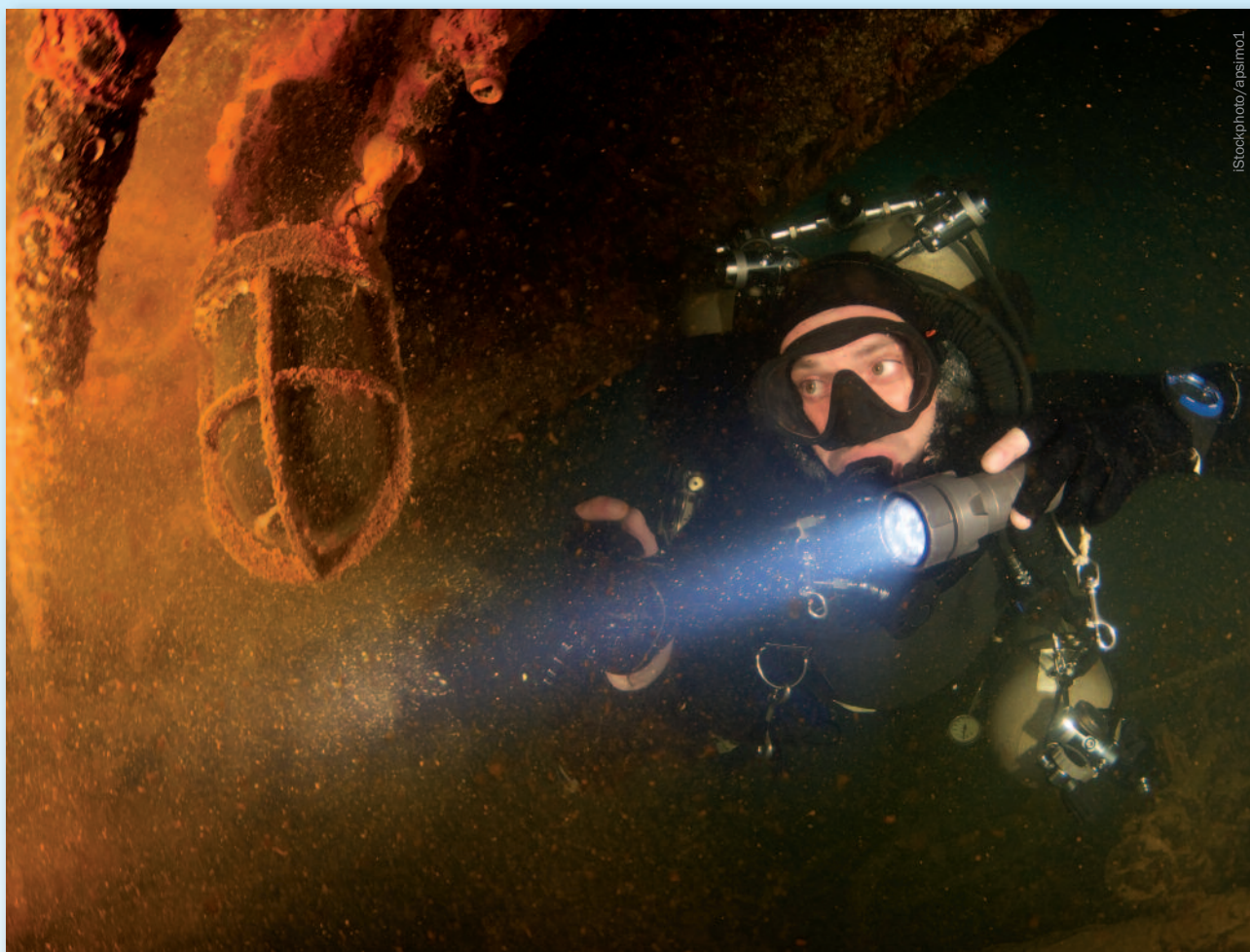
The effects of the US Navy-carrier-borne Operation Hailstone against the Imperial Japanese Navy in February 1944 were devastating for the Japanese fleet in Chuuk Lagoon (also known as Truk Lagoon), Federated States of Micronesia. Although many of the large naval vessels had beat a retreat before the massive bombing raids, more than 65 ships were wrecked and more than 250 aircraft sunk. This devastation saw the initiation of a wonderful corrosion experiment with the wrecks placed at different depths and orientations on the seabed. Five sets of measurements recorded between 2002 and 2008 enabled development of a new understanding of what controls corrosion of iron shipwrecks.

Corrosion processes on tropical iron wrecks

After an iron ship sinks, seawater gradually penetrates its protective coatings. This increases the underlying corrosion rate until marine organisms have colonised the wreck. The marine growth provides a barrier between the oxidising medium, dissolved oxygen, and the underlying metal, separating the anodic (metal oxidation) and cathodic reactions (oxygen reduction) of the corrosion cell. Chloride ion levels increase with the concentration of Fe^{2+} corrosion products, up to three times the levels found in normal seawater. Hydrolysis of the primary corrosion product FeCl_2 under the concretion results in a range of iron corrosion products that contain mixtures of oxides, hydroxides and

chlorides as well as iron carbonates. Thus, the acidity recorded underneath the concretion layer, penetrated by a compressed-air-driven drill, is controlled by the corrosion rate. A combination of in-situ pH, corrosion potential (E_{corr}) and measurements on the combined thickness of the corrosion products and marine growth provide measures of the localised corrosion rate.

The bio-availabilities of iron and phosphorus are key factors in controlling the thickness of the marine growth, and higher corrosion rates provide more iron to the local microenvironment. Anaerobic bacteria under the protective concretion blanket convert iron phosphide (Fe_3P) present in cast iron into volatile phosphines, which are growth



iStockphoto/apsimo1

A diver explores the engine room of the *Fujikawa Maru* wreck in Chuuk Lagoon.

stimulants. When vessels have been subjected to periodic 'dynamite fishing' from exploding (recovered) munitions, differences in concretion thickness on horizontal and vertical surfaces are perhaps more of a measure of the movement of shock waves than a reflection of differences in composition of the underlying alloys. Suddenly exposed corroded iron undergoes accelerated corrosion and results in premature disintegration of the wreck. Areas of the armed merchant vessel *Fujikawa Maru* showed five concretion terraces, which is consistent with multiple episodes of concretion shedding followed by regrowth. Comparisons with an 'undiscovered' wreck from the same period showed that repeated bombings of the *Fujikawa Maru* have

increased the overall corrosion by 46%. Since the corrosion rate is controlled by the flux of dissolved oxygen over the concreted surface, objects at the same depth with a higher surface profile will decay more rapidly than flat objects such as hatch covers or deck plates.

Corrosion profiles of cast iron structures on the wrecks provide a cumulative index of the annual corrosion rate. Such profiles are measured after removal of an area of concretion and drilling with a metal drill-bit into the corroded matrix and recording the depth of the hole with a micrometer. The corrosion rate in mm/year (d_y), or depth of graphitisation, is averaged by dividing the depth of corrosion by the age of the wreck. Each wreck can be

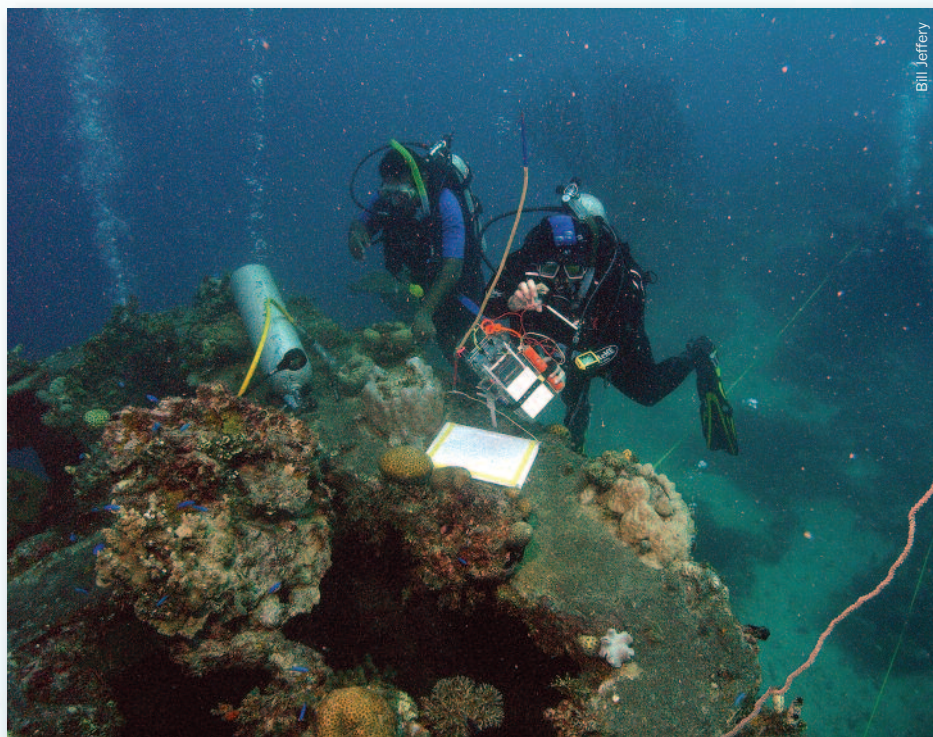
Comparisons with an 'undiscovered' wreck from the same period showed that repeated bombings of the *Fujikawa Maru* have increased the overall corrosion by 46%.



Bill Jeffery

Holes in deck plates of the *Fujikawa Maru* due to accelerated corrosion from 'dynamite fishing'.

Sunny starboard side with extensive marine growth on the *Suzuki* patrol boat.



Bill Jeffery

The orientation of the wreck site, in terms of proximity to islands, channels ... has a major impact on the corrosion rate.

characterised by a site-specific corrosion equation of the form:

$$\log d_y = a E_{\text{corr}} + b$$

The dependence of the corrosion rate on the corrosion potential (a) is controlled by the amount of dissolved oxygen, which in turn is interdependent on the salinity and the water temperature. The values of a are determined by the empirically derived formula:

$$a = 10.33 \log [\text{O}_2] - 4.57$$

where the concentration of oxygen is recorded in $\text{cm}^3 \text{dm}^{-3}$. The constant b is determined through solving a series of simultaneous equations associated with E_{corr} and depths of graphitisation measurements on a series of cast iron objects on the same wreck site.

Calculation of the original thickness of metal is possible from a series of equations using the length, breadth and height of the hull. By subtracting the accumulated corrosion loss, the residual metal thickness of the structures can be calculated.

Experience has shown that when there is less than 3 mm of residual metal, the combined weight of concretion and stresses associated with storm surges lead to collapse of the wrecks.

Corrosion and in-situ pH

Measurements on the *Fujikawa Maru* found that the log of the corrosion rate increased linearly as the pH fell, according to the expression:

$$\text{Fujikawa Maru } \log d_y = 0.758 - 0.26\text{pH}$$

Since both the corrosion rate and the H^+ concentration show logarithmic

dependence on each other, the acidity from hydrolysis is a direct measure of the localised corrosion rate. Increased corrosion results in a higher background concentration of FeCl_2 , greater hydrolysis and a decreased pH. Objects corroding in an identical microenvironment have the same depths of graphitisation, e.g. the port and starboard bollards had 6.5 and 6.6 mm of graphitisation respectively. Higher profile objects such as the deck windlass had a corrosion depth of 8.4 mm, while the base of the forward gun was corroded to a depth of 11.6 mm. Higher profiles catch more current to create a greater flux of dissolved oxygen and so they corrode faster. Plotting E_{corr} and pH data on a Pourbaix diagram showed that the points were connected by straight lines that had a slope of -29.5 mV/pH , which is consistent with the reaction:



It is logical that the increased corrosion rates are associated with a higher acidity level beneath the protective concretion layer.

Studies on the *Suzuki* patrol boat showed that branching and massive corals were dominant on the sunny starboard side of the wreck, while molluscs dominated the darker port side, as the wreck lists to the port side at about 15° . The *Fujikawa Maru* lists in the opposite direction where the average E_{corr} on the sunny port side is 6 mV more anodic than the darker side, which equates to a difference of 4.5% in the corrosion rate. The sunny sides have higher rugosity or surface roughness, which increases turbulence and the flux of dissolved oxygen and so corrosion increases. Measurements of the rugosity of the marine concretions showed a direct dependence between the corrosion potential and the surface profile. Rugosity decreases in response to loss of sunlight at greater depths, which in turn lowers the corrosion rate, but as a second-level effect.

The iron corrosion rate rapidly falls with increasing depth as most water movement comes from wind chop. The *Fujikawa Maru*, *Suzuki* and *Shinkoku Maru*, which have been subjected to repeated dynamite fishing attacks, showed less sensitivity of the rugosity on depth than the undamaged parts of the *Suzuki*, the Tonoas dock boat and the so-called Yamamoto gun boat, as there had been insufficient time for the full regrowth of the colonies of marine organisms.

Data from all the wrecks shows that for the first 20 metres, there is a logarithmic drop in the corrosion rate (mm/year) with increasing water depth as shown here:

$$\log d_g = -0.732 - 0.018d$$

where d is the average water depth of the measurements. Wrecks in the open ocean have essentially the same dependence on depth but the intercept value at -0.630 is 102 mV more anodic, which equates to 26.5% faster corrosion due to increased wave action. Owing to reduced



Biological diversity of a pristine wreck at the Tonoas dock boat site.

wave action at depths between 21 and 38 metres, the corrosion rate of the deeper lagoon wrecks are 3.5 times less sensitive to depth. Shallower wrecks are the ones most at risk of leaking oil from their fuel bunkers and they should be targeted with ameliorative measures, such as the application of sacrificial anodes on the fuel tanks.

The orientation of the wreck site, in terms of proximity to islands, channels etc., has a major impact on the corrosion rate. The *Gosei Maru*, which lies on its port side at depths between 4 and 37 metres in the lee of a nearby island, has corrosion rates 36% lower than expected for the depth. The stress on the upside-down *Yubae Maru*, at a depth of 28 metres, makes it corrode 60% faster than expected. Large numbers of hull plates are scattered across the site as rivets have given way under stress loads that were never engineered into the structure.


The capacity to discern the nature of the variables that control the deterioration of historic shipwrecks can only be developed by a team approach, as there are so many variables to consider. Engagement with marine biologists, maritime archaeologists, diving tourism operators and local heritage managers is essential. Awareness of the cultural sensitivities associated with shipwreck graves is also a vital element in getting things right.

Acknowledgements

Special thanks to Bill Jeffery, Maria Beger, Vicki Richards and the volunteers from the Earthwatch Institute and staff of the Heritage Protection Office in Moen.

Ian D. MacLeod FRACI CChem is Executive Director, Fremantle Museums & Maritime Heritage, Western Australian Maritime Museum, Fremantle, Western Australia.

See the September 2014 issue of *Chemistry in Australia* (p. 16) to find out more about underwater cultural heritage conservation relating to these and other shipwrecks.



Fundamentals of the fourth state

Quiet corona and upper transition region of the sun. This image, taken on 31 December 2013 by the AIA instrument on NASA's Solar Dynamics Observatory at 171 Å, shows the current conditions of the quiet corona and upper transition region of the Sun.

NASA/SDO

Tiny particles do extraordinary things at incredible temperatures, discovers **DAVE SAMMUT** as he looks on the sunny side.

Most of us will encounter only three states of matter: solid, liquid and gas. We know the chemistry and behaviours in these states quite intimately. But the sun offers us a look at the fourth state – plasma – and matter(s) get interesting.

Being a complete novice in this area, I've been reading. Particular among these, Golub and Pasachoff have produced a readily accessible work in *Nearest star: the surprising science of our sun* (Cambridge University Press, 2014).

Let's start at the corona. What an astounding region this is. So very hot that the temperature can only be estimated spectrally, at something around one million kelvin. So dilute that on average it is barely more than vacuum, yet it is subject to movements of vast quantities of matter, all of which twists and turns at enormous velocities under the influence of unimaginable magnetic fields.

At coronal temperatures, the energy of its matter is so great that a portion of it is able to escape the sun's gravity as a solar wind. Each second, the sun ejects approximately 1.5 million tonnes of matter and emits 3.8×10^{20} MJ of energy into space, vastly more energy in a second than is produced in all of the world's power plants in a year.

The corona is so hot that the photons are shifted mostly beyond the visible spectrum into the violet, ultraviolet and higher-energy short-wavelength regions. The earliest studies of coronal spectra were actually misled by these extraordinary

energy conditions. While the 'D3' line, first seen in 1868, was correctly used to identify the new light element helium (named for *Helios*, the sun, and in 1895 identified in uranium materials on Earth), a strong green coronal emission line was attributed to a new element called 'coronium' in 1869.

Due to its presence in the corona, it was assumed that coronium must be lighter than hydrogen. But this was a problem, particularly in light of Mendeleev's breakthrough work on the periodic table of the elements. It wasn't until 1939 that spectrologists Bengt Edlen and Ira Bowen at Caltech and Walter Grotrian in Potsdam, Germany, correlated the green coronium emission to spark discharge spectra in Grotrian's laboratory, and it was found to be Fe^{XIII} . That's 13 lost electrons of only 26.

Strangely, the corona is two to three orders of magnitude hotter than the surface of the sun itself, which is 'only' 6000 K (calculated by taking the total power emitted by the sun and dividing by its surface area). Yet we aren't sure why this should be. Why would it be cooler in closer, and why does the temperature spike so rapidly with distance? One of many theories is that magnetism carries energy from the inner layers of the sun directly to the corona, but there is as yet no agreement on the topic and it remains a key mystery.

But how do we even define the surface of the sun? It is a ball of gas, yet it appears to the naked eye to have a distinct edge. Here's two fascinating facts: first, light is being constantly emitted, adsorbed and re-emitted at

At coronal temperatures, the energy of its matter is so great that a portion of it is able to escape the sun's gravity as a solar wind.

every level of the sun from the surface to the core, everywhere that nuclear fusion is taking place. Yet with the constant adsorption and re-emission, it takes light produced at the core 100 000 years to reach the surface.

Second, the sun's gas is itself opaque. Measuring 'opacity' (effectively the opposite of transparency) on a logarithmic scale, zero is completely transparent while we can see only murkily at 1, and by 5 a gas is completely opaque. Most of the light that we see from the sun is from a level at which the opacity is 0.67, and that is the point that we generally use to define the surface of the sun. Although the photosphere is several thousand kilometres thick, from our distance* that thickness yields less than a minute of arc, much too small to be resolved by the human eye.

*Approximately 150 million kilometres, give or take, with a nod to 400 years of researchers who worked hard to determine that particular datum, including Captain James Cook.

The truly unique aspect of a star is fusion itself – the forge of the elements. Chemist Carolyn Ruth put it pretty succinctly for the American Chemical Society in *ChemMatters* (October 2009, pp. 6–8): ‘In stars less massive than the sun, the reaction converting hydrogen into helium is the only one that takes place. In stars more massive than the sun but less massive than about eight solar masses, further reactions that convert helium to carbon and oxygen take place in successive stages before such stars explode. Only in very massive stars (that are more massive than eight solar masses), the

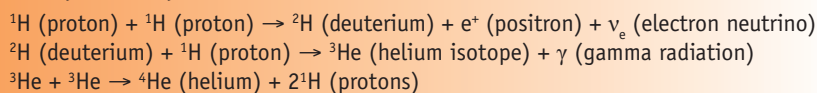
chain reaction continues to produce elements up to iron.’

Different stars go through different fusion processes. Stars like our own undergo the proton–proton chain described below, while more massive stars undergo the C–N–O (carbon–nitrogen–oxygen) process, which is a multistep cycle starting and finishing with carbon, also transforming

hydrogen to helium. Mature stars rich in helium undergo helium fusion by the triple-alpha process, via beryllium to carbon.

That gets us just one element up the periodic table. The reactions just keep getting more complex and layered, and although the detail is way too much for this article, it is absolutely fascinating.

The proton–proton chain



Ocean floor dust gives new insight into supernovae

Scientists plumbing the depths of the ocean have made a surprise finding that could change the way we understand supernovae, exploding stars way beyond our solar system.

They have analysed extraterrestrial dust thought to be from supernovae, which has settled on ocean floors, to determine the amount of heavy elements created by the massive explosions.

‘Small amounts of debris from these distant explosions fall on the Earth as it travels through the galaxy,’ said lead researcher Dr Anton Wallner, from the Research School of Physics and Engineering at the Australian National University.

‘We’ve analysed galactic dust from the last 25 million years that has settled on the ocean and found there is much less of the heavy elements such as plutonium and uranium than we expected.’

The findings are at odds with current theories of supernovae, in which some of the materials essential for human life, such as iron, potassium and iodine are created and distributed throughout space.

Supernovae also create lead, silver and gold, and heavier radioactive elements such as uranium and plutonium.

Wallner’s team studied plutonium-244, which serves as a radioactive clock by the nature of its radioactive decay, with a half-life of 81 million years.

‘Any plutonium-244 that existed when the Earth formed from intergalactic gas and dust over four billion years ago has long since decayed,’ Wallner said.

‘So any plutonium-244 that we find on Earth must have been created in explosive events that have occurred more recently, in the last few hundred million years.’

The team analysed a 10-centimetre thick sample of the Earth’s crust, representing 25 million years of accretion, as well as deep-sea sediments collected from a very stable area at the bottom of the Pacific Ocean.

‘We found 100 times less plutonium-244 than we expected,’ Wallner said.

‘It seems that these heaviest elements may not be formed in standard supernovae after all. It may require rarer and more explosive events such as the merging of two neutron stars to make them.’

The fact that heavy elements such as plutonium were present, and uranium and thorium are still present on Earth, suggests that such an explosive event must have happened close to the Earth around the time it formed, said Wallner.

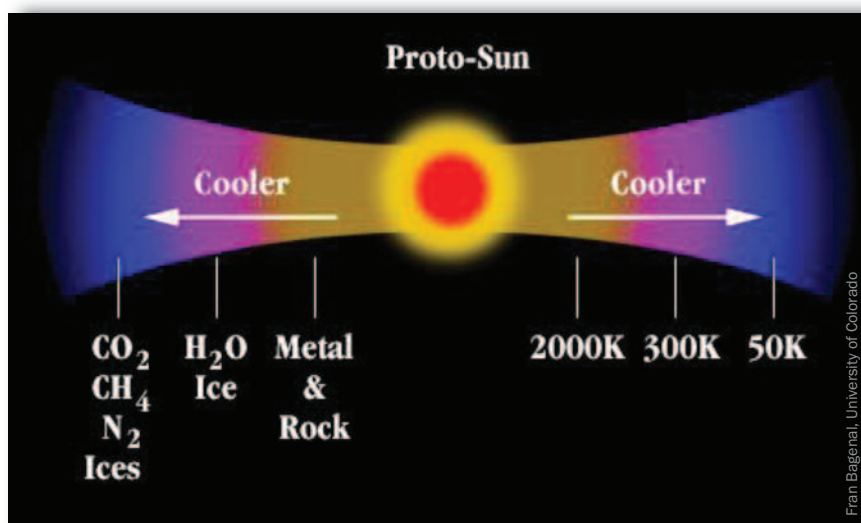
‘Radioactive elements in our planet such as uranium and thorium provide much of the heat that drives continental movement; perhaps other planets don’t have the same heat engine inside them,’ he said.

The research is published in *Nature Communications*.
AUSTRALIAN NATIONAL UNIVERSITY

The Crab Nebula is a supernova remnant in the constellation Taurus.

iStockphoto/Mantfred_Konrad

Neutron by neutron, elements larger than helium are created within these stars and flung off into the empty vastness of ever-increasing space, slowly or with cataclysmic force.



Separation of refractory and non-refractory materials during formation of our solar system (Laboratory for Atmospheric and Space Physics, University of Colorado Boulder, <http://lasp.colorado.edu/home>).

Fran Bagenal, University of Colorado

Here's where I leave the dry commentary. I cannot say how inspired I am to think that the substances that we work with every day as chemists, the very materials of our own bodies and minds, are quite literally stardust.

From the infernal maelstrom of the Big Bang, in a matter of just minutes, are born the hydrogen and helium isotopes that underlie our entire universe. Some 100–300 million years later, in these roiling clouds, massive, fast-burning stars form, ejecting huge quantities of matter into space before exploding spectacularly. Over literally billions of years, generations of stars are born in galaxies in the densest areas of the ever-expanding, churning clouds of matter. Neutron by neutron, elements larger than helium are created within these stars and flung off into the empty vastness of ever-increasing space, slowly or with cataclysmic force.

And somewhere, in some far-flung and remote cloud of matter, a ripple passes. Pushed together, gravity takes hold of the particles and a new system begins to form. As the cloud of hydrogen, helium, various molecules and dust contracts, it spins faster, conserving angular momentum. The various elements and compounds

separate – lighter materials such as water, methane, carbon monoxide and nitrogen on the outer, heavier elements towards the centre. In the hot, dense bulb at the centre, a proto-sun flares.

Critically, our own planet forms in one of the sub-ripples. Again, condensation and accretion separate the materials, iron and heavier elements mostly to the proto-Earth's core, lighter silica and alumina outer. Perhaps some of the lighter materials came back to Earth later in the form of planetissimals or comets, and the like.

Of course, the whole process would have been incredibly complex, and our understanding is still limited. But that's not the point. The point is that by whatever variation in the mechanisms of formation, our planet came together from the various material of the stars.

Whether chemically formed or falling in from space, the various chemicals of life collected on this one little planet – methane, ammonia, carbon dioxide and more. Warmed by a sun to temperatures between freezing and boiling, at some point life began.

So here we are, each of us part of a global effort to advance our knowledge of the universe and our

place within it. Daily, we work in theory and practice with physical materials born uncountable millennia ago, each day in the hope of making our world a better place to exist. And daily, whether shining directly or clouded by a bit of water vapour, our sun continues its inexorable processes. How can we feel anything but optimistic?

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



iStockphoto/Kamruzzaman Ratan

Postgrad check-up

In late 2013,* Caroline Kyi and Michael Leeming were in the throes of postgraduate study at the University of Melbourne. We've asked them what they're up to now.

Caroline

I finally submitted my thesis on 5 December 2014. Others had informed me that this would be an anticlimax after the whole chaotic experience of candidature. Personally, I found the actual submission of the thesis a welcome experience. Evidence of the celebratory tone of the event was provided by the congratulatory balloon, offered by the staff at Examinations Office – pink of course, chosen by my four-year old daughter. The rest of the day was spent mentally unwinding, feeling calm and walking around with a big smile on my face.

The last 18 months have been very busy. In October–November 2013, I was given the opportunity to present posters at two international conferences – the Conference for Cultural Heritage Conservation Science and Sustainable Development (Paris) and Monitoring Conservation Management: Built Heritage (Milan) – and work with colleagues from the Courtauld Institute of Art, University of London, and the Department of Food, Environmental and Nutritional Sciences, University of Milan. Financial support for these endeavours was kindly provided by the ARC Centre of Excellence for Free Radical Chemistry and Biotechnology as well as through the Bio21 Student Travel Award Scheme. This time spent overseas provided the opportunity to exchange research ideas and gain a sense of how my research was placed within an art conservation context.

In March 2014, I was fortunate enough to be invited to work in a conservation project at the Nagaur Fort, Rajasthan, India. More recently, through funding provided by a Staff Engagement Grant (University of Melbourne), I have been working with community members and students from the Centre for Cultural Materials Conservation (CCMC), at the University of Melbourne, on the conservation of painted mercantile signs in the City of Port Phillip. These experiences have enabled me to maintain practical conservation skills while studying a highly specific aspect of conservation through my thesis research.

The experiences in 2014 and over the period of my candidature have been innumerable and varied. They have reaffirmed my belief in the benefits of working in collaborative and community laboratory environments. They have exposed me to the pros and cons of cross-disciplinary research as well as identifying the opportunities available to me as a working mother and those opportunities that will remain just beyond my reach. I have been required to write like a scientist and think like an art conservator.

Overall, undertaking a PhD has been an immensely rewarding pursuit and I wish to thank the ARC Centre of Excellence for Free Radical Chemistry and Biotechnology and the School of Chemistry, University of Melbourne, for providing me with the opportunity to undertake this research, as well as those



individuals who have supported me in this rather long endeavour.

At present I am working on identifying aspects of my research that can be published. The aim is to finalise a few publications while still effectively in writing mode. Beyond this, seeking roles/opportunities that will continue to enable me to be active in both conservation and the scientific research fields is a broader aim. For the moment I am content to enjoy the sunshine.

Michael

Can I just say that research would be, without a doubt, the greatest job in the world if everything just worked first shot. Actually, I'd even settle for third shot: three tries then you get the result. Easy.

People always talked about the 'second-year blues' for PhD students. I always thought it was a myth ... Nope. For me, it's definitely not motivation that's lacking though. It's more that you're one year in and the novelty has evaporated away but the end is still a long way off. You also have no idea if or how all those disparate results will eventually come together with any semblance of coherence to form your thesis. But your supervisors help and, to be fair, you do think about it virtually every waking moment of the day so a plan slowly develops and eventually it starts to seem achievable.

Fortunately though, I've managed to fit in a lot of things this year that take my mind off it. First, I had the opportunity to go to a conference (and have a holiday) in Switzerland. That was fun. There's definitely nothing like seeing some big name prof covered in sweat on the dance floor at the conference dinner to cast all of their papers in a completely different light. You get back to the office



thinking 'I know you're the editor of that journal we just submitted to, but, man, do I have some photos of you in my Dropbox folder!' Ha! What second-year blues?

I also enrolled in a course called Graduate Certificate in Advanced Learning and Leadership. The title seems a little gaudy but, to describe it in one sentence (which is a criminal undersell), it's a leadership course crossed with an ethics course crossed with a philosophy course. We spent a week at Mt Eliza Business School debating Machiavelli and Plato and Thomas Hobbes as *The Prince* and *The Republic* and *Leviathan* applies to politics as it applies to privacy and identity – which brought us up to lunch on day one.

There's no way I can possibly do it justice here but suffice to say that it was the single most challenging and yet inspiring week of my university career so far. It had me considering concepts that I never thought would see the light of day in my PhD studying drug metabolism.

Back in the lab, I'm nearing the end of my second year and I have a reasonably good idea of what my thesis will look like and what I have to do to get there. Now it's just a matter of reeling off the experiments. If only everything worked first shot.

*Caroline's and Michael's original career profiles were published in the September (p. 30) and October (p. 34) 2013 issues of *Chemistry in Australia*.

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New Fellow



Dave Sammut is a career technologist with degrees in industrial chemistry (BSc Hons) and business (MBT) from the University of New South Wales. He has worked for 20 years in active R&D, R&D corporate management and commercialisation, and in

professional communications to government, investor and non-technical audiences.

Sammut spent the first years of his career in a series of roles with Intec Ltd, a small minerals processing technology company, participating in and eventually running its laboratory and demonstration plant R&D programs.

Subsequently, he performed a variety of combined business development/operational roles in recruitment, industrial waste processing, consulting and commodities analysis. After a couple of years in Canada, Sammut returned to Intec Ltd in a combined technical/corporate role incorporating a broad range of business development, investor relations and project management duties.

Sammut started DCS Technical Pty Ltd (www.dcs technical.com.au) in early 2013. He divides his time between consulting to a broad range of clients on the federal R&D tax incentive, and consulting to the minerals processing industry as an expert in chloride hydrometallurgy. After 20 years developing the Intec Process technology, Sammut is on the cusp of becoming an overnight success, with the contract signed for the first use of the technology at the full commercial scale for the gold industry.

Sammut is an active participant in the Australian Industrial Ecology Network and the RACI, including semi-regular feature articles for *Chemistry in Australia*. He also mentors young scientists as they make the transition from university into their first career roles. In his spare time, Sammut indulges his hobbies in stone carving, writing, and truly amateur stand-up comedy.

Bob Mathews receives inaugural OPCW-The Hague Award



The inaugural OPCW-The Hague Award was awarded to VERIFIN, accepted by the Director Paula Vanninen, left, with Mr Jozias van Aartsen, the mayor of The Hague; and Dr Robert (Bob) Mathews, second from right with Director-General Ahmet Üzümcü at the 19th Conference of States Parties on 1 December 2014.

On 1 December 2014 the OPCW, in partnership with the City of The Hague, hosted the OPCW-The Hague Award Ceremony at the World Forum conference centre. The Award recognises outstanding achievements in advancing the goals of global chemical disarmament. This year's inaugural Award was presented jointly to Dr Robert Mathews FRACI CChem and the Finnish Institute for Verification of the Chemical Weapons Convention (VERIFIN).

The Director-General of the OPCW, Ambassador Ahmet Üzümcü, and the Mayor of The Hague, Mr Jozias van Aartsen, presented the Award, with Professor Paula Vanninen receiving it on behalf of VERIFIN.

Mathews and VERIFIN have made valuable contributions to advancing chemical disarmament since well before the signing of the Chemical Weapons Convention and the founding of the OPCW. They have been credited with providing 'sustained leadership and support to the development of key concepts of the Convention, as well as to initiatives to promote chemical disarmament and non-proliferation around the world.'

Mathews is an eminent scientist and expert who has dedicated his career to

the disarmament and non-proliferation of chemical weapons. He made significant contributions to the final drafting of the Chemical Weapons Convention, as well as to its establishment, implementation and promotion as a unique instrument eliminating an entire category of weapons of mass destruction.

Speaking at the Award ceremony, Ambassador Üzümcü emphasised the key role played by both recipients in bringing an almost 20-year diplomatic negotiation to a successful conclusion and setting the stage for the implementation of the world's most inclusive and comprehensive treaty, which bans an entire category of weapons of mass destruction. Mayor van Aartsen welcomed the long-standing partnership between the OPCW and the City of The Hague.

The OPCW-The Hague Award was established to preserve the legacy of the 2013 Nobel Peace Prize to the OPCW. The Award comprises a certificate, a medal and a cash prize of €90 000, divided equally between VERIFIN and Mathews. At his request, Mathews' €45 000 was transferred to the OPCW Chemical Weapons Victim Fund.

OPCW

Ian McKay Ritchie

Corrosion expert

Australia recently lost one of its brightest stars with the death of Professor Ian Ritchie AO DSc FAA FTSE, a most gifted and delightful human being. From the perspective of the Electrochemistry Division of the RACI, the passing of Ian Ritchie represents a loss of critical analysis and understanding of interfacial phenomena that was second to none.

Ian began an academic career with his primary degrees from Trinity Hall, Cambridge, in 1958 and he graduated in chemistry, physics, mathematics and biochemistry and topped it off with chemical engineering. Cambridge University awarded him a Doctor of Science in 1999 in recognition for his contribution to the field of electrochemistry.

Ian began his postgraduate career in the US in the new and rapidly developing field of semiconductors, making transistors by hand and developing a life-long passion for the chemistry of the solid state. Turmoil in the semiconductor industry and an inner drive towards researching the fundamentals proved America's loss and Australia's gain in 1962, when he moved to a teaching post and PhD enrolment at the University of Melbourne. His thesis was acclaimed as 'a new approach to the ... derivation of rate laws for tarnishing reactions ... using for the first time a random walk analysis, represents a significant original contribution to the field'.

His knowledge of solid-state chemistry, talent for elegant experimentation and practical problem-solving skills led him to become a leading expert in corrosion science. His 1981 paper in *Corrosion Australia* on the reaction of nitrite with aluminium, which definitively convicted nitrite 'inhibitors' as the culprit in the early failure of alloy engines in Perth's brand-new fleet of Mercedes buses, is a great example of his ability to apply fundamentals to the solution of practical problems. He also made many significant contributions to the development of the fundamentals themselves.

Ian moved to a position of Associate Professor at the University of Western Australia in 1972, and subsequently Professor of Chemistry and Pro-Vice Chancellor (Research) at Murdoch University. The best students clamoured to join his dynamic research groups. His lectures shone out from all the rest as interesting, challenging and, particularly, fun!

While at the University of Western Australia, Ian developed a strong friendship and fruitful collaboration with Jim Parker, out of which the vision of Perth as a world centre for hydrometallurgy was born. Jim's sudden and tragically early passing was a potentially terminal setback for that dream.

But Ian picked up the baton with furious determination and, by dint of masterful negotiation, creative adaption and just sheer hard work, brought the dream to fruition in the form of the A.J. Parker CRC for Hydrometallurgy. Under his leadership, the Parker Centre rapidly grew to become an acknowledged world-leading institute in its field. Its breadth of collaboration,

research output and education programs were second to none by the time he stepped down after a decade at the helm.

Ian also made many contributions to public life, including as a member of the WA Premier's Science Council, the Joint Minerals Council Tertiary Education Taskforce and AVCC Committee, and the Working Group of the WA Minerals and Petroleum Education Research Institute. He worked tirelessly with the WA Clean Air Committee for over 20 years, in particular to bring effective emissions controls and regulation to the strategically important Kwinana industrial strip south of suburban Perth. He led a strategic review of the Chemistry Centre of WA (now ChemCentre) in 1982 and thereafter worked tirelessly to enhance the role and functionality of the Centre, which was then the largest single employer of chemists in the southern hemisphere. ChemCentre's position was finally enshrined in legislation in 2007, and the laboratories have been relocated to bespoke, world-class laboratories (named 'The Ritchie Wing' in his honour) in the Chemistry Precinct at Curtin University. The annual Ian Ritchie Achievement Awards have been established to recognise employee excellence at ChemCentre.

His many civic and academic honours include the Australasian Corrosion Medal (1979), the Stokes Medal for Electrochemistry (1997) and the Applied Research Medal of the RACI (1997), Doctor of Science from Cambridge University (1999) and the President's Award of the Australasian Institute of Mining and Metallurgy (2001). In 1997, he was made West Australian Citizen of the Year (Professions), and he was awarded an Honorary Doctorate by Murdoch University in 2002. He was a Fellow of the RACI, the Australian Academy of Science and the Australian Academy of Technological Science and Engineering.

In 2014 he was made an Officer of the Order of Australia (AO), a crowning honour that came as a bittersweet, counterpoint to the raging sickness that was taking hold of his body. Hiding his illness with characteristic stoicism, this brilliant but humble man was astonished by the flood of congratulations that provided him comfort and reassurance in his final weeks. Family, friends, students and colleagues came from far and wide to farewell him and to recall not so much his achievements, but his heart of gold, soft humanity, real humility, and deep commitment to service and truth.

Ian Ritchie died of cancer on 12 August 2014. He is survived by Ann, their daughter Katherine Olsen, sons Andrew and Alex, and five grandsons.



Ian MacLeod FRACI CChem and Greg Power FRACI CChem

Bringing about an earthquake in human behaviour

Douglas A. Lockard/Chemical Heritage Foundation



Australian chemists will always be endeared to Carl's links with one of our natural product greats, Arthur Birch, and through his half-dozen or so Australian postdocs and research fellows, who went on to become renowned practitioners.

The passing of Professor Carl Djerassi (1923–2015) on 30 January at the age of 91 was followed by numerous obituaries in the international press focusing on his synthesis in 1951 of norethindrone, the key component of the first birth control pill.

He was proud to be called the 'father of the pill', but in his own typically humble words: 'identifying scientists is really only a surrogate for identifying the inventions or discoveries.' He was convinced that if he had not done it, someone else would. The result was the sexual revolution of the 1960s, and the occurrence of a substantial 'earthquake in human behaviour'.

The President of Stanford University John Hennessy recently wrote: 'Carl Djerassi was first and foremost a great scientist', and his former colleagues noted: 'he is probably the greatest chemist our Department ever had'.

Carl's research focused on natural products (steroids, alkaloids, antibiotics, lipids and terpenoids, but also on the applications of physical measurements (optical rotatory dispersion, magnetic circular dichroism and mass spectrometry) and computer artificial intelligence techniques to organic chemistry. In medicinal chemistry he was a pioneer not only in the field of oral contraceptives but also on antihistamines (pyribenzamine) and topical corticosteroids (Synalar). This work is published in over 1200 articles and seven monographs.


Add to these achievements that Carl was the author of about 19 literary works dealing with ethics and the human aspects of scientific research, with many dealing with aspects of human reproduction including the 'pill'. His terms 'science-in-fiction' and 'science-in-theatre' will forever ring in my ears backed by his plays *NO* and *Oxygen*. Carl was a strong advocate of exposing the human side of scientists and the personal conflicts they face, including the need to focus on 'how we do what we do!'

Another side of Carl, not frequently displayed, was his love for the fine arts, especially as a collector of the work of Paul Klee and many emerging artists.

Australian chemists will always be endeared to Carl's links with one of our natural product greats, Arthur Birch, and through his half-dozen or so Australian postdocs and research fellows, who went on to become renowned practitioners. Unfortunately, Carl's visits to Australia, while highly valued, were all too few and infrequent.

This is not an obituary, but rather a tribute to a truly versatile scholar and a gentleman.

Dr Alan J. Jones FRACI CChem



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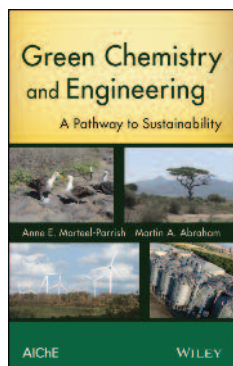
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Green chemistry and engineering: a pathway to sustainability

Marteel-Parrish A.E., Abraham M.A., American Institute of Chemical Engineers, Inc./John Wiley and Sons, 2014, hardback, 376 pp., ISBN 9780470413265, \$114.95

Green chemistry, first described in 1998, has subsequently assumed a significant role in global politics, economics and education. The driving forces behind the

movement to 'greener' chemistry and engineering include an increasing awareness of environmental issues coupled with a realisation of the finite nature of the Earth's resources. Academia, industry, the professional societies (including AIChE, the sponsors of this book) and governmental agencies have enthusiastically adopted this paradigm shift from considering, not just the end product of some (chemical) action, to viewing, additionally, the means and the broader consequences and impacts, both intended and consequential/unintended. In some ways, the ideas of green chemistry are not rocket science, but they are a significantly different way of viewing the world: a coalescence of the inventiveness and innovation of chemistry with the basic tenets of sustainability and good husbandry of the environment. This book is an attempt at providing higher education students with the basic notions of green chemistry.

There are three main divisions within the book. First, the fundamental ideas embodied in green chemistry and engineering are discussed along with some of the essential underpinnings of chemistry. The former are well presented and clear: the latter seemed to be covering much fundamental material, which an Australian tertiary student could be assumed to know. Some material seemed very elementary in a book such as this, but, of course, it all depends on where you are starting.

The second section of the book is altogether at a more advanced level, covering the core areas of chemistry, including chemical reactions, kinetics, catalysis and reaction engineering, and thermodynamics, separations and equilibrium. This is all good material, well presented and logical and an excellent basis for a first-year Chemistry/Chemical Engineering course.

The third section of the book could be described as applications. Chapters are devoted to renewable materials, current and future states of energy production and consumption, the economics of green and sustainable chemistry, and green chemistry and toxicology. This is where this book shines. In the first section, you get the principles and a touch of elementary chemistry. In the second section, you get some good solid material, central to chemistry. In the third section, the preceding sections are tied together and green chemistry becomes real and meaningful. To draw an analogy, it is a bit like a good meal: the entrée piques the interest; the main course fills the needs; and the dessert satiates and lingers in the memory! I must admit that I found the entrée partly

interesting (the principles) and partly boring (the elementary chemistry). At that stage, I very nearly dismissed the book and the ideas as pabulum. However, perseverance paid off – the main course and the dessert were well worth sticking round for: I learnt a lot and enjoyed it too!

Throughout the book, there are highlight boxes. This seems to be a popular stratagem for authors to delineate material, for all sorts of reasons ranging from 'quite interesting but skip if you are in a hurry' to 'if you don't like hard-core mathematics, just ignore'. The ones in this book are well placed, relevant and worth reading.

Overall, this is a timely and worthwhile book. Caring for our planet is ultimately all about putting our money where our mouths are, and, let's face it, for most of us, this needs a reasonably radical shift in our inculcated perceptions. What we see is not merely a function of what is there, but of what we have been taught to see. So, it is important that the next generation of chemists are taught this new, 'green', way of viewing. This book offers a good way of doing this, either as the basis of a stand-alone course, or as a useful resource for material and examples for incorporation in tertiary courses. Professional chemists and chemical engineers will also benefit from reading this book, particularly the bits on principles and applications.

R. John Casey FRACI CChem

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Tweaking the R&D tax incentive

Companies generally perform R&D in order to reduce risk, reduce costs, increase market share, increase margins and create new market opportunities. These all can lead to increased profits and enterprise value. It is a rare company in the 21st century that can flourish or even survive without continuous innovation, some of which will be underpinned by R&D performed within the company or elsewhere.

Despite the demonstrated benefits of successful R&D, it is often argued that Australian companies do not do enough R&D. As a result we have an R&D tax incentive that is designed to encourage companies to perform more R&D in an attempt to boost 'competitiveness and productivity' in the Australian economy. Specifically, the R&D tax incentive offers a:

- 45% refundable tax offset for R&D expenditure for companies with an annual turnover less than \$20 million
- 40% non-refundable tax offset for companies with an annual turnover greater than \$20 million.

A more likely explanation for the existence of the R&D tax incentive is that many Western countries also have an R&D tax incentive and not having one is deemed a market failure by some commentators (or, at least, a point of non-competitiveness), the argument being that Australian and/or (more likely) multinational/global companies can readily move their R&D overseas to more 'R&D friendly' environments.

The aforementioned low rates of business expenditure on R&D (BERD) in Australia compared to other OECD countries is quite a persuasive argument with policy-makers for the continued necessity of the R&D tax incentive. However, this reasoning is somewhat flawed when the make-up of the Australian economy is considered sector by sector. With Australia's predominant focus on resources, agriculture and services, the nation's BERD as a percentage of GDP is actually quite close to what it would be when calculated using average global expenditures on R&D as a percentage of revenues in these particular business sectors.

Elsewhere in the world, economists argue that losses to government coffers as a result of an R&D tax incentive are more than offset by increased economic activity resulting from the resulting R&D, which then acts to increase tax revenues. That is, the net benefit of an R&D tax incentive is effectively positive, according to a 'Laffer curve'. When this impact cannot be shown, economists sometimes fall back on 'net public good' or 'social benefits' in order to promote R&D tax incentives.

My feeling (which is contrary to most articles on this subject) is that the R&D tax incentive in Australia is not as effective as might be imagined for three readily identifiable reasons.

- Much of the R&D performed only leads to changes in market share and profitability of competing and non-exporting domestic companies in the services sector (a sector that accounts for nearly 68% of GDP), with little net benefit to the tax office or to society at large.
- Many companies choose to use the R&D tax incentive to undertake multiple lower-risk and lower-return R&D projects,

rather than to simply accelerate their single-most promising R&D project. In fact, returns on R&D expenditure follow the classic 'long tail' curve, indeed much the same long tail curve as is seen in venture capital investment in technology start-ups. Not only can we say that 'not all R&D is equal', we can also say that much of what is claimed under the R&D tax incentive has no credible potential, at any time from inception to completion, to create high-value business outcomes.

- There is no substantive tax incentive in place to promote the commercialisation of R&D outcomes.

Here are three tax-related changes that could encourage higher value business investment in R&D in Australia.

First, the R&D tax incentive should be reserved for companies that are using R&D outcomes to generate foreign revenue opportunities (in addition to domestic opportunities) but only where these revenues are repatriated to Australia for taxation purposes. This would act to isolate the cost and benefits of the R&D tax incentive into globally focused companies with both an R&D and taxation presence in Australia. This equates to focusing our limited government resources for business sector incentives into a much higher return program.

Second, companies should be encouraged to put all their efforts into fewer R&D projects with more optimal risk and return profiles. Having spent my working life in and around technology companies, both large and small, I have learned that: (1) outcomes are better when a company has a concentrated R&D 'focus', and (2) it is far better to invest more into a sole R&D project in order to quickly catch the market opportunity, and/or to 'fail fast' and then quickly move on to other projects.

Therefore, I propose that the benefits of the R&D tax incentive should scale with project size relative to company revenues. For example, expenditure on each identifiable project would be eligible for the R&D tax incentive, starting at a low percentage figure for projects with expenditure less than some nominal percentage of corporate revenue, increasing to a higher percentage figure for projects accounting for higher percentage of corporate revenues.

Third, the Patent Box tax scheme (bit.ly/1BBlyaj) (which Australia does not yet have) effectively gives companies an extra tax break on patent-protected products and services (see February issue p. 36). Whereas the R&D tax concession is designed to encourage investment by companies into domestic R&D, possibly many years prior to receiving any income from that R&D, the extremely complementary Patent Box tax scheme is designed to encourage investment into commercialisation at the back end, once R&D is completed. In combination, the R&D tax incentive and the Patent Box tax incentive have the power to promote much higher quality R&D with greater economic impact.



Ian A. Maxwell (maxwell.comms@gmail.com) is a serial (and sometimes parallel) entrepreneur, venture capitalist and Adjunct Professor in Electrical and Computer Engineering at RMIT University, who started out his career as a physical polymer chemist.

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Direct Action: a precipitate reaction?

The Government of Australia has adopted a climate change strategy based on Direct Action to reduce emissions and improve the environment (bit.ly/1DDGMTb). 'Direct action' on soil carbons constitutes the major 'plank' of the strategy.

Speaking at a carbon price forum in Sydney in July 2011, the Hon. Andrew Robb stated in relation to Direct Action that:

On some farming land, soil carbon has dropped from 5% to 1% and even less. Increased soil carbon enhances microbial activity and water retention and has a marked impact on productivity. Rehabilitating millions of hectares of existing agricultural soil would seriously contribute to food security issues of the 21st century. If you increase soil carbon by one per cent, that will add 15 tonnes of carbon per hectare into the soil. There are 3.77 tonnes of CO₂ per one tonne of carbon, so if you increase soil carbon by one per cent, that equates to taking 50 tonnes of CO₂ out of the atmosphere.

Soil is the unconsolidated mixture of mineral and organic matter that has developed on the surface of the Earth by physical, chemical and biological processes, and is the natural medium in which land plants grow. Soil carbon exists as plant residues, humus and biologically stable charcoal. It has biological, physical and chemical functions that affect soil structure, aeration, moisture retention and drainage, cation exchange capacity, plant nutrition and pH buffering.

The purpose of Direct Action is to offset CO₂ emissions from the burning of coal for power generation. About 50 tonnes of CO₂ is emitted from burning 21 tonnes of NSW anthracite coal.

In principle, storing carbon in the ground might be considered analogous to part of the natural carbon cycle. Sources of carbon that can be stored for a long time in agricultural soils include animal wastes; crop, food and timber industry residues and tyres; also garden and other compostable material.

A grower would reasonably expect the value of increased crop yield and the Direct Action incentive to exceed the costs of carbon storage. The taxpayer would expect Direct Action to deliver verifiable long-term, if not permanent, carbon storage. Is Direct Action likely to meet its stated objectives by encouraging farmers to apply large amounts of organic carbon to their land?

The amount of carbon stored in soil is the difference between inputs and outputs, like a budget. Inputs include plant matter such as crop and pasture residues, manure, and the remains of microbes and fungi. Outputs include uptake by animals, crop removal, decomposition and soil erosion.

Well-structured and aerated soils receiving ample nutrients and rainfall are the most productive. The rate of soil organic carbon sequestration, with adoption of recommended technologies, depends on soil texture and structure, rainfall, temperature, farming system, and soil management. Water and nutrient use efficiencies are critical factors that determine if carbon is retained or released to the atmosphere. A perhaps counter-intuitive suggestion is that the mass of soil biota increases with rising atmospheric CO₂ and that additional

organic carbon further increases respiration within, and carbon release from, soils (bit.ly/1Lv3Ze).

The annual loading of biosolids (see box) or other organic matter to land is often limited by the nutrient requirement of the crop, especially of phosphorus, and the phosphorus buffering capacity of the soil. Management, fertiliser history, salinity and groundwater must also be considered.

Biosolids and biochar

Large and growing stockpiles of biosolids, derived from sewage treatment, have accumulated near our cities. Biosolids contain useful quantities of plant nutrients and carbon but they are bulky and would have to be transported long distances to suitable farmland. Transport costs, regulation, real or perceived food safety risks and uncertain benefits tend to inhibit their uptake for agricultural use. Environment protection agencies encourage the use of biosolids in agriculture. Relatively small amounts are used in soil conditioners, compost and potting mixes etc.

Biochar is a stable, carbon-rich solid product resulting from the heating of organic matter in an oxygen-limited environment. Although experimental, biochar looks promising as a concentrated and stable form of carbon. Biosolids can readily be turned into biochar and the latent energy can be recovered in the process (bit.ly/18LIzfa). On the basis of carbon equivalence, transport costs and vehicle emissions for biochar would be far less than for biosolids or other bulky organic matter. Biochar would have little impact on soil nitrogen levels but offers potential benefits for productivity as well as longer-term carbon storage in soils.

Not all of the factors that influence the soil carbon budget are predictable or constant. It would be a brave climatologist who would dare to predict with confidence when, where and if seasonal rainfall distribution patterns will shift. But seasonal rainfall distribution can be more important to yield and quality than the annual rainfall aggregate.

Australian soil carbon levels have been falling and there is no doubt these soils could hold more. Accumulation of soil carbon is a slow process subject to the vagaries of weather, climate and land management. The challenge is to do this while still maintaining an economically viable farm enterprise.

Australian dryland agricultural soils contain about 50 tonnes of carbon per hectare in the top 30 cm of soil, with the overall average being closer to 30 t/ha. Raising the carbon content of soils to depths greater than 30 cm will not often be achievable due to the presence of heavy clay, rock or ground water etc. Furthermore, nearly 90% of Australia's agricultural land is

devoted to low-to-medium-intensity grazing of natural vegetation; soil and/or climate conditions are generally not suitable for more intensive agricultural practices and, given these constraints, soils are not likely to be able to store large quantities of carbon (bit.ly/1u52Be2).

By inference, the example given by Robb refers to a soil rich in organic matter. Soils with already high carbon content are unlikely to benefit from Direct Action in terms of increased productivity. Nor would these soils be the most suitable for long-term carbon storage.

Biosolids are an abundant source of organic carbon likely to attract interest under Direct Action. Taking, for example, the phosphorus requirement of a crop to be 50 kg/ha, and assuming a reasonable estimate of phosphorus content of the biosolids as 10 kg/t, the biosolids loading would be limited to 5 t/ha for that crop.

If the 'background' carbon content of a soil is 50 t/ha, adding 5 t/ha of organic matter with, say, 20% carbon content to a moderately heavy soil could raise the carbon content by around 4%, assuming all of this carbon were to be retained. In any case, 1 tonne is well short of the Direct Action example of 15 tonnes of carbon added to the soil. The CO₂ emission offset, at the nutrient (P) limit in this example, adopting 3.67 tonnes of CO₂ per one tonne of carbon is:

$$5 \times 0.2 \times 3.67 = 3.67 \text{ t/ha}$$

If the incentive under Direct Action is \$10/t of carbon stored, for 100 ha at 1 t C/ha, the incentive is:

$$10 \times 100 \times 1 = \$1000$$

It has been estimated that 1 tonne of added soil carbon pool on degraded cropland soils may increase wheat yield by 20–40 kg/ha. Many variables influence the response of soils to carbon additions. It may take some years to reach measurable levels or it could be masked altogether by other factors such as rainfall or management changes.

Assuming a farmgate price of \$A250/t for general purpose wheat and a yield increase of, say, 40 kg/ha, the indicative value of the additional production is:

$$250 \times 0.04 \times 100 = \$1000$$

The costs of transport, spreading, cultivation, sampling and testing cannot be accurately determined. However, some estimates and common sense suggest that transporting 500 tonnes of biosolids would cost a lot more than the value of the yield increase attributable to carbon in this example.

Soil cultivation results in losses of organic carbon, which is released as CO₂ into the atmosphere. Agricultural soils, mainly through the use of nitrogenous fertilisers, are also significant emitters of N₂O, a greenhouse gas more potent than CO₂ (bit.ly/1Cu4nbD).

Direct Action appears to be 'evolving' into a more generalised funding concept with less emphasis on specific incentives such as the \$10/t of carbon stored.

For general agricultural purposes, the carbon to nitrogen ratio of the applied organic matter should not exceed 20, and preferably be less than 15. Without appropriate management, high C:N ratios may cause soil nitrogen depletion and loss of productivity. Good land management can slow the rate of soil carbon loss but growing demand for increased production is not consistent with the aim of long-term carbon storage.

Under Australian conditions, continuous organic inputs are needed to convert agricultural soils to carbon sinks. To increase organic carbon by 1% in the topsoil over 10 years, 15–30 tonnes of organic matter are required per year, in addition to crop residues (bit.ly/1uVKaUe). As shown earlier, organic matter addition may be limited by nutrients, toxicants or salts that can affect plant growth, damage soil structure or contaminate ground water. Special management, land use changes and soil amendments may then add to costs. Given that cropping is a gamble, especially in marginal rainfall areas, a grower would want to be sure that additional inputs can potentially increase productivity without increasing risk.

Experience with recycled water has shown that farmers require hard evidence that the value of any productivity increase will exceed the associated costs while providing a competitive return on their investment. The possibility or market perception that soils may be contaminated by imported carbon-rich organic matter adds a degree of risk that producers may find unacceptable.

Direct Action appears to be 'evolving' into a more generalised funding concept with less emphasis on specific incentives such as the \$10/t of carbon stored. The policy may yet turn out to be an example of the 'market' intervening to save the government from the folly of its own good intentions.



Max Thomas Dip. Agric. (retired) (maxthomas4@bigpond.com) worked in the public sector and in private consulting on a range of land, water and waste management projects. He prepared guidelines for irrigation with recycled water for EPA Victoria and developed a number of environmental management systems in the water industry. References for data are available on request.

Mineral processing at the margins

For more than a century, Australia has had a major competitive advantage in the production of raw materials. During this period, many industries have added value to the basic minerals; perhaps the best known has been the establishment by BHP of the Newcastle steelworks in 1912, using iron ore from South Australia and Hunter Valley coal.

Most mineral ores are processed in some way by a broad cross-section of chemical processes. This may range from using chemically doped water for froth flotation to extract metals, for example cyanide extraction of gold ores.

For some added-value industries, extensive chemical processes are used in the beneficiation of ores, production of refined intermediates and production and refining of metals. Of pertinent interest is the production of aluminium from bauxite ore via alumina intermediate. This series of processes involves value addition from US\$40/t for bauxite to US\$2000/t for aluminium metal.

Although bauxite is not unique to Australia, we have some of the largest and richest deposits in the world. This hydrated alumina occurs in vast beds around the Gulf of Carpentaria and in significant deposits south of Perth. Exports of the bauxite deposits based around Weipa on the Gulf of Carpentaria help set the world price, typically in the range US\$35–50/t FOB (free-on-board).

The first stage in the aluminium production process is the purification of the bauxite to produce a refined alumina by the Bayer process. In this process, the raw bauxite ore is dissolved in sodium hydroxide (caustic soda) at high temperatures, forming a supersaturated sodium aluminate solution. This separates the impurities, which contain a high proportion of iron, known as red mud.

The sodium aluminate is then cooled and alumina seed crystals are added to precipitate the alumina from the supersaturated solution. The excess caustic is concentrated and recirculated.

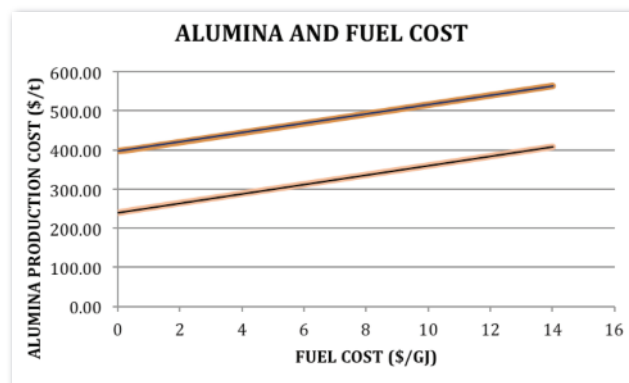
The alumina is calcined to produce the refined alumina for metal production. Apart from bauxite, the main inputs are caustic soda and energy; some smaller inputs in some refineries are lime for assisting the handling of silica and starch for clarifying the liquors. Typical statistics are shown in the following table.

Aluminium metal production requires an enormous input of electricity, up to 15 MWh/t of aluminium, and aluminium production statistics usually go hand-in-hand with a major power investment.

Statistics for alumina production (\$US 2013) capital \$1071/t

	\$/t
Bauxite (2.37 t/t @ \$34/t)	80.58
Caustic (0.1 t/t @ 400/t)	40.00
Lime (0.05t /t @ \$120/t)	6.00
Starch (0.01 t/t @ \$300/t)	3.00
Power (0.347 MWh/t @ \$50/MWh)	17.36
Fuel (11.7 GJ/t @ \$8/GJ)	71.20
Subtotal	240.54
Return on capital (20 year life; 3 year construction)	156.45
Cost of working capital	2.92
Operating cost at 10% of capital cost	107.14
ALUMINA PRODUCTION COST	507.05

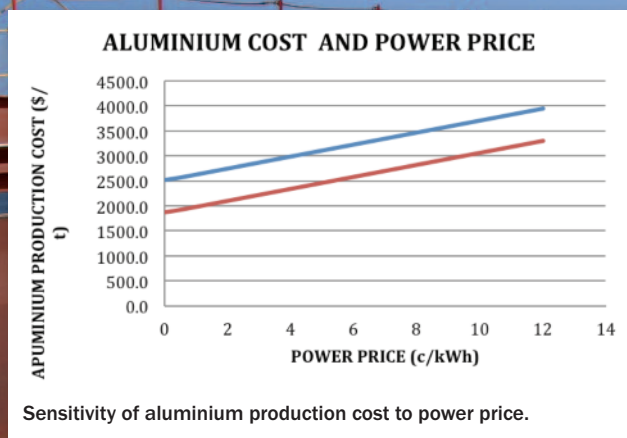
This estimate is for a basic alumina refinery. Most refineries seek to reduce the fuel demand by extensive heat integration of the various operations and many refineries have co-generation facilities providing both power and heat (steam). Apart from bauxite and caustic, the only other major input is fuel (as gas or fuel oil). The sensitivity of the alumina production cost to the prevailing price of fuel is shown as the top line in the following graph.



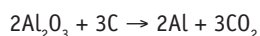
Sensitivity of alumina production costs to fuel cost.

At the present time, the typical selling price for alumina is \$350/t. The graph indicates that this price cannot be achieved on the above statistics and this production cost can only be achieved by writing off the capital investment (lower line). This marginal production cost curve indicates that alumina refineries require fuel prices below about \$9/GJ to achieve the international export price.

For refineries using fuel oil (the Gove refinery in Northern Territory), fuel costs are typically \$9/GJ or more, making these facilities non-viable. For refineries using gas (Kwinana (Western Australia) and Gladstone (Queensland)), on-going viability depends on securing gas contracts at below parity LNG export prices, currently higher than \$8/GJ. Recent falls in crude oil price may assist the viability but this is unlikely to spur investment in new refineries.



Aluminium metal is produced by electrolysis of alumina (dissolved in molten cryolite), using a carbon anode that is oxidised in the process. The reaction stoichiometry is:



Aluminium metal production requires an enormous input of electricity, up to 15 MWh/t of aluminium, and aluminium production statistics usually go hand-in-hand with a major power investment. Often the aluminium smelter becomes the foundation customer, receiving power at the marginal price (sometimes lower) from the utility, which makes up its costs from other customers. To help cap such a subsidy, return on capital is aligned to the utility investment, which is generally over a longer period and with a lower capital return than typical commercial costs (30-year project, 7.5% discounted cash flow (DCF) compared to a more typical 20-year project with 10% DCF). Typical statistics for a 200 000 t/year smelter are shown in the following table.

Statistics for aluminium metal production (200 kt/year, \$US 2013)

	\$/t
Capital cost	6445.8
Total capital charges (\$M/year)	662.5
Operating costs* (\$M/year)	1791.2
Power costs (278 MW @ 2c/kWh)	240.0
TOTAL COSTS (\$M/year)	2693.7

*Operating costs include alumina, anode carbon plus other non-feedstock operating costs (labour, maintenance, chemicals etc.)

With a power cost of 2c/kWh, the unit production cost of aluminium is about \$2600/t. Unfortunately, this is well above

the current world traded price for the metal at about \$2000/t. The impact on the cost of production against the power price is shown in the graph above (upper line). Again we see these prices achieved by writing down the capital investment to near zero (lower line).

As is apparent from the stoichiometry, aluminium smelters are large emitters of carbon dioxide even without the consideration of emissions from fossil fuel power plants. With addition of carbon emission taxes, this further marginalises Australian operations relative to other operations on the Pacific Rim. With power prices typical of the Australian wholesale price of about 5c/kWh, the production cost well exceeds the international price of the metal even if the capital cost is fully written off.

Over the past decade, China has invested heavily in alumina and aluminium production and Australian producers have to match the Chinese export price of typically \$2000/t.

The poor standing of the economics of the aluminium value chain has other implications for processing of advanced metals, such as titanium and magnesium, often touted as a potential major growth area for Australia. The production of light metals is energy intensive and until the present trend of increasing energy prices in Australia can be reversed, there will be little likelihood of attracting the required investment.



Duncan Seddon FRACI CChem is a consultant to coal, oil, gas and chemicals industries specialising in adding value to natural resources. He is indebted to CRU International Limited (www.crugroup.com) for market information on bauxite, alumina, anode carbon and metal prices.

Product stewardship and Australia's nuclear industry

David Dupont's article about e-waste and closed loops (December 2014/January 2015 p. 40) sparked more than a few memories for me. When I joined the mining industry in 1987, my first project was to look at process improvements in the recovery of precious metals (Ag, Au, Pt and Pd) at a copper refinery at Port Kembla, New South Wales. Most of the metals were contained in the copper concentrate feed, with silver and gold at typical concentrations of grams per tonne (ppm).

Another source of silver was residues from photographic processing, which came from a few major photographic companies. The photo residues were combined with those from the copper refinery and the silver was recovered, and refined



iStockphoto/matthiashaas

electrolytically. Major customers for the refined silver were the same companies who supplied the residues in the first place, and who then processed the refined silver into photographic chemicals. Of course, they later recycled the silver residues back to the refinery, and it was close to a closed-loop operation.

Precious metals are relatively easy to keep from the environment, because their high value gives an incentive to users to recover that value. Other metallic contaminants (say nickel and cadmium) do not have the same value and may end up in waste streams more readily.

As a way of encouraging recycling and resource recovery, Dupont suggested that when new phones are purchased, a discount should be offered from the purchase price if the old phone is 'traded' or returned at the same time. However, this puts the onus on the retailer to recover the discount value by recycling the old phone. Perhaps an alternative would be to pay an upfront levy when buying the new phone, which could then be recovered when upgrading later. The levy could be called a 'deposit' and the refund would be available to whoever trades in the phone when upgrading, just like the deposit on beverage containers in South Australia.

Much is made of South Australia's container deposit scheme having operated since 1977, and other states are considering it. However, in the 1960s and 70s, soft-drink bottles (glass back then) carried a 5-cent deposit in South Australia, well before the legislated scheme. The deposit was paid back at the corner shop or (later) supermarket, unlike the dedicated recycling depots in use now. We call it 'product stewardship' these days, although I suspect that the soft-drink manufacturers worked this way to avoid buying expensive new glass bottles. Beer bottles did not have a deposit, but they all had an embossed message stating that they always remained the property of the Adelaide Bottle Supply Co-operative, a joint venture between the two brewing companies. A smaller amount of cash could be recovered when returning beer bottles by the wheat bag full to a 'marine dealer'.

While economics probably drove product stewardship in the past, plenty of need and opportunity still exists to practise it, both for sustainability reasons and to protect the environment. One priority area could be the nuclear fuel cycle, and given that Australia is home to the largest single known resource of uranium, we should have a big role to play. Yellowcake exported from Australia is the source of the isotopes that need to be reprocessed and ultimately stored, and we also operate on the premise that whoever buys the yellowcake also buys the waste management problem. Depleted uranium produced during the production of reactor-grade ^{235}U has found several uses, including as aeronautical and marine ballast, and conventional armaments. It has its own toxicological effects, and was implicated in Gulf War syndrome, suffered by US soldiers after the 1991 invasion of Iraq, where it was used extensively in armour-piercing munitions. Other, more significant, wastes are produced during the operation of reactors, and contain a range of isotopes with toxicity and radiological concerns.

Ultimately, reprocessed nuclear wastes are stored in long-term repositories, usually near the reprocessing centres, which tend to be in developed countries with higher population densities and fewer remote areas than Australia. What better place to permanently store these reprocessed wastes than a dry, geologically stable environment like Australia, which also happens to be the source of the material? We could also meet our international treaty obligations by actually operating, rather than just insisting on, the safeguards that are supposed to be followed in the nuclear fuel industry. It wouldn't quite be a closed loop production, because some of the mass would have been converted into energy, but it would enable us to demonstrate our bona fides about safe operation of the nuclear fuel cycle, and also capture more of the economic benefit of our natural resources that is currently captured by others.



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Copper and hydrogen sulfide in wine

The chemistries of copper(II) and hydrogen sulfide in wine have been intimately linked for many decades. In the past, vineyard sprays and the use of copper or brass fittings contributed to copper concentrations in finished wine that were high enough to induce the formation of *copper casse* (a copper-based haze involving protein) or lead to enhanced oxidative spoilage. The actual copper concentration in wine that induces these effects is still the subject of active research and an article on the Australian Wine Research Institute website summarises the present state of understanding (bit.ly/1LKaLOP).

At least two strategies have been proposed to remove excess copper to stabilise the wine from spoilage. One approach uses potassium ferrocyanide (blue finings) to remove a range of heavy metals, including copper. In some cases, iron(III) ferrocyanide was more effective, especially if the iron concentration of the wine was low. The method works well, but, of course, the excess ferrocyanide may break down under the acidic wine conditions to release hydrogen cyanide, a somewhat unfortunate consequence!

In 1935, Jean Ribéreau-Gayon, a former professor of oenology at the University of Bordeaux, argued that the addition of sodium sulfide would lead to a reduction of the copper concentration by precipitation of copper(II) sulfide. The process was claimed to be efficient, the copper concentration being lowered to around 0.2 mg/L, although the basis for this concentration has been difficult to find. I suspect it was based on observation and without theoretical justification. In essence, this approach to removing copper from wine is not that different from using sulfide to remove copper from wastewaters. While I am somewhat reluctant to draw many parallels between wine and wastewater, I have over time tasted some experimental and student wines that would rival wastewater in both aroma and taste.

In current winemaking practice, the copper/sulfide situation is reversed. As I outlined in the March issue (p. 39), copper(II) sulfate or citrate may be added during winemaking to remove the H₂S aroma or added just prior to bottling, in the hope that the presence of copper(II) will minimise off-odour development during bottle ageing.

The success of this copper fining, as it is known in wine practice, appears to depend on the stage of the wine processing when it is added. The experiments that I described in the March issue mimicked copper(II) additions to the finished or ready-to-bottle wines. In these experiments, we observed that the H₂S aroma was removed by the addition, but essentially no precipitation or loss of copper was found (see doi: [10.1111/ajgw.12114](https://doi.org/10.1111/ajgw.12114)). The experimental results imply that the copper(II) sulfide particles are very small, and certainly less than 0.2 µm, the smallest filter used. There has always been considerable anecdotal evidence for the small particle size, although detailed experiments to validate this have been missing until we published our data. Ribéreau-Gayon

recommended heating the wine to ensure removal of copper(II) sulfide: shades of the barium sulfate gravimetric analysis come to mind here. However, the heating would be detrimental to wine quality overall, so it is not really an effective approach unless one is seeking a Madeira style of wine.

The addition of copper(II) earlier in a wine's history may be more effective in removing H₂S aroma. The two 'H₂S hot spots', to use a term borrowed from Geoff Johnston of Pirramimma, are at the end of the primary fermentation and during malo-lactic fermentation. The presence of copper(II) at these two stages may well be effective in reducing or even eliminating the need for copper additions later in the wine's life. The important issue here may well be the presence of residual protein. Most proteins possess a positive charge at wine pH and Ribéreau-Gayon in 1935 proposed the addition of isinglass, a protein used in wine fining, to assist in removing the copper(II) sulfide. This approach was based on the claim that the CuS particles possess a negative surface charge, an issue that requires further investigation. If protein addition is to be effective, then it is only feasible to use it while the wine is in tank or barrel, allowing time for the protein/copper/sulfide combination to coagulate and be removed by settling or filtration. Once the wine is ready for bottling, adding protein may lead to its instability in the bottle and give rise to an unattractive brown haze.

Recent work indicates that the role of protein in copper/sulfide chemistry is more complicated. Certainly, in wastewaters, gelatin has been shown to generate monodisperse copper sulfide particles, exactly the opposite of what is claimed for wine. But maybe pH plays an important role here. Further, in a recent commercial trial on a non-protein stabilised Riesling, the wine with the highest measured concentration of H₂S also had the highest concentration of residual copper (bit.ly/1zGSdub). This was after extensive copper/protein precipitation had occurred, and opens up a series of new questions on copper/sulfide chemistry, at least in white wines.

To add one more factor to the complexity of the copper/sulfide chemistry, we found in the precipitation study mentioned above that tartrate was one wine component that influenced the effective removal of the CuS precipitate. Using 'model wines' with and without tartrate and after filtration through a 0.2 µm filter, the copper concentration was reduced by around 80% for the tartrate-free model compared to 60% in the tartrate model. The surface activity of tartrate in protein instability and tannin aggregation in wine has been separately demonstrated and similar principles may apply here also. But that is a story for another day.



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Pray hunter, pray

Job hunting. To me there is a certain mis-match in the imagery that the word *hunter* puts into my mind and the actual position of the average job seeker. A hunter, to me, is a powerful, confident, brusque individual who storms into a territory that is not their own, takes what they need and nonchalantly leaves without a passing thought for the devastation left in the wake of their departure. A job seeker, on the other hand, tries absolutely assiduously to make a good first impression, using enthusiastic and inviting language, dotting the i's and crossing the t's, playing out interview scenarios in their head, polishing shoes, trimming fingernails and taming hair. It is an absolutely different person from one you'd find stalking lions in the savannah. It is behaviour more like that of a bowerbird, studiously crafting a nest to attract the attention of the most promising mate. And bowerbirds aren't known to be the world's greatest hunters. In fact, they are more likely to be prey.

I find myself reflecting on this because I am, once again, looking for a job. It is an occupational hazard of a postdoc, but I look forward to the change: the new challenges, opportunities, cultures and countries and colleagues. I like moving, but at the same time, the job-hunting process is one I undertake with utmost trepidation and perhaps far too much introspection. Ahem.

The thing is, there is no sure-fire formula to landing a job. One school of thought says that your cover letter is of paramount importance, while another claims with equal certainty that it is the CV. Some people claim CVs longer than two pages are fast-tracked to the shredder, while others claim that brevity is a sign of an un-lived life. Even with the content matter of CVs, there is no consensus on what is necessary and what is superfluous. Do you list your hobbies? Your elementary fluency in Japanese? Your high school grades? Your job at the supermarket when you were a freshman/freshwoman? In Europe, it is customary to include your photograph on your CV. In the US, this may be viewed as a kiss of death. Duh!

I write fluently and often (articles, proposals, stories, reports and columns for *Chemistry in Australia*), but nothing makes me as nervous as contacting a potential employer. I stare at the screen and compose and recompose sentences in my head. I write and delete sentences with equal frequency until I finally arrive at a paragraph I think my intended audience will find satisfactory. And even then I might change my mind two sentences into the next paragraph. Dang!

Speaking of writing, there is the other blight of the modern job application process – the letter of reference. So many jobs require these nowadays. It is essential that you get a glowing one from a referee who both thinks highly of you and is likely to be highly thought of by the employer. Referees are busy people so I tend to provide mine with a draft that they are then free to embellish as they like before they send it on. And if you thought writing a glowing evaluation of yourself is hard, it is even harder to write one from another (more senior) person's point of view. Ugh!



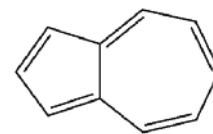
Then the final hurdle of job-seeking these days: social media. Luckily I do not have time for Facebook and Twitter so I don't have to expunge non-flattering comments from those sites. But I do have take care of anything Google may have to say about me. This usually means keeping all my scientific profiles up to date: LinkedIn, Google Scholar, Research Gate, Researcher ID and ORCID all have to reflect my education, publications, achievements and awards. Phew!

And lastly, after you and your referees have submitted the perfect job application, you sit and wait. No, wait, you don't! You can't just apply for one job. It is a numbers game. Only a certain number of submitted CVs will make it past the online portals and HR reviewers to finally be seen by the person who makes the final decision. And that number is small. So what you have to do is submit many high-quality applications and pray to the gods of capriciousness that at least one makes it to the top of the pile of CVs on someone's desk. Gah!

I am a job hunter, sure, but I think of myself more as prey. An odd type of prey, to be sure: one who actually wants to be found, but a meek, powerless prey nonetheless. Sigh!

The author just knows that there is a position out there for a verbose scientist with a proclivity for ending paragraphs with interjections.

Out of the Blue. A blue about a blue



azulene

During my MSc research, I isolated a sesquiterpene alcohol, β -eudesmol, from the timber of *Pterocarpus indicus*, the tree I was working on under the direction of Ray Cooke. In an effort to identify the carbon skeleton, I heated the natural product with sulfur so as to dehydrogenate it to a substituted naphthalene. The distillate from the dehydrogenation was bright blue, and Cooke advised that the colour was probably due to an azulene impurity, formed by molecular rearrangement. Washing the crude product with sulfuric acid removed the blue colour, thus confirming the azulene hypothesis, and I went on to identify the hydrocarbon as having 1,7-disubstitution on the basis of infrared and ultraviolet spectra.

Cooke remembered that when azulene was first shown to an Australian science audience, the speaker was challenged by a member of the audience who felt that a hydrocarbon simply could not be blue. Who were the protagonists and when did this confrontation occur?

Norm Lahey told me he knew of the incident and that T.G.H. Jones had shown azulene at a meeting of the Royal Society of Queensland in 1937 or 1938. In fact it was Lahey, then a student of Jones', who had synthesised the C-15 azulene by selenium dehydrogenation of a natural product. For the presentation, a small quantity was dissolved in ether so that the colour could be easily seen. Few chemists attended meetings of the RSQ, and Lahey was not present at this one, but Dorothy Hill, whom he asked about it for me, remembered it well. She confirmed Jones' role and felt that the challenger was Tyack Blake, who 'had a little knowledge about everything' and often spoke at meetings and was described by some as 'a boring self-opinionated pseudo-scientist'.

Another former Queenslanders who I approached was Ralph Bick. His father, who was Treasurer of the RSQ for many years, had told him that it was Henry Tryon who had spoken out against the idea of a blue hydrocarbon, suggesting instead that there was contamination with copper. Lahey provided me with information from the *Proceedings* of the RSQ for 1938, in which it was recorded that 'Dr T.G.H. Jones showed a specimen of azulene and commented on its properties'. Tactful reporting of the meeting continued with the comment that 'The exhibits were commented on by Messrs H. Tryon' and others.

Tryon (1856–1943) was an authority on entomology but confidently extended his expertise to science in general and frequently questioned speakers. His high-pitched squeaky voice, moustache and short beard, and formal dressing that included dark suits, a waistcoat with gold watch-chain draped across it, black tie and a starched collar caused some people to make fun of him and to underestimate his intelligence. A posthumous biographer described him as 'an erudite and versatile scientist ... with a brilliant brain, a sarcastic tongue and a cantankerous nature'. Clearly a divisive character, Tryon was remembered by

his biographer in the *Australian Dictionary of Biography* as 'irascible and over-critical in both personal and public relationships' and 'the terror of inexperienced or ill-prepared speakers'. Jones seemed to have his measure, speaking in terms of resonance theory and bringing about closure of the 1938 meeting with a confident air.

The structure of azulene was a mystery for many years, and a number of structures were suggested for the molecule, with the final proof of the cyclopentadienylcycloheptatriene (bicyclo[5.3.0]decapentaene) structure, an isomer of naphthalene, being provided by the synthesis of a number of azulenes by Pfau and Plattner in 1936. So Jones was pretty much up with the latest and well placed to fend off a critic.

While I was compiling notes for this Letter, I came across a commercial product, Blue Cypress Oil, that contains guaiazulene (1,4-dimethyl-7-isopropylazulene) and really is blue. It comes from a native Australian cypress, *Callitris intratropica*, growing in tropical Australia and is marketed by Australian Cypress Oil Pty Ltd. The leaves of this tree contain some essential oils of terpenoid nature, but the blue oil is steamed out of the heartwood. A related substance, chamazulene (1,4-dimethyl-7-ethylazulene) occurs in flower oils of chamomile, artemisia, matricaria and tansy, which lack the fragrance of the blue cypress oil. *C. intratropica* is grown in plantations, originally established to provide timber for housing construction. A decline in the use for housing has led to the development of alternative applications for the wood.

Part of the azulene story is that oils like this had been reported over the years and the colour had been a source of speculation. At the soirée and exhibition held as part of the celebration of the Jubilee of the Chemical Society of London in 1891, J.H. Gladstone, President of the Society 1877–9, had exhibited 'cœruleine, a blue substance found in many essential oils'. Although he was better known for his work on optical properties of substances, John Hall Gladstone (1827–1902) studied a number of essential oils and in his 1864 paper in the *Journal of the Chemical Society* he reported a blue hydrocarbon (probably a mixture) that he called cœrulein. Others had seen a similar thing, one referring to it as azulene, but Gladstone pointed out possible confusion with the blue coal-tar dye known as azuline and also that cœrulein was the name of a blue pigment marketed by artists' suppliers Winsor and Newton. The final 'e' appeared unremarked in 1891. Was it a typo?



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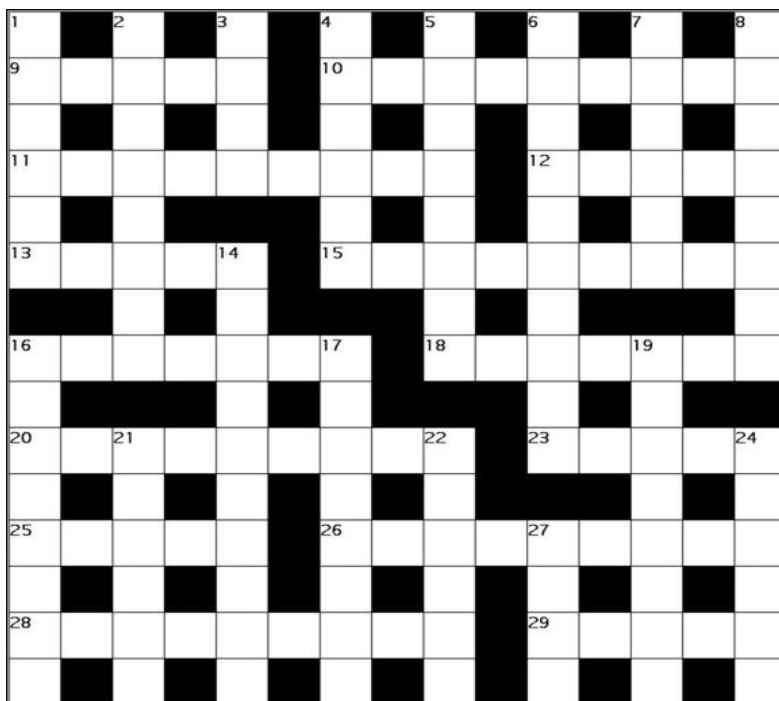
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www.flogen.org/sips2015

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

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Across

- 9** Starts adding zeolite into diatomaceous earth to form $R-N=N^+=N^-$. (5)
10 So hot re free radical. (9)
11 Strangely semifluid $H_2S=NH$. (9)
12 A group of investigators with sulfur producing hydronium ions in aqueous solution. (5)
13 Turns S_2 over fix. (5)
15 Count of blasts composed using sets. (9)
16 Spooner's dirt consumed move. (7)
18 Secretly watches over Enzyme Commission class. (7)
20 Unspecified item of ghost mine pyrotechnics. (9)
23 Give up product. (5)
25 Tellurium in our exterior. (5)
26 In particular, 18 Across loses 99 but gains supporter. (9)
28 Makes one sour re wrong. (9)
29 Shackle 27 Down x 792. (5)

Down

- 1** Goes by propositions. (6)
2 Conceding 23 Across in unit of mass. (8)
3 Use of lime hydrate rising to include a type of internal combustion engine. (4)
4 29 Across band on the way. (6)
5 Again lets discharges . . . (8)
6 . . . contaminate river, lately less radical by comparison. (10)
7 Taken in for a period, identifying a salt. (6)
8 Carries on and ends programmable repetitious, incongruous tests. (8)
14 Not many confused calcium and tellurium with 4 Down. (10)
16 One element is replaced by two others in monomer naming error. (8)
17 Discharge electron assignment. (8)
19 Dig a sale (jumble) governed by $PV = nRT$. (5,3)
21 Oddly, *Meet the Press* might give a measured response. (6)
22 Fat bribe. (6)
24 Grind yttrium turnings to eliminate water. (6)
27 Move slowly in terminating caustic potash. (4)

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

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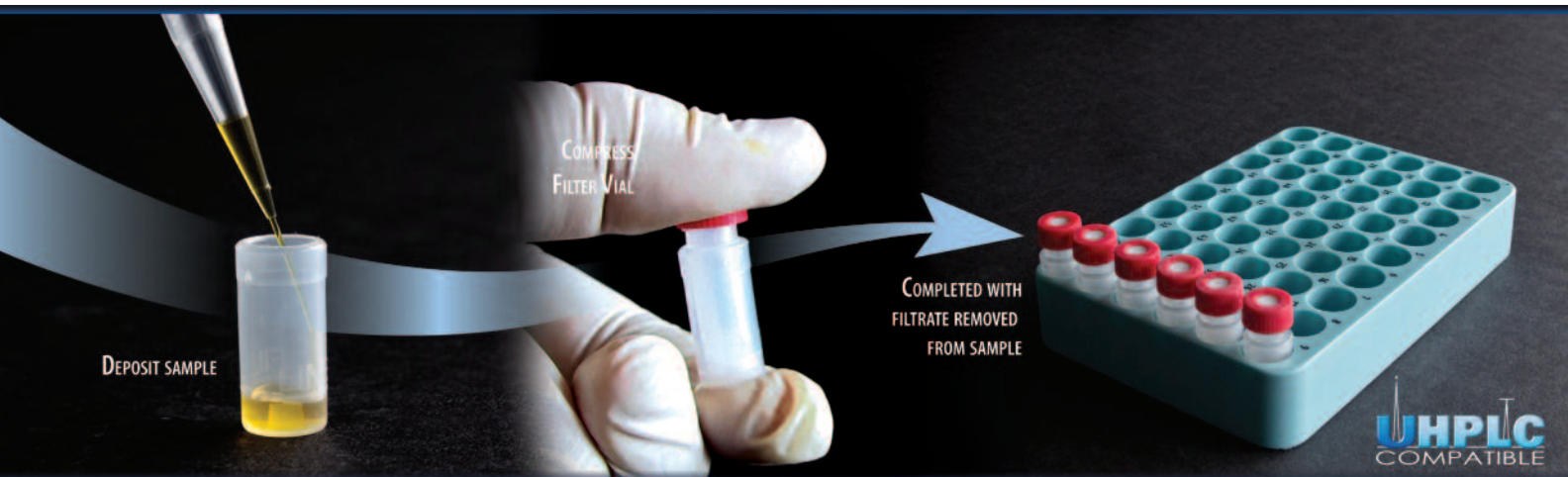


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