Chemistry in New Zealand

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NZIC Chemistry IN NEW ZEALAND

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Articles and features

Other columns

Comment from the President

Welcome to the October issue of *Chemistry in New Zealand*. The new NZIC website is now fully operational, thanks to the hard work of Joanna Dowle and Paul Plieger, and many members have already used it to renew their membership. There are still members who have not renewed, so if this is because of issues with using the website please contact Joanna Dowle (*nzic.office@gmail.com*).

There are more changes afoot at NZIC as our long serving Honorary Treasurer, Associate Professor Colin Freeman, has indicated that he will step down from the role at the end of this year. Council and I thank Colin for his long and distinguished service to NZIC. This means that NZIC will need a new Honorary Treasurer for 2019. If you are financially minded and willing to help (or know of a member who is) please get in touch with myself, Joanna Dowle or the incoming president Dr Sarah Masters.

Emeritus Professor Brian Halton is also stepping down from his role as Consulting Editor for *Chemistry in New Zealand*. Professor Halton has been associated with NZIC for many years and held a variety of roles within the Institute. He has provided exemplary service to NZIC. Council and I thank Professor Halton for all he has done for NZIC and wish him well.

In sad news, Emeritus Professor Andrew Brodie passed away in August. Professor Brodie was a highly respected member of the chemistry community, was the President of NZIC in 2004 and was awarded the NZIC Chemical Sciences prize in 2007. Andrew's obituary is in this issue of *Chemistry in New Zealand* and on behalf of the NZIC I want to pass on our condolences to his family and friends.

The 2018 NZIC awards were voted on at the recent Council meeting. Continuing the trend from recent years there were many excellent nominees for all of the awards which suggests that chemistry in New Zealand is currently in a good state. However, this made the deliberations very difficult. This year the **Shimadzu Prize for Industrial and Applied Chemistry** went to Mr Darren Saunders from ESR in Christchurch. The **Denis Hogan Chemical Education Award sponsored by ABA Books** was awarded to Dr David Warren (Department of Chemistry, University of Otago). The **Maurice Wilkins Centre Prize for Chemical Science** was awarded to **Antony Fairbanks** (School of Physical and Chemical Sciences, University of Canterbury). Congratulations to all the award winners.

As I stated in a previous President's column, 2019 is the 150th anniversary of Dmitri Mendeleev's first report of the periodic table and will be the International Year of the Periodic Table of Chemical Elements (IYPT 2019, *https://iupac.org/united-nations-proclaims-international-year-periodic-table-chemical-elements/*). This represents a huge opportunity to get chemistry out into the public eye. So I hope everyone within NZIC has been thinking about events we could hold during 2019 to publicise our discipline and the Periodic Table.

The deadline for submitting a research article to the special issue of *Chemistry – An Asian Journal* that will focus on chemistry in New Zealand is coming up (Friday 30 November 2018). I hope many of you will consider submitting some work.

Finally, Christmas is fast approaching and if you know of people who are interested in chemistry then a copy of *Scientific Sleuthing* (*http://clerestorypress.co.nz/scientific-sleuthing/*) might make an excellent Christmas present.

James Crowley
NZIC President

Erratum

In the July 2018 issue it was incorrectly stated in the President's Report and in the Auckland Branch News that Distinguished Professor Margaret Brimble was elected FRSNZ. Professor Brimble has of course been a Fellow of the Royal Society Te Aparangi for many years already, having been elected FRSNZ in 2001. Margaret's most recent achievement was being made a Fellow of the Royal Society (FRS) this year, becoming the first New Zealand-based female and the first organic chemist to be elected FRS. The correct information was supplied by the contributors and the editor apologises for this error. The corrected electronic version of the July 2018 issue is available on the NZIC website.

New Zealand Institute of Chemistry

supporting chemical sciences

October News

AUCKLAND

University of Auckland

Welcome

Dr *Rebecca* ***Deed*** has been appointed as a lecturer in wine science. She has a background in plant molecular science and wine microbiology, with a PhD in biological sciences from the University of Auckland. Her thesis investigated the effect of low temperature fermentation on the transcriptome of wine yeast and the production of yeast-derived wine aromas. After graduating in 2013, Rebecca worked as a technician to develop improved commercial yeast strains for the NZ wine industry. From 2014-2018, Rebecca became involved in the University's wine science teaching programme, lecturing in viticulture, wine microbiology and sensory evaluation, while working on postdoctoral research with Dr *Bruno* ***Fedrizzi*** in the School of Chemical Sciences, centred on unravelling the biosynthesis of volatile sulfur compounds in wine. Rebecca's current research areas are focused on using molecular biology and analytical chemistry techniques to understand the mechanisms behind the biological and chemical formation of aroma compounds in grape juice and wine, as well as understanding yeast metabolic pathways leading to good fermentative ability.

Dr Rebecca Deed

Professor *Juliet* ***Gerrard*** has recently become the second Prime Minister's Chief Science Advisor after Professor Peter Gluckman. At the announcement of Juliet's new role, the Prime Minister talked about the value of having scientists inform policy and the advantage to New Zealand of having a network of science advisors embedded in government ministries. Juliet stated that she saw key parts of her role as earning trust of the wider community in scientific advice, making science accessible, and ensuring people appreciated both the relevance and the limitations of scientific advice. She noted that this could be termed "social license to operate (SLO)". A recent article in the Journal of the Royal Society Te Aparangi defines that term in the following way:

"An SLO is granted based on communicating the knowledge, metrics and predictive basis for deciding if something is worthwhile. This requires trust. Trust is brought about by robust and understandable reporting; a sense that the system is fair, there is equitable sharing of benefits and that enough is known to make the decision." (Stevens and O'Callaghan, *J. Royal Soc. N.Z.* **2015**, *45*, 89)

We benefit as scientists and citizens from these science advisor roles, and we wish Juliet well in her new position.

Farewell

Members of the Auckland Branch attended the funeral of Professor Sir *Neil* ***Waters***. Neil was a graduate and then academic staff member at the University of Auckland, being promoted to a personal chair in recognition of his x-ray crystallography research in 1970 and then being appointed to the Chair in Physical Chemistry in 1981 (in those days professorial chairs were awarded in key subfields of chemistry, while personal chairs were awarded to recognise individual research excellence). Neil then left the University of Auckland to become the second Vice-Chancellor of Massey University, starting in 1983 and retiring in 1995. Neil's main physical legacy is the establishment of the Massey Albany campus. But his influence on academic colleagues was also significant, as reflected for example in two current Vice-Chancellors (Professor Stuart McCutcheon from the University of Auckland and Professor Grant Guilford from Victoria University of Wellington) attending his funeral, both having benefitted from Neil's leadership and advice, along with Distinguished Professor Ted Baker, whose PhD research was co-supervised by Neil.

Events

On 6 July the 2nd annual University of Auckland mass spectroscopy symposium showcased a diverse range of applied and fundamental mass spectrometry research from overseas and across the university. Keynote speakers included Professor Brett Nixon (University of Newcastle, Australia) investigating male fertility and Professor *Christian* ***Hartinger*** (University of Auckland) working on anticancer drug development. Mass spectrometry is transforming our understanding of the chemical and biological world.

On 1 August the School of Chemical Sciences (S=C=S) social club had its first meeting of the semester, with a pizza/karaoke/games night. About 50 students attended from first year to postgraduate, along with six staff members. Thank you in particular to Jianyong Jin, Natalija Vyborna, Joseph Vella, Timothy Christopher, and James Brady for organising the event.

The International Chemistry Olympiad competition was held 19-29 July in Bratislva, Slovakia and in Prague, Czech Republic. The practical and theory exams were extremely difficult, particularly as the time spent on each was limited to five hours. For the practical, the students had to do three experiments. The organic experiment involved carrying out a reaction, separating the products by solvent extraction, carrying out a further reaction on one of these, TLC analysis and product crystallisation. The kinetics experiment involved determination of a rate law (using initial rates) for a reaction with luminol. The third experiment was a titration of the metal ions in mineral water after separation of these using an ion exchange column. Each student was provided with a plastic box (30 x 20 cm) of equipment to support each experiment. In addition, other pieces of equipment were available on the bench: burette, stirring motor, wipes, stop watch, etc. The amount of equipment at each of the 300 student places was staggering – the total was just over 100 pieces of equipment provided for each of the 300 students (with each piece absolutely sparkling). Our results were pleasing as three of the four team members received bronze medals (Russell Boey from St Andrews' College in Christchurch and Steven Ma and Callun Loomes from Auckland Grammar). A big thanks to *Katrina* ***Graaf*** and her team for helping us with preparing the team for their laboratory experience.

We congratulate all winners of the various talk and poster competitions of the annual Research Showcase held on 6 June.

Second Year Poster Competition:

First Prize: Elyse Williams (***Brimble***)

Second Prize: Martijn Wildervanck (***Brothers***)

Third Prize: Ryan Dixon (***Sperry***)

General Poster Competition:

First Prize: Jared Freeman (***Brimble***)

Second Prize: Naasson Mbenza Mbambi (***Leung***)

Third Prize (shared): Andrew Chan (***Simpson***) and Rasangai Sabaragamuwa (***Perera***)

First Year PhD Oral Presentations:

First Prize (shared): Nabangshu Sharma (***Leung***) and Natalie Haverkate (***Barker***)

Second Prize (shared): Lakshini Thewarashige (***Simpson***) and Timothy Christopher (***Sohnel***)

Audience choice 1st session (shared): Taniela Lolohea (***McGillivray***) and Rebecca Richards (***Elliot***)

Audience choice 2nd session (shared): Timothy Christopher (***Sohnel***) and Thomas Grant (***Brimble***)

Invited PhD Oral Presentations:

First Prize: Matthew Sullivan (***Hartinger***)

Second Prize: Stephen Lo (***Barker***)

Third Prize: Hans Choi (***Brimble***)

Congratulations to all of you!

Visitors

On 27 July Professor Harm-Anton Klok from Ecole Polytechnique Fédérale de Lausanne, Switzerland gave a seminar on *Polymers at synthetic and biological surfaces.*

On 6 August Professor Janice Aldrich-Wright from Western Sydney University gave a seminar on *Multiple action platinum (IV) prodrugs.*

On 8 August Professor Terry Collins presented a lecture entitled, *Learning how to love the future through green science* as part of the University's Winter Lecture Series. Professor Collins is a Distinguished Alumnus of the University of Auckland and is a world leader in the field of green chemistry. He currently holds the Teresa Heinz Chair of Green Chemistry and is the Director of the Institute for Green Science at Carnegie Mellon University, Pittsburgh PA, USA.

Congratulations

Congratulations to *Margaret* ***Brimble***, *Jon* ***Sperry*** and *Paul* ***Harris*** who have been invited to submit full standard proposals for the Marsden grant, and *Paul* ***Hume*** and *Ivanhoe* ***Leung*** who have been invited to submit full Fast-Start proposals.

Congratulations to Jamal Cheema, supervised under Professor *Jadranka* ***Travas-Sejdic*** and Dr Andrew Kralicek (Plant and Food Research), for success in receiving the Australian Institute of Nuclear Science and Engineering (AINSE) postgraduate research award (PGRA). His PhD research is based on development of conducting polymer-based biosensors.

Congratulations to the MOCHIYO team for winning the Velocity Innovation Challenge, Science Category 2018. The team included food science undergraduates Bohee Moon, Joyce Baroro, Kamille de Guzman and Ester Kiriwang and food science PhD candidate Anand Mohan (Supervisor: Associate Professor Siew-Young Quek)

Congratulations to PhD students Stephen Lo and Rebecca Jelley (supervisor: Associate Professor *David* ***Barker***) for being $1000 prize winners at Velocity Challenge.

Congratulations to *David* ***Barker***, *Viji* ***Sarojini*** and *Tilo* ***Sohnel*** on being named as Associate Investigators in the MacDiarmid Institute for Advanced Materials and Nanotechnology.

Congratulations to Dr Guantian Li who was awarded the Chinese Government Award for Outstanding Self-financed Students Abroad ($US 6,000) for his PhD work. Guantian has worked on the properties and structure of starches from quinoa under the main supervision of Dr *Fan* ***Zhu***. He has published 12 peer-reviewed journal articles in top Food Science journals.

Congratulations to Professor *David* ***Williams***, who was selected as a finalist in the Baldwins Researcher Entrepreneur Award, which is awarded by the Kiwi Innovation Network (KiwiNet). His nomination was for *Air quality measurement for everyone: sensors, systems and networks*, and is in recognition of the small, low-cost air quality sensors that his company Aeroqual Ltd produces.

The most recent issue of *Physics World* has an interview with Professor *Cather* ***Simpson*** about Engender Technologies Ltd, and about what is required to take an idea and turn it into a successful company. Great inspirational interview Cather!

Congratulations to *Michelle* ***van Rensburg***, *Brent* ***Copp*** and *David* ***Barker*** for their recent article in *Eu-*

ropean Journal of Organic Chemistry. The paper entitled, *Synthesis and absolute stereochemical reassignment of mukanadin F: a study of isomerization of bromopyrrole alkaloids with implications on marine natural product isolation* was determined to be a VIP (Very Important Paper) and was awarded the front cover of the current issue.

Congratulations to *Margaret* ***Brimble*** for successfully securing $1.19 million from the Health Research Council (HRC) of New Zealand for research entitled, *Naturally occurring peptaibols: "Magic bullets" for targeting breast cancer.*

Congratulations to PhD student Chloe Cho in the polymer lab of Dr *Jianyong* ***Jin*** for winning the best poster award at the IUPAC World Polymer Congress (commonly known as MACRO 2018), which is the world's largest biennial polymer event organised by IUPAC. This year, MACRO 2018 was held from 1-5 July in Cairns and attracted 845 delegates from all over the world. Among 199 poster presentations, Chloe won the second best poster award.

Congratulations to Dr *Dongxiao* ***Sun-Waterhouse***, who received the NZ Institute of Food Science and Technology (NZIFST) Award for Excellence in Leadership, which recognises leadership above and beyond "business as usual". Dongxiao's commendation recognised "leadership excellence for a notably sustained period". This award was presented at the NZIFST annual conference in Hamilton.

Congratulations to Professor *Conrad* ***Perera***, who received the J C Andrews Award from the NZ Institute of Food Science & Technology. This is their most prestigious award, given to Fellows who have made significant contributions to the food industry, research and academia. This is in recognition of his wide-ranging contributions which include initiating and contributing to four major changes in food science curricula (two at the University of Auckland, one in Brazil and one in Singapore), acting as a consultant with international organisations such as FAO and the UN Industrial Development Organisation, and of course supervising many postgraduate students in food science. Well done Conrad!

Congratulations to the student winners at the NZIFST Conference on 3-5 July. Yaoyao Peng, a second year PhD student was the 1st prize winner for the poster presentation while Manasweeta Angane won the 2nd prize. Both students are supervised by Associate Professor *Siew-Young* ***Quek***.

Congratulations to Yi-Chern Li who won the NZ Young Food Technologist Award. Yi-Chern Li graduated from the Food Science Programme in 2011 and is currently a product manager (Consumer & Foodservices, Global Operations) at Fonterra.

Congratulations to Shinji Kihara, a PhD student in Associate Professor *Duncan* ***McGillivray***'s group for his appearance on Seven Sharp. He was one of the scientists helping to answer the question, *Bottled water or straight out of the tap – which is best?*

Congratulations to Allan Zhang in *Margaret* ***Brimble***'s group who won the prize for the best poster at the 15th Chinese International Peptide Symposium, Shenzhen, China, 3-7 July, entitled, *Total synthesis and conformational study of the anti-tubercular cyclic peptide callyaerin A.*

Congratulations to *Tony* ***Chen*** for his newborn. Wishing you and your newborn many years of good health, love, and happiness.

Congratulations to Dr *Kaitlin* ***Beare***, who is the only Faculty of Science staff member to be awarded a Centre for Learning and Research Fellowship in 2019. Kaitlin's Fellowship is based on the theme, *A new canvas for teaching and learning* and she intends to develop methods for Canvas to provide feedback to both staff and students, and to develop new ways to assess student achievement in large classes. We look forward to the results from a successful Fellowship!

Congratulations to Elyse Williams who is a PhD student in the ***Brimble*** peptide group in the School of Biological Sciences. Elyse's Honours work has just been published in *Angewandte Chemie* (*Solid-phase thiol-ene lipidation of peptides for the synthesis of a potent CGRP receptor antagonist*) and a patent application for this work has also been filed. The work reported in the paper resulted from a collaboration with Debbie Hay and Kerry Loomes. Investment has also now been secured to carry out a pilot *in vivo* animal study to evaluate whether Elyse's compounds can be taken to the clinic. Elyse has also just had a review published in *Chemistry – A European Journal* (*Chemical synthesis of bioactive naturally derived cyclic peptides containing ene-like rigidifying motifs*). After these stellar outputs from her Honours work Elyse is now working on a completely different project for her PhD.

Congratulations to PhD student Mahsa Motshakeri, who has received a runner-up prize for the Metrohm Young Chemist Award open to students enrolled at academic institutions in Australia, New Zealand and the Pacific Islands. Mahsa received AUD $750 for her research on the topic of *Rapid electroanalysis of uric acid and ascorbic acid using a Poly(3,4-ethylenedioxythiophene)-modified sensor with application to milk*. This work was recently published in *Electrochimica Acta*, and is being supervised by Professor *Paul* ***Kilmartin*** and Associate Professor *Anthony* ***Phillips*** of the School of Biological Sciences.

Congratulations to Professor *Penny* ***Brothers*** who has been named as a finalist in the Innovation & Science category of the 2018 Women of Influence Awards.

Congratulations to Dr *Michel* ***Nieuwoudt*** and her team who won first prize for their idea for a personal stress sensor at the Optical Society of America Innovation School. The School is a four-day programme that aims to foster entrepreneurial thinking among early-career professionals. Michel is back and keen to commercialise the idea!

Congratulations to the following PhD candidates who successfully presented and defended their theses*:*

Paul Baek – supervised by Professor *Jadranka* ***Travas-Sejdic*** and Associate Professor *David* ***Barker***. Paul's thesis was based on development of stretchable and self-healing conducting polymers for organic electronics.

James Wood – supervised by Distinguished Professor *Margaret* ***Brimble*** and Dr *Dan* ***Furkert***. James is now undertaking postdoctoral work at the University of Bristol.

Nina Novikova – jointly supervised by Professor *Cather* ***Simpson*** and Professor *Penny* ***Brothers***. Nina's thesis is entitled, *Distorted porphyrins: photophysics and singlet oxygen photosensitisation in boron porphyrins and porphyrinoids*.

Auckland University of Technology

New faces

Dr *Marcus* ***Jones*** joins the Department of Chemistry at AUT as a senior lecturer. Marcus completed his BA and PhD degrees at the University of Oxford and University of Cambridge respectively followed by postdoctoral positions with Garry Rumbles (National Renewable Energy Laboratory, Colorado) and Greg Scholes (University of Toronto) before achieving tenure at the University of North Carolina at Charlotte. Marcus' research is broadly focused on the photophysics of quantum dots and their potential applications.

We welcome a new MPhil student, Bhanumathi Bandi, who will be working with Dr *Jack* ***Chen***, a new MSc(Research) student, Anau White, who will be working with Professor *Allan* ***Blackman*** and welcome back Emma Matthewman who will be performing her 3rd year research project with Dr *Cameron* ***Weber***.

Events and invited talks

AUT hosted an NZIC seminar from Dr *Bill* ***Hawkins*** (University of Otago) entitled, *One ring to rule them all: the synthesis of biologically relevant compounds from cyclopropanes*.

Pablo Solís Muñana, PhD student of Dr *Jack* ***Chen***, spent 5 weeks in June/July working in the laboratory of Professor Leonard Prins in Padua, Italy, as part of a collaboration funded by a Catalyst Seeding Grant (Royal Society Te Aparangi).

Congratulations

Professor *Nicola* ***Brasch*** was appointed to the PBRF Physical Sciences assessment panel and has been appointed as an Associate Investigator of the Dodd-Walls Centre.

Ruth Cink, PhD student of Professor *Nicola* ***Brasch***, has been selected for the finals of the AUT Three Minute Thesis competition. Ruth also received an award for her oral presentation at the Dodd-Walls symposium at the University of Auckland.

A paper by Vinay Bharadwaj and Professor *Nicola* ***Brasch*** in collaboration with researchers from Kent State University, USA has been featured on the frontispiece of *Chemistry – A European Journal*. The paper describes the preparation and characterisation of a molecule capable of rapidly producing HNO under neutral pH conditions.

Pablo Solís Muñana, Dr Jack Chen and Professor Leonard Prins

Massey University Albany, Institute of Natural and Mathematical Science (INMS) and The New Zealand Institute of Advanced Studies (NZIAS)

Welcome

Jonathan ***Kitchen*** joined the chemistry department at the beginning of the year. Before joining Massey, Jon completed a PhD at the University of Otago, a PDRF at Trinity College Dublin and was a lecturer at the University of Southampton, UK. Jon's research focuses on supramolecular materials characterisation/development and the applications of new (soft) materials containing functional/responsive *d*- & *f*-block systems. His research aims to develop control and predictability over the preparation of supramolecular materials, and in doing so develop new generation functional nano-devices including thin-film luminescent sensors, porous networks for sensing and switchable magnetic materials. Jon delivered a local branch NZIC seminar (*Responsive supramolecular materials*) at the University of Auckland and has also recently been invited to guest edit a *Magnetic materials for sensing* special issue in the journal *Chemosensors*.

Events and invited talks

Distinguished Professor *Peter* ***Schwerdtfeger*** just came back from Oslo spending 5 months at the Norwegian Centre for Advanced Study. He was part of a large team working on *Chemistry at extreme conditions* including large magnetic fields and high pressure. Two of his PhD students joined him there working on related topics, i.e. melting simulations of heavy rare gas solids (Odile Smits, see *Angewandte* **2018**, *57*, 9961) and quantum electrodynamic effects in superheavy elements (Morten Piibeleht). Peter also gave talks at the several meetings and congresses in Menton, Rome, Rota and Paris and visited Universities in Tromsoe, Stuttgart and Marburg. In Spain he launched a new Wiley journal together with Professor Jesus Vigo Aguiar entitled, "*Computational and mathematical methods*. Two of his students (Lukas Trombach and Odile Smits) gave invited talks at the CMMSE congress in Rota. Peter started a new Marsden contract in July (together with E. Pahl) on superheavy element chemistry and physics, establishing a new collaboration with the nuclear physics group of Professor Witek Nazarewicz at Michigan State. He will soon be off again to visit universities in Shanghai, Stuttgart and Boston (Harvard). Peter has also become a "critical mind" on twitter (believe it or not).

Professor *Al* ***Nielson*** attended the 28th international conference on organometallic chemistry, ICOMC 2018, held in Florence, Italy. He gave an invited oral presentation entitled, "*New complexity for aromatic ring agostic interactions in ligand assisted cyclometalation reactions of palladium (II)* and presented a corresponding poster entitled, *Interplay of steric and electronic effects on the bonding components in aromatic ring agostic interactions*.

Debbie ***Jordan*** attended the IUPAC International Conference on Chemical Education in Sydney where research was presented and discussions had on teaching methods and the value of different aspects of a chemistry student's undergraduate education.

Marie-Anne ***Thelen*** and *Debbie* ***Jordan*** organised workshops for over 300 year 12 & 13 students in the Chemistry Teaching labs. The students participated in one of two workshops, either a synthetic experiment (making aspirin and assessing the purity using IR spectroscopy) or a *Chemical Cluedo* using NMR and IR spectroscopy to establish the identity of chemicals in Professor White's lab.

CANTERBURY

Events

NZIC Canterbury held its inaugural Winter Warmer on 21 August at the Rutherford Regional Science and Innovation Centre (RRSIC) featuring mulled wine, mince pies and numerous attendees.

University of Canterbury

The University of Canterbury celebrated the history of an award-winning building that captures both the past and present of UC, with a free public exhibition about the Old Chemistry building at the Christchurch Arts Centre in July. The exhibition featured tools and instruments that would have been used on site, photos from this time and more. The display was a collaboration between chemistry alumni and staff and students of the College of Arts and the College of Science.

UC Open Day, the biggest day on the UC calendar, was held on 12 July. The new Ernest Rutherford building was open all day for self-guided tours of the labs and interactive displays. Staff and students were on hand to showcase the labs, provide demonstrations and answer questions. Papanui High School Head Girl Nina Sales was one of the 4200 attendees. She was given a GoPro to capture her experience as she checked out UC Science and the campus – if you weren't there, here's the next best thing *https://www.facebook.com/universitycanterbury/videos/1987993384844879/*

The documentary *Paul Callaghan: Dancing with Atoms,* directed by Shirley Horrocks, screened in early August at the NZ International Film Festival. Shirley Horrocks is the cine-biographer of many notable New Zealand artists and delivered an invaluable survey of the work and legacy of one of our most exceptional scientists and public figures. Sir Paul Callaghan - physicist, science communicator, entrepreneur and 2011 New Zealander of the year - died in 2012 of cancer when he was in his prime. As well as his NMR research, he wrote books, gave public lectures and shared his vision of a prosperous and predator-free New Zealand – "…a place," he said, "where talent wants to live." Shirley Horrocks, who met Callaghan while making her 2012 film *Venus: A Quest*, focused here on his life in science. Through big brother Jim, classmates, colleagues and Callaghan himself – in a series of interviews filmed in 2010 – we journey from Callaghan's childhood in Whanganui, to his work at Massey University, then to Victoria University of Wellington and the MacDiarmid Institute for Advanced Materials and Nanotechnology. There are dramatisations of schoolboy high jinks and footage from Callaghan's trips to Antarctica. Callaghan's life, and the film, takes a turn after his move to Wellington, where he applied himself beyond physics to art–science collaborations, economics and conservation. "Suddenly it became OK for scientists to work with artists," says physicist Shaun Hendy about his former mentor. Poet Bill Manhire, cartoonist Dylan Horrocks, broadcaster Kim Hill and Weta Workshop's Richard Taylor are among those who describe how Callaghan expanded the conversation between science and wider society and rallied people to his causes, many of which continue after his death. Anyone who knew Paul, or was affected by his work, will want to see this tribute.

Awards

Dr *Deborah* ***Crittenden*** was a 2018 Kiwi Innovation Network (KiwiNet) Research Commercialization Award finalist: *https://idealog.co.nz/venture/2018/05/revealed-2018-kiwinet-awards-finalists*. The 12 finalists were selected to celebrate the impact from science through successful research commercialisation within New Zealand's universities and CRIs. Deborah is a senior lecturer in the School of Physical and Chemical Sciences, developing exciting new technologies delivering environmental sustainability, including infinitely rechargeable batteries and real-time nitrate sensors. She is currently working on designing new energy storage liquids for use in redox flow batteries, a novel nitrate sensor system based upon laser-induced photochemistry coupled to simple, low-cost detection methods, and developing a new platform technology for predicting how drug molecules bind to their targets on a very large scale. In 2017, a spin-out company, Flow Holdings, was established based upon Dr Crittenden's molecular design work to develop a prototype redox flow battery. Discussions are ongoing around partnering with industry to further advance and commercialise her nitrate sensor design, which has already attracted pre-incubation funding. Additionally, Deborah is in early discussions with a tech incubator around commercialising her computational drug design tool.

*Samantha **Bodman*** (Physical and Chemical Sciences) won Best Doctoral Student Presentation at the University of Canterbury's Thesis-in-Three finals in mid-August: *https://blogs.canterbury.ac.nz/intercom/2018/08/15/thesis-in-three-champ-shares-joys-and-challenges-of-competition/*

MANAWATU

The ***Telfer*** group welcome+d four new members: John Clements (postdoc), Nicholas Symon (MSc), Laurine Friche (intern) and Shikeale Harris (summer student).

Maulik Mungalpara won an NZIC sponsored award for best presentation at the Annual Post Graduate Symposium organised by the Institute of Fundamental Sciences, Massey University.

Suraj Patel and Laura Brand joined the ***Rowlands*** and ***Jameson*** groups respectively to work on their undergrad projects.

The ***Plieger*** group joined in celebration with Michael Brown as he handed in his MSc thesis. Caitlyn Miles joined the group for her undergrad project.

*Shane **Telfer*** gave a lecture on *Ethane/ethylene separation* at the CFE-CEES meeting in Cairns, Australia. In early July, he gave two seminars on metal-organic frameworks, one at KAIST, Daejeon, South Korea and another at the SRC mini-symposium at UNIST, Ulsan, South Korea.

*Paul **Plieger*** participated in several conferences in Europe and Asia. He presented a keynote lecture on *The design and synthesis of high nuclearity metallo-macrocycles for magnetic applications* at the 10th International Symposium on Nano & Supramolecular Chemistry, ISNSC-10, in early July then followed this up with a lecture on *Tuning beryllium coordination with outer-sphere hydrogen bonding* at ICCC43 (43rd International Conference on Coordination Chemistry) in Sendai, Japan. Paul will also attend the Asian Chemical Editorial Society (ACES) meeting in November as the NZIC representative on the Board.

Sidney Woodhouse (MSc) also attended the ICCC43 conference and presented her poster on *Salicylaldoxime derivatives capable of 3d/4f coordination*. Sydney was a recipient of an NZIC travel grant for attending this conference.

Dr Nathaniel Davis (VUW) gave a presentation on *Chromophore control : nanoscale to devices* on 25 July.

On 1 August, the Manawatu branch organised a public seminar on the invention of spreadable butter. The talk was jointly delivered by Robert Norris and David Illingworth, the inventors of spreadable butter. More than 60 people attended the event which was held at the Palmerston North Central Library. Copies of the book *Scientific sleuthing – chemical discoveries made in New Zealand* were sold after the seminar.

Justin Bendall gave a public talk on *A commercial perspective on chemical analysis for protection against food safety risks* which was jointly organised by the Manawatu branches of NZIC and the Royal Society Te Aparangi.

Kyle Van de Bittner of Ferrier Research Institute of VUW spoke on *Microbial factories: an efficient avenue to valuable natural products* on 24 August.

Robert Norris and David Illingworth delivered a public lecture on the invention of spreadable butter

Copies of *Scientific sleuthing - chemical discoveries made in New Zealand* were sold after the public seminar

OTAGO

The branch held the 3rd NZIC Otago Chemistry Quiz on the evening of 8 August in the School of Pharmacy. Nine teams from across the university entered, with strong participation from undergraduate and postgraduate students. The overall winners were *Live free and diethylamine*, with *The gnomeless gardeners* and *Lab rats* taking second and third place respectively. Members of the Branch committee, in particular *Andrea* ***Vernall***, *Christina* ***McGraw***, *Caitlin* ***Casey-Stevens*** and *Dave* ***McMorran*** are thanked for their work in writing quiz questions and running what was an enjoyable night.

The Aurora Otago Science and Technology Fair was held at Otago Museum in early August. The Branch supported the event through student prizes. Branch chair, *Nigel* ***Lucas*** awarded prizes to ten students, a difficult job considering the high standard across hundreds of entries. The projects awarded prizes all had an underlying chemistry theme and were: *Maori traditional – new medicine* (Kate Coates), *Cold science* (Bethany Miller), *Stain stain go away* (Emily Smith), *Fizz away* (Kate Allan-Chalmers), *Race to rust* (Koru Edwards, Oliver Thompson), *Chlorine residual in our water* (Liam Robertson), *Pearly whites and the perfect smile* (Zara Deans), *Exciting enzymes* (Morganne-Lee Greene), *What's in my water?* (Ethan Lau), and *Ambulance at the bottom of the cliff – an investigation into the relationship between leaf pigmentation and NZ's native horopito and predation at Orokonui eco-sanctuary* (Ollie Meikle).

University of Otago, School of Pharmacy

Allan ***Gamble*** presented at the Gordon Research Conference on Bioorganic Chemistry in New Hampshire in June. Allan also visited and presented a research seminar at the National Cancer Institute (NIH) in Frederick and the University of Delaware. PhD student *Jessica* ***Fairhall*** also presented at the Gordon Research Conference in Bioorganic Chemistry and at the Genetic Code Expansion Conference held in Oregon in August. Finally, congratulations to PhD student *Sumit* ***Dadhwal*** for submitting his PhD thesis.

University of Otago, Department of Chemistry

PhD student *Alistair* ***Richardson***, who is supervised by *Nigel* ***Perry*** and *Dave* ***Larsen***, won the Sciences Division *Three minute thesis* competition with his talk entitled, *Transport of vitamin C: giving apples a healthy boost*. There were a total of nine three minute talks from PhD students plus eight MSc talks. All were very good, especially another talk by chemistry student *Kavindra* ***Wijenayake*** on *"Fingerprinting" the world's milk*. However, the three judges had to make a choice, and their summary was that Alistair "really nailed it".

Dave ***Warren*** and two undergraduate chemistry students (*Jess* ***Beevis*** and *Jessie* ***Blyth***) spent three days at Araiteuru Marae in Dunedin on a Science Wānanga. They delivered a hands-on activity about the analysis of copper ore using colorimetry, performed a 'magic show' and made liquid nitrogen ice cream during the event. Their final item was a teddy bear explosion using liquid nitrogen (see photo). This was Dave's 17th Science Wānanga since 2009.

In news from the group of *Christina* ***McGraw***, PhD student *Wayne* ***Dillon*** joined Professor *Cliff* ***Law*** at Sanford's Ecofarm in the Marlborough Sounds to participate in *A feasibility study of coastal acidification mitigation strategies for the mussel industry*. Wayne deployed a suite of his sensors to study variability in the marine carbonate system. In August, two new students joined the lab: *Denise* ***Chen*** and *Anna Lunde* ***Hermansson***. In July, Christina participated in the Gordon Research Conference on Ocean Global Change Biology. This meeting coincided with the annual meeting of the Scientific Committee on Oceanic Research working group #149 (Changing Ocean Biological Systems (COBS): *How will biota respond to a changing ocean?*), which Christina attended to continue work on the development of a best practice guide for marine multidriver research.

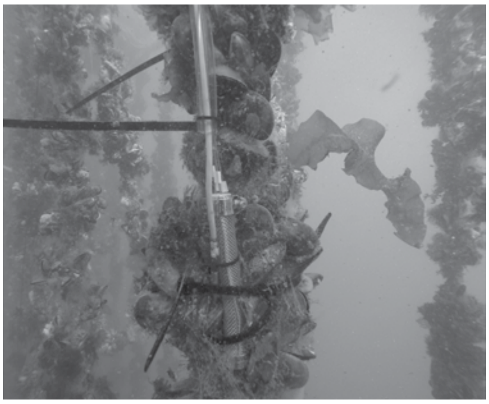
Professor *Lyall* ***Hanton*** and Associate Professor *Stephen* ***Moratti's*** Gel group which included Dr *John* ***McAdam***, Dr *Jaydee* ***Cabral*** and PhD candidate *Bagus* ***Santoso*** travelled to Adelaide between 8-10 August for a mini symposium with Professor P.J. Wormald's surgical research group at Adelaide Medical School to share everyone's latest findings. Other

Liquid nitrogen teddy explosion at the Araiteuru Marae, Dunedin (photo courtesy of the Otago Chemistry outreach team)

The 2018 NZIC Otago Branch Quiz Night winning team, *Live free and diethylamine* news from the Gel group includes the recent departure of Dr *Shailesh* ***Goswami*** and *Marina* ***Roxburgh***. Shailesh is now the Process Development Chemist at Chitogel, Ltd. Marina is taking time off travelling through Asia and Europe.

The group of *Anna* ***Garden*** have been travelling this winter with Anna presenting an invited lecture in the symposium *From clusters to the solid state* at the 18th International Conference on Computational and Mathematical Methods in Science and Engineering in Costa Ballena, Spain in July. PhD students *Charlie* ***Ruffman*** and *Caitlin* ***Casey-Stevens*** presented posters of their hydrogen evolution and nitrate reduction work respectively at the International Workshop on Computational Electrochemistry in Aalto, Finland in June and Charlie, Caitlin and *Geoffrey* ***Weal*** presented posters at the CAMD Summer School on Electronic Structure Theory and Materials Design in Helsingør, Denmark in July. Geoff, Caitlin, Charlie and Anna also visited the groups of Hannes Jónsson and Egill Skúlason at the University of Iceland and Anna visited PhD student (co-supervised with *Sally* ***Brooker***) *Luca* ***Bondì*** in Florence.

Professor *Sally* ***Brooker*** visited Professor Roberta Sessoli's large research team in Florence in early July to discuss collaborative research and start setting up a co-tutelle. Her PhD student, *Luca* ***Bondì***, is currently working in Roberta's team for four months, on studies with Professors Federico Totti and Matteo Mannini. Sally then visited Professor Annie Powell at the Karlsruhe Institute of Technology, where she presented an invited seminar and had the pleasure of catching up with her summer student from long ago, Dr Shaun Presow. Shaun did his PhD with Professor Karl Wieghardt, then worked as an advisor in Brussels, before he moved to his present position with BASF in Ludwigshafen – he now has German residency. Sally then went to Dresden where she presented an invited keynote lecture at the 10th International Symposium on Nano and Supramolecular Chemistry (ISNSC). Dr *Humphrey* ***Feltham*** made another visit to the group of Professor *Alison* ***Downard*** (Canterbury) in August, to progress our MacDiarmid-funded collaborative project on surface at-



A carbonate sensor attached to a mussel dropper line at Sanford's mussel farm in the Marlborough Sounds

From left to right: Bagus Santoso, John McAdam, Stephen Moratti, Sarah Vreugde, Jaydee Cabral, Simon Robinson, Raj Sindwani, Catherine Bennett, Lyall Hanton and P.J. Wormald

Top: Roberta Sessoli hosted Sally in Florence. Bottom: Luca (back left) and Matteo Mannini (front right) discussing our collaborative work in Florence

Garden group members at the CAMD summer school in Helsingør, Denmark. From left to right: Alexei Ivanov and Vilhjálmur Ásgeirsson (PhD students, University of Iceland), Geoffrey Weal, Caitlin Casey-Stevens and Charlie Ruffman tachment of hydrogen production catalysts.

Keith ***Gordon*** was recently a finalist for the Otago University Science Division Supervisor of the Year award. He was nominated for his dedication to the growth of his students, both scientifically and personally. Keith gave an invited talk entitled, *Insight into organic photovoltaic materials through Raman spectroscopy and computational chemistry* at the International Conference on Raman Spectroscopy, ICORS 2018, in Jeju, Korea.

Jonathan ***Barnsley*** graduated with a PhD in August for his work on *Spectroscopy of donor-acceptor dyes*. Jonathan is currently working as a research associate and is planning for a short postdoc position on the photochemistry of hops in collaboration with Plant and Food Research. The recent publication *Frequency dispersion reveals chromophore diversity and colour-tuning mechanism in parrot feathers* in Royal Society Open Science gathered widespread attention and was featured by TV3 news, The Scientist, Forbes and ABC Australia.

Georgina ***Shillito*** presented a poster at the Electron Donor-Acceptor GRS conference in Newport, RI, USA. While overseas, Georgina visited Julia Weinstein's lab in Sheffield. *Joshua* ***Sutton*** presented a poster at ICORS 2018 entitled, *Raman spectroscopy from low frequency to overtones – insight into the electronic structure of self-assembling materials*. Joshua will also visit the Mike George lab in Nottingham, UK, to make some time-resolved IR measurements and visit Han Young Woo's group at Korea University Seoul. Joshua received funding from a Claude McCarthy Fellowship to assist in this travel. He published a number of papers this year including *A nona-nuclear heterometallic* Pd_3Pt_6 *"donut"- shaped cage: molecular recognition and photocatalysis* in *Angewandte Chemie*. *Joseph* ***Mapley*** presented a poster at ICORS 2018 entitled, "*Electronics of β-indandione modified zinc porphyrins* and also published a number of papers including *Computational and spectroscopic analysis of β-indandione modified zinc porphyrins* in *Journal of Physical Chemistry A*.

Jeremy ***Rooney*** is currently writing up his PhD thesis entitled, *Low temperature cured waterborne coil coatings* and recently gave a presentation to NZ Steel and Callaghan Innovation in Auckland. Jeremy and Matt Tarling have published a paper titled, *Distinguishing the Raman spectrum of polygonal serpentine*. *Ruth Eloisa* ***Sales*** presented a talk entitled, "*Vibrational spectroscopy of lake snot: conquering the New Zealand lakes invader* at the Dodd Walls Centre Symposium for which she won the prize of Best Oral Presentation. Ruth also presented a talk entitled, *Vibrational spectroscopy of New Zealand lake snot* at ICORS 2018. *Garagoda Arachchige Piumika* ***Samanali*** presented a poster entitled, *Probing consolidant penetration into Harakeke fibres using Raman microscopy* at the Dodd Walls Centre Symposium for which she won the prize of Best Poster Presentation.

Kārlis ***Bērziņš*** from Latvia has joined the Gordon group as a PhD student. Kārlis's background is in pharmaceutical studies, and he will use Raman spectroscopy and multivariate analysis to probe solid state pharmaceutical systems. We are also joined by *Chima* ***Robert*** from Nigeria as a PhD student. Chima's background is in forensic chemistry and he will use Raman spectroscopy for a number of different analytical projects. *Elliot* ***Tay*** has been working on frequency dispersion in the Raman spectra of parrot feathers. This work follows on from the initial study using Raman spectroscopy to probe the nature of pigments in parrot feathers. Elliot plans to carry on research in the Gordon group next year.

Undergraduate students *Sam* ***McIntyre*** and *Lachlan* ***Gaudin*** are also in the Gordon labs as part of their CHEM390 studies. Sam is using Raman spectroscopy to investigate quality control of apricots, while Lachlan is using low-frequency Raman spectroscopy to investigate crystallinity within organic photovoltaics. Sam recently got back from a Chemistry Outreach program in Malaysia and Lachlan and Keith were part of the winning team *Live free and diethylamine* for the NZIC quiz

Sally and Shaun Presow (BASF) catching up in Karlsruhe night.

Wanghyo ***Kim*** is a visiting student from UNIST (Ulsan National Institute of Science and Technology), Ulsan, South Korea. Wanghyo has a background in organic synthesis of photosensitive dyes for dye-sensitised solar cells (DSSCs). He has come here to run some resonance Raman spectroscopy measurements with his supervisor, Professor Tae-Hyuk Kwon who is on sabbatical. Professor Makoto Yamaguci (Akita University) is also on sabbatical with the Gordon group. Makoto is an expert in aeroplastics and will be investigating low-frequency Raman as a novel way to measure crystallinity in these systems.

WAIKATO

University of Waikato

Analytical Chemistry Competition 2018

This annual event was held on 12 June. Invitations were sent to schools in the wider Waikato/Bay of Plenty region to send teams of four students to the University of Waikato for the day to carry out an analysis. 24 teams of 4 students from 19 schools across the Waikato/Bay of Plenty region entered in this year's competition.

The task was to analyse a sample of $NiSO_4.nH_2O$ using a gravimetric procedure for Ni^{2+} and a volumetric method for SO_4^{2-}. This allowed the value of n to be calculated in the empirical formula by difference. This was a demanding task in the time available but some excellent results were achieved. "A number of teams produced excellent results and the winning team produced results which were very close to the true values", said competition judge and key organiser, *Michèle* ***Prinsep***.

Although rivalry was fierce, the main emphasis was on enjoying the experience of working in a chemistry laboratory at the university and meeting students from other schools. The winning team received $240 and a trophy, with prize money also awarded to all other place-getters thanks to the generosity of the sponsors.

The competition allowed enthusiastic Year 13 chemists to spend a day in the university laboratories working on an experiment that would be beyond the resources of their schools. Rivalry was fierce but the main emphasis was on enjoying the experience and meeting students from other schools.

Results were:

1st Prize: Waikato Diocesan School for Girls (Belinda Chong, Georgina Harris, Caitlin Ryan, Day-eth Smit)

2nd Prize: Pukekohe College (Sophia Chen, Charlotte Coyler, Bella Perham, Cameron Woods)

3rd Prize: Trident High School 1 (Megan Lai, Jack Nelson, Christian van der Gulik, Simon Winship)

4th Prize: Hamilton Boys' High School (Patrick Dowd, Jason Mace, Joshua Monteiro, Logan Trigg)

5th Prize: Tauranga Girls' College 2 (Clara Chang, Chloe Ieong, Holly Topp, Shari Webber)

The day involved many of the Chemistry Department staff in setting up the competition and supervising the labs. Bryant Hall and Student Village provided excellent lunches (sponsored by the Waikato Branch of the NZIC) and Hill Laboratories and the Waikato Branch of the NZIC generously donated the prizes.

Scion

We welcome Dr Bart Challis, our new Chief Operating Officer. Bart comes to us from Hill Laboratories in Hamilton, where he was General Manager – Commercial.

Florian ***Graichen*** and *Dawn* ***Smith*** attended the 2018 Bio-Environmental Polymer Society (BEPS) meeting in Troy, New York and met with US-based collaborators.

Stefan ***Hill***, *Marie Joo* ***Le Guen***, *John* ***McDonald-Wharry*** (Waikato University) and *Jerome* ***Leveneur*** (GNS) travelled to the SAXS/WAXS beamline at the Australian Synchrotron (Melbourne) as part of a National Science Challenge project looking at fibre alignment in 3D printed objects.

Drs Susanne Zibek and Gerd Unkelbach (Institute for Interfacial Engineering and Biotechnology, Stuttgart, Germany) participated in a Scion-organised *Bark Biorefinery Workshop* with NZ companies interested in developing new bio-based chemicals and materials from bark side-streams and were hosted during their stay by *Warren* ***Grigsby***. *Stefan* ***Hill*** and *Laura* ***Raymond*** hosted Dr Michelle Coote (ANU Canberra, Australia) as part of a RSNZ Catalyst-funded collaboration looking at the computational modelling of natural product solubilities in supercritical carbon dioxide.

First place winners at the 2018 NZIC Analytical Chemistry Competition, from left: Dayeth Smit, Georgina Harris Belinda Chong and Caitlin Ryan, Waikato Diocesan School for Girls

WELLINGTON

The 2018 Ferrier Lecture was given on 7 June by Professor Nicola Pohl, professor of chemistry and the Joan and Marvin Carmack Chair in Bioorganic Chemistry at the University of Indiana. Her lecture, *Next wave biotherapeutics: a marriage of sugars and proteins*, looked at the challenges in developing the next wave of biotherapeutics - modifying proteins with sugars - and discussed how these problems fit into the larger questions facing the field of chemistry today.

On 25 July *Martyn* ***Coles*** gave a talk titled, *Fluorescent rocks and minerals: a (hopefully) illuminating talk*. He described some of the science behind why some rocks glow or change colour under UV light, and demonstrated with some samples from his own collection. The talk was followed by pizza.

August's meeting, *The chemistry of chocolate making*, was on 15 August. George Havlik from Bohemein Fresh Chocolates spoke about where chocolate comes from, the components of chocolate and the crystallisation of chocolate during the tempering process, among many other things. He really knew his stuff and was able to answer all our questions about the chocolate making process. There was also some chocolate tasting involved.

Professor Nicola Pohl presenting the 2018 Ferrier Lecture (photo credit: Scott Cameron)

VUW

The NZIC Wellington high schools quiz was held on 20 June in the VUW Recreation Centre, with 35 teams of four students competing to give a total of 140 students. They came from 18 schools in the Wellington region: Onslow College, Scots College, St Patrick's Silverstream, St Catherine's College, Samuel Marsden, Hutt Valley High School, Wellington College, Wellington East Girls' College, Wellington Girls' College, St Bernard's College, Hutt International Boys' School, St Oran's, Paraparaumu College, Wa Ora Montessori College, Sacred Heart College, Newlands College, Tawa College and Heretaunga College. The MC for the night was *Fraser* ***Hughson*** who also wrote the questions for the quiz. Prizes were provided in the form of gift certificates from NZIC as well as some items donated by SCPS, the MacDiarmid Institute and VUW student enrolments. These were given as spot prizes between each round as well as in addition to the main quiz prizes. The winning teams were:

1st place – The Spice Boys from Scots College

2nd place – A Wellington College team

3rd place – A-Meme from Wellington College

The best team name went to, *We're in a bit of a* PCl_3 from Wellington Girls' College. However, this was somewhat contentious as there were some brilliant names including *Markovnikov and the funky bunch* from Samuel Marsden and *East Cis-ters* from Wellington East Girls' College. First place for best dressed went to *St Auran's golden girls* from St Orans with second going to *NaBrO* from Paraparaumu College. Other spot prizes included the Buckyball race, build a model steroid (complete with name and backstory), and recite the periodic table (a student from Tawa College got up to 75). *Amanda* ***Berger*** demonstrated three experiments (elephant's toothpaste, chemical traffic light, flame tests) all accompanied by a spot prize question. Thanks to all the student volunteers and Wellington Branch student liaison *Renee* ***Goreham***!

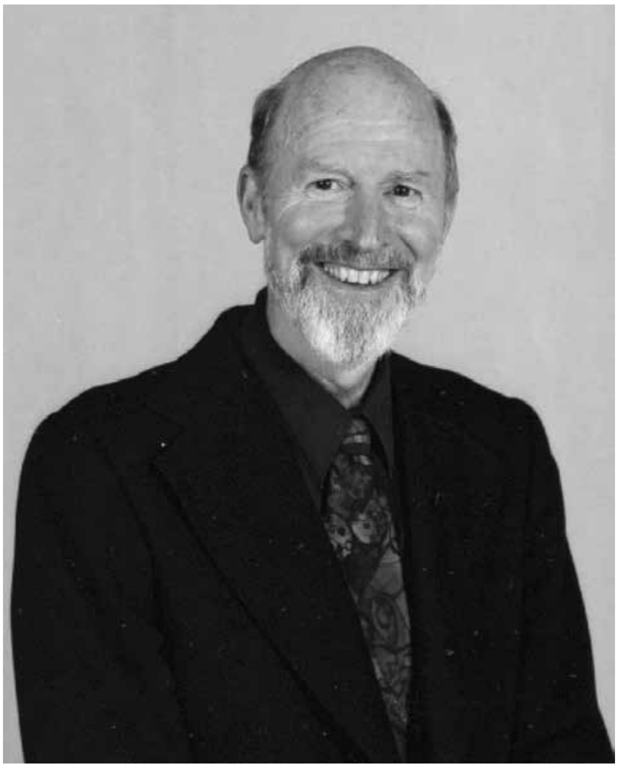
Taylor ***Cooney*** presented *Antigen loading in synthetic vaccines – is more better?* as an oral and a poster at the European Molecular Biology Laboratory (EMBL) Chemical Biology conference 2018 in Heidelberg, Germany, in late August. She was awarded an EMBL Advanced Training Centre CPP Fellowship.

Ryan ***Schwamm*** has been awarded an 1851 Fellowship and will be starting a postdoctoral project with Michael Hill in Bath. Ryan recently completed his PhD under the supervision of *Martyn* ***Coles***.

The Ferrier Research Institute won the Discovering Gold category at the 2018 Wellington Gold Awards for the development of the cancer drug Mundesine. The winners were announced at the TSB Arena on 5 July.

Andrew Martin Brodie PhD (Cant.), DSc, FNZIC, CChem, FRSC, 1945 – 2018

It is with great sadness but with many fond memories that we remember Andrew Brodie, who passed away peacefully surrounded by his family on Tuesday 7 August at the age of 73. Not only did Andrew contribute greatly to chemistry and to New Zealand science generally, but he was also a stalwart, and often a leader, of a remarkably diverse range of community groups. These included tramping groups, bridge club, Tai Chi club, church groups and trusteeship of Fergusson Hall, the Massey University Hall of Residence. All of these communities held him in the highest regard.



Apart from a year in Papua New Guinea when he was 10, Andrew spent his early life in Christchurch. Fresh from Cashmere High School, he was invited into an accelerated chemistry programme at the University of Canterbury in 1963 and in slightly less than 5 years – an outstanding achievement – had completed a BSc Honours degree and PhD in chemistry. The latter, with Professor Cuthbert (Cuth) Wilkins as his mentor, included no fewer than 5 high quality publications. Equally importantly during this time he met and married a fellow chemistry student, Carolyn Ramsay, and they set out for London in mid-1968. Andrew aimed high, taking a Postdoctoral Fellowship with Professor Jack Lewis (later Sir Jack, then Lord Lewis) at University College, London.

Returning from London to Palmerston North, where Andrew was to take up a lectureship in chemistry at Massey University, must have felt like a rather drastic step. Yet both the university and the city and its surrounding environment offered a remarkable freedom to develop both personally and scientifically. New research was developed, families grew and new friends were made. Ted and Heather Baker recall the many occasions when they and their children went camping at local beaches – and later on joint skiing holidays at Ruapehu – with Andrew and Carolyn and their growing family. Later on, Andrew and Carolyn also joined tramping groups to explore the back country in the Tararua and Ruahine ranges.

At Massey, Andrew found himself in a newly formed Department of Chemistry and Biochemistry that was still busy recruiting. Teaching loads were high, new courses had to be developed and resources for research were limited. Yet the sense of starting off together as young staff was also liberating; no worries about numbers of publications, performance criteria, PBRF or the like. Crucially, the Head of Department, Professor Dick Batt (a biochemist) and Head of Chemistry, Professor Geoff Malcolm, were enormously encouraging of new initiatives.

To build up research strengths, academic staff were encouraged to find common interests and work together. This led Andrew to a lifelong and remarkably productive and successful research partnership with Eric Ainscough, who had arrived some months later. Despite different ways of working – or perhaps because of this – they complemented each other perfectly. There were no egos involved; they simply both loved chemistry. Andrew was a superb supervisor of graduate students, totally supportive and helpful, but also giving them freedom to find their own way. Many of the students that he and Eric trained have gone on to exciting careers in various branches of science round the world.

Between them, Andrew and Eric published more than 130 papers together, shared graduate students, shared ideas and shared resources. It was entirely fitting that in 2007 they were jointly awarded the New Zealand Institute of Chemistry Prize for Excellence in the Chemical Sciences. The partnership ended with Eric's death in early 2017. Their last publications were a trio of papers in 2016. Much of their work was in metal coordination chemistry, but both Andrew and Eric had enquiring minds and other opportunities came from having chemists and biochemists together in one department. Thus, another strong theme of research was in bioinorganic chemistry, collaborating with Ted Baker in work on metalloproteins. This, too, led to many highly-cited publications. Andrew's adventurous spirit also came out when he and his family decided to spend a sabbatical year in Japan, in 1976. He told of his surprise when, on arriving at the airport his host presented him with great wads of banknotes (expenses for him and his family) and asked him to please count them, right there! There must have been big cultural adjustments to make, but for Andrew, Carolyn and their young family it was a very positive and enriching experience.

In the mid-1980s, Andrew became head of the Department of Chemistry and Biochemistry and then head of the Department of Chemistry when the Department of Biochemistry was formed. Science flourished under his gentle guidance and a new generation of chemists were hired in the mid to late 1990s. Andrew was a strong supporter of the New Zealand Institute of Chemistry, becoming its President in 2004, and also contributed greatly to science education at the secondary-tertiary interface; his award of a New Zealand Science and Technology Medal in 2007 recognised his exceptional contribution to the promotion of science.

In the early 2000s Andrew and Eric embarked upon two new areas of research: a wide-ranging exploration of metal complexes that featured a cyclotri- and cyclotetraphosphazene core (alternating P and N atoms) with pendant arms attached to the P-O groups bearing metal-coordinating ligands. This work, supported by the Marsden Fund of the Royal Society of New Zealand and in collaboration with Professor Harry Allcock, Penn State University, extended also to polymeric phosphazene systems. The other area, for which chemistry technician Graham Freeman prepared many of the complexes, was in metal(I)-halo complexes of bulky phosphane ligands. Some remarkable metal(I)-halo clusters were characterised. Structural characterisation by X-ray diffraction was a key technique and Andrew had enduring partnerships with first Joyce Waters, then Tony Burrell and Geoff Jameson.

On retirement in 2009, Andrew was made Professor Emeritus and as indicated by the flow of publications remained actively engaged in chemistry.

Andrew was a proud and supportive father of five children and a loving husband to Carolyn. His empathy to others carried over into all he did. His teaching was characterised by order and quiet enthusiasm; his leadership by careful listening and advocacy of chemistry; his research by thoroughness and accuracy. His papers enjoy a long shelf-life and a high average citation rate. Thus, his research lives on to inform succeeding generations of chemists.

Contributed by Ted Baker and Geoff Jameson

Pacifichem 2020

The Pacifichem2020 congress is on track to be as successful as Pacifichem2015. The organising committee received 380 first round symposia submissions which is similar to 2015 levels. The committee has taken a more active role in locating gaps in the programme and coordinating symposia across different topics, and the call for second round symposia will be targeted towards the areas that the committee feels are missing.

I'd like to thank the NZIC members that are part of the contributed symposia so far. I'd also like to thank the NZIC symposia reviewers - the NZIC was second only to the Canadian Chemical Society in terms of active reviewers and this was a great effort given our relative size and that we asked for 3 extra reviewers in 2020. This is one area that NZIC can make a contribution to Pacifichem on an equal footing with the larger societies, so our reviewer efforts are certainly appreciated and are noted by the organising committee too (and this was a point that I stressed when the profit sharing was re-negotiated after 2015, so I am very pleased that we have been able to deliver on the reviewing efforts).

To make the most of the new profit sharing arrangement the NZIC should aim to encourage as many members as possible to attend the 2020 congress. Even a handful of extra attendees will make a significant difference to the NZIC return from 2020.

There are some changes for 2020. The student poster competition will become a student research competition where the format will be a "2 minute thesis" presentation. Entry is open to all current students. Entrants will submit their presentation slide for judging in the first round and the best 240 entrants will be taken through to the second round which is the presentation round.

Mark Waterland

New chemical space for the discovery of bioactive compounds

Daniel J. Foley

School of Physical and Chemical Sciences, University of Canterbury
(email: *daniel.foley@canterbury.ac.nz*)

Keywords: *molecular discovery, synthetic chemistry, 3-D fragments, hit optimisation*

Dan was born in 1989 and grew up in the UK. He carried out his undergraduate studies at the University of Manchester (2007–2011), which included an industrial secondment at Syngenta, before completing his PhD (2011–2015) with Prof. Steve Marsden and Prof. Adam Nelson at the University of Leeds. Dan subsequently held an EPRSC Doctoral Prize Fellowship (2015–2017), which he carried out at Leeds and the Diamond Light Source. Further postdoctoral studies (2017–2018) followed in the group of Prof. Herbert Waldmann at the Max Planck Institute of Molecular Physiology in Dortmund, Germany, where he held a Marie Skłodowska–Curie Fellowship. Recently, Dan joined the School of Physical and Chemical Sciences at the University of Canterbury. His research interests concern the synthesis of novel sp^3-rich compound libraries, the establishment of their biological relevance, and the development and application of synthetic toolkits to enable the reliable synthetic advancement of hit compounds towards leads and tools.

Introduction

The discovery of functional small molecules endowed with biomedically relevant activities is a significant challenge, with major implications towards the development of next generation pharmaceuticals and agrochemicals.[1–3] Novel molecular medicines typically take more than 10 years to develop and cost around US$ 2bn.[4] Approaches that can improve efficiency and productivity in this process are therefore of significant interest to the drug discovery community.[2,3,5] To enable molecular discovery in a target-agnostic manner, the systematic exploration of chemical space is an area of intensive ongoing research.[6] To realise this, the judicious development and application of enabling synthetic methodologies for the preparation of compound libraries (and optimisation of any subsequent hits) is of paramount importance.[1–3] My career has encompassed a number of projects that have sought to address the challenge of developing new routes to novel functional small molecules.[1,7–10] Here, I will briefly summarise some of the key strategies developed and discuss my plans to aid the discovery of the next generation of bioactive compounds.

Scaffolds in molecular discovery

A scaffold is a minimum core component of a compound series which ideally, once decorated with suitable peripheral substituents, binds to and effectively modulates a specific biological target. Historically, the over-exploitation of a small number of (typically flat, aromatic) scaffolds has led to the unsystematic exploration of chemical space,[6] limiting the number of suitable scaffolds available to address novel and intractable biological targets. For instance, an analysis of the CAS database found that around half of the 24 million cyclic compounds were based on just 0.25% of the known scaffolds,[11] a situation that has likely arisen because of the use of only a small number of reaction classes in discovery programmes.[12] Chemical space is vast, so guidelines have been defined to help chemists prepare compounds that are relevant to particular classes of functional small molecules. For example, ideal molecular properties (e.g. molecular weight, lipophilicity *etc.*) have been defined to facilitate the preparation of pharmaceutically relevant compounds (e.g. drugs,[13] leads[2] and fragments[5] - see Fig. 1a).[1] Recently, emphasis has been placed on the synthesis of scaffolds with diverse three-dimensional shapes featuring high fractions of sp^3-hybridised carbons, a property generally exhibited by natural products that has been shown to be valuable for the clinical progression of drug candidates.[14] With careful synthetic planning to prepare scaffolds bearing suitable functionalisable handles (amines, carboxylic acids *etc*), their molecular properties may be subsequently fine-tuned (by decoration with capping groups) towards use in a range of discovery applications (Fig. 1b).[1]

Methods to prepare diverse scaffolds

I have been involved in a range of investigations to prepare diverse molecular scaffolds.[7–10] Firstly, a 'bottom-up' (building) synthetic approach was investigated (Fig. 2a).[7,8] Alternative building blocks were exposed to a toolkit of reactions, which were pre-validated for robustness in the laboratory. Allylic alkylation of amino acid derivatives delivered key building blocks, which could then be cyclised using a suite of cyclisation methodologies (ring-closing metathesis, iodine-mediated cyclisations, lactamisations and Heck reactions) to give more than 20 novel scaffolds.[8] By using computational tools, virtual decoration of the scaffolds with typical medicinal chemistry capping groups demonstrated that they had the potential to

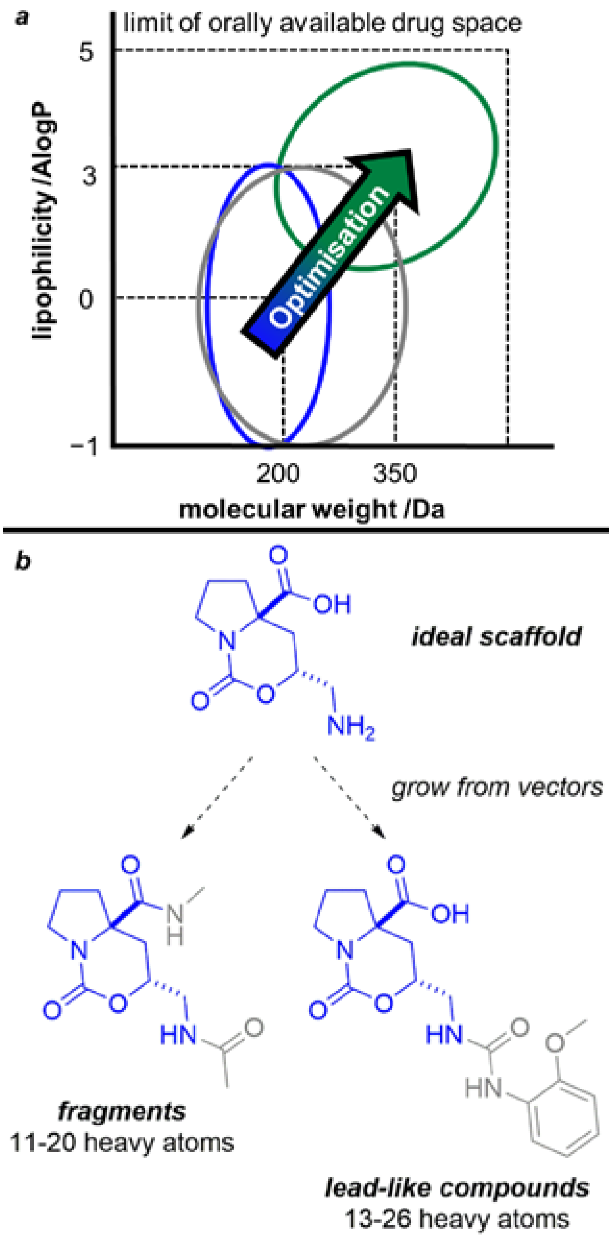


Fig. 1. **Panel A:** Useful chemical spaces for molecular discovery, including ideal scaffolds (blue ellipse), ideal screening compounds (including fragment and lead-like spaces, grey ellipse), and optimal drug-like space (green ellipse). Image adapted from ref. 2 and reproduced with permission. **Panel B:** An example of an ideal scaffold, and some decorated derivatives that would be suitable for different screening libraries.

provide access to valuable lead-like compound libraries. Secondly, a 'top-down' synthetic approach was investigated (Fig. 2b).[9] This concerned the preparation of a small number of complex polycyclic intermediates. These assemblies were designed to include functional handles which were then exposed to a suite of reactions to enable the ready modification of the core scaffold topology. [5+2] cycloadditions were used to prepare the polycyclic intermediates, which were then systematically modified to prepare over 25 scaffolds.

Demonstrating biological relevance

The scaffolds prepared were harnessed for use in alternative molecular discovery programmes.[9,10] As part of the European Lead Factory initiative, which is a public–private partnership that aims to produce novel lead and tool compounds, scalable synthetic routes to selected scaffolds were determined, and their utility for the preparation of screening compounds was established. Translation of the developed synthetic chemistry to the pharmaceutical company, Edelris, culminated in the synthesis of > 2900 medicinally-relevant compounds with properties appropriate for early-stage molecular discovery.[10] These compounds are currently undergoing screening in a wide variety of biological assays. Furthermore, decoration of the scaffolds using a range of small capping groups provided a collection of > 50 fragments. The collection was screened against a range of epigenetic proteins using high-throughput fragment soaking and X-ray crystallography at the Diamond Synchrotron.[9] A range of distinctive hits were identified against the cancer-related epigenetic proteins: bromodomains ATAD2 and BRD1, and the histone demethylase JMJD2D, which may have value for further development (Fig. 2c).

Future directions

The discovery of novel bioactive compounds remains an ongoing challenge, particularly with a view to generating starting points for drug discovery that have a high probability of successful progression (i.e. that are biologically effective and have favourable toxicological profiles). Furthermore, the discovery of reliable chemical probes for specific biological targets is often the key stimulus that promotes new research activity to understand novel molecular processes underpinning disease.[15] Organic synthesis will continue to play a crucial role in realising these processes.[3,5]

Fragment-based drug discovery (FBDD) is an established strategy that has culminated in the investigation of more than 30 compounds in clinical trials, along with two approved drugs.[16] FBDD enables the efficient exploration of chemical space by screening collections (~ 100-1000) of small compounds (typically ≤ 20 heavy atoms) using biophysical techniques (e.g. X-ray crystallography and NMR spectroscopy). Fragment hits tend to be weak binders (typically µmol-mmol affinity), yet frequently form high quality interactions with the target that often need to be maintained for successful hit-to-lead progression. Commercial fragment libraries have historically been dominated by flat (het)aryl compounds.[17] In contrast, sp^3-rich 'three-dimensional' fragments have tended to be underrepresented in screening collections, and their value in FBDD remains an open question that has not been systematically investigated. It has been suggested that the introduction of more shape-diverse fragments into screening collections may enable modulation of more challenging molecular targets.[16,17] The paucity of sp^3-rich fragments in screening collections may have arisen due to challenges in preparing such compounds, and because toolkits to allow the reliable synthetic optimisation of any derived hit compounds from unconventional growth vectors (e.g. from carbon centres rather than from heteroatom centres) are lacking.[5]

I intend to focus my research efforts on the synthesis of new sp^3-rich fragments, the investigation of their biologi-

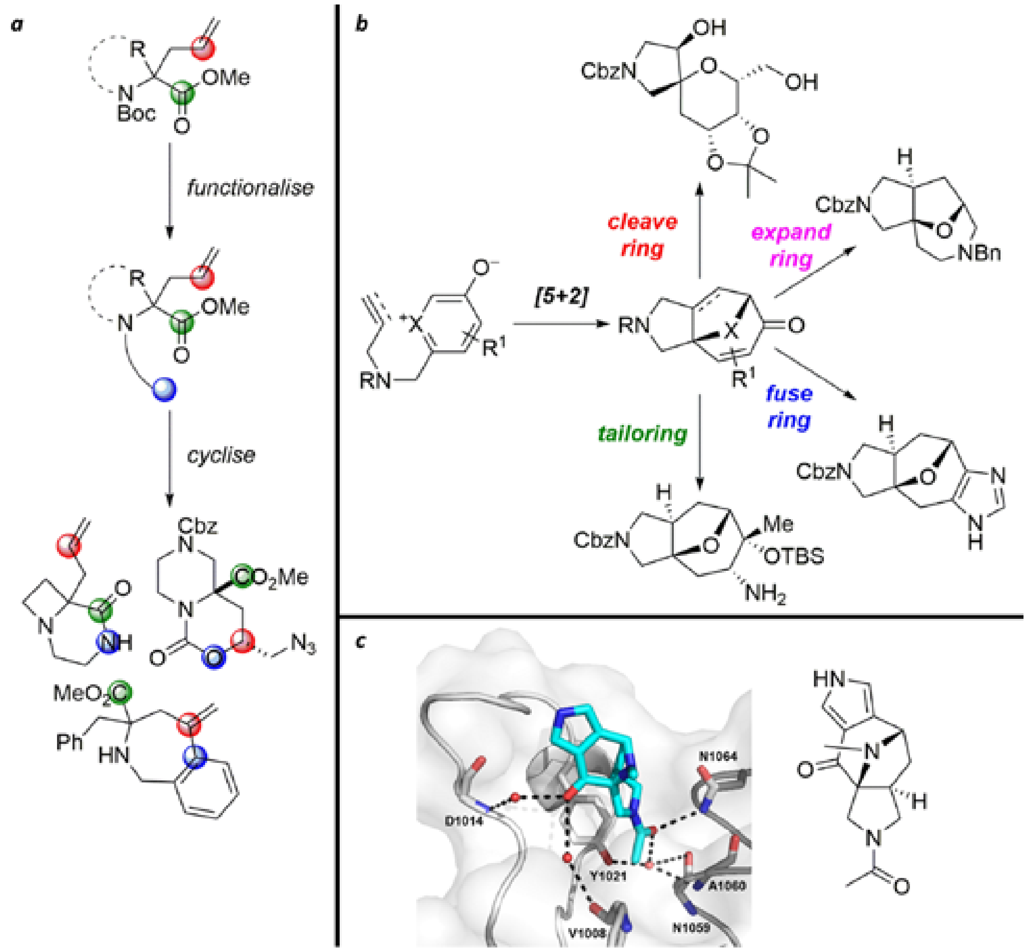


Fig. 2. Strategies to prepare scaffolds. **Panel A:** A bottom up approach to diverse scaffolds. Image adapted from ref. 8 and reproduced with permission. **Panel B:** A top down approach to scaffolds. Image adapted from ref. 9 and reproduced with permission. **Panel C:** An example of a fragment hit bound to the bromodomain of ATAD2. Image adapted from ref. 9 and reproduced with permission.

cal relevance, and the development and application of synthetic toolkits that may enable the synthetic advancement of hits towards higher affinity compounds (leads and tools). I would be very interested in collaborating with researchers who are looking to investigate novel fragment libraries against interesting biological targets, and/or using new biophysical screening methods, along with researchers who are interested in investigating fragment libraries computationally (e.g. using virtual docking) with a view towards subsequent biological validation. I am excited to have joined the scientific community in New Zealand, and I look forward to establishing fruitful collaborations to realise these endeavours.

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Opening of the Rutherford Regional Science and Innovation Centre (RRSIC) at the University of Canterbury

The Ernest Rutherford building which accommodates a major proportion of the Rutherford Regional Science and Innovation Centre (RRSIC) was officially opened on 15 February 2018 by Prime Minister The Right Honourable Jacinda Ardern. The Ernest Rutherford building is the first of two new science buildings to be built for the RRSIC. The building is named after Ernest Rutherford, father of nuclear physics and UC's most famous alumnus. It is one of the only buildings in Australasia that combines multiple science disciplines in one space. With 20,000 square metres of floor space, it houses teaching and research laboratories for physics, astronomy, chemistry, geological sciences, geography and biological sciences.

Ernest Rutherford (1871–1937) was the father of modern atomic and nuclear physics - one of the greatest scientists of the twentieth century. Rutherford was born near Nelson in 1871. He entered the University of Canterbury, then called Canterbury College, in 1890. After three degrees and two years of research at the forefront of electrical technology of the day, he won an 1851 Exhibition Scholarship, which he took up at the Cavendish Laboratory, Cambridge. He made discoveries about radioactivity, transmutation of elements in nuclear interactions, and most notably the discovery that all atoms consist of a dense, charged nucleus surrounded by tiny electrons in mostly empty space. Rutherford was awarded the 1908 Nobel Prize for Chemistry and was later made a Baron (Ernest, Lord Rutherford of Nelson) for his contributions to science.

Cultural themes have been interwoven into the building, and the many communal spaces promote interaction. The design and feel of the Ernest Rutherford building is influenced by the concept of "Te Ara a Tāwhaki – the Pathway to Knowledge". Tāwhaki was an ancestor from Māori mythology who climbed the heavens and acquired great knowledge. The central atrium provides a central link and a major arterial route both up and through the building. Much like the journey taken by Tāwhaki through the heavens, students, faculty and visitors will move up the main staircase acquiring knowledge and encountering new experiences and challenges at each level.

This is a new era for science at University of Canterbury, one where excellence is at the forefront of everything we do – from teaching, research and learning, right through to the spaces where it happens. The new RRSIC is a hub for Canterbury's science and innovation network in state-of-the-art facilities that encourage collaborative teaching, learning and research.

KiwiNet
Kiwi Innovation Network

Green chemistry project aims to create lipids for nutraceuticals

HAMILTON, NZ, June 20, 2018 – Nelson research scientist Dr Ivan Kurtovic has received a $25,000 boost from KiwiNet's Emerging Innovator Programme for a green chemistry project to create specialised lipids for use in nutraceutical and functional food manufacture.

Dr Kurtovic, an enzymologist in the Marine Industrial Biotechnology Team at Plant & Food Research, is working on enzyme technology that transforms lipids to have higher levels of desirable fatty acids for nutritive and therapeutic applications.

Dr Kurtovic says, "The demand for sustainable green chemistry in industrial processes is increasing. Lipid transformation is often carried out using solvents or other techniques that are not environmentally-friendly. I'm exploring methods for enzymatic interesterification that can be used as an alternative, to achieve lipid transformations and produce highly bioavailable lipids enriched with Omega-3 fatty acids."

The Emerging Innovator funding has also allowed Dr Kurtovic to purchase several custom-built immobilised enzyme (lipase) reactors for transfer of the technology from the laboratory to prototype pilot scale. This has helped achieve the proof of principle needed to validate the new technology and attract further investment.

"Thanks to KiwiNet, this is the first time I've been able to scale up my enzyme research and to test improvements in a more industry-relevant way," says Dr Kurtovic. "I'm continuing to test different enzyme systems and optimise the scale up process to improve conversion and enrichment of the final product."

Dr James Hutchinson, CEO of KiwiNet, says: "One of New Zealand's fastest-growing food export categories is nutraceuticals. Consumers are increasingly interested in sustainable, natural and environmentally friendly products. Ivan and his team at Plant & Food Research are developing valuable enzymatic methods for creating lipids for the therapeutic market. This research represents a great commercial opportunity for industry, in New Zealand and farther afield, to develop IP that can be used in their processes."

Sue Muggleston, Intellectual Property Manager and Business Manager at Plant & Food Research, says: "It's been fantastic working with Ivan, KiwiNet and partners to progress the commercial application of this research. In conjunction with an industry partner, we're keen to further develop the commercial potential of this technology and make the most of opportunities in the nutraceuticals market."

Dr Kurtovic, who completed his PhD at McGill University in Canada in 2011 while on sabbatical from Plant & Food Research, says his biggest takeaway from the Emerging Innovator Programme is being able to appreciate the transition from pure research to scale up, and then to commercialisation. "It's been invaluable learning how to simplify and present my story, how to engage with IP experts, to understand how research can be commercialised and what the steps are. I now have the confidence to attempt further scale ups and further applications of my research."

The KiwiNet Emerging Innovator Programme, open to early career researchers based at universities and Crown Research Institutes across New Zealand, is designed to enable researchers to partner with a business and refine their project for market. It also boosts research with a commercial application at a critical time.

Programme recipients receive expert legal advice from KiwiNet corporate partner MinterEllisonRuddWatts and IP advice from Baldwins, as well as $25,000 in cash towards the project from donations from the Norman F. B. Barry Foundation, which owns the Quality Hotel Parnell Limited.

John Smith, Chairman of the Norman F. B. Barry Foundation says, "KiwiNet and the Foundation share the common goal to inspire young scientists to seek out opportunities to apply their knowledge to benefit the community and the economy. We're very proud of Ivan and the other emerging innovators – they're creating some seriously clever science with a commercial focus."

Further information:

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About KiwiNet Emerging Innovator Programme

The KiwiNet Emerging Innovator Programme was established in 2015 by KiwiNet with the generous philanthropic support of the Norman F. B. Barry Foundation. The aim of the Emerging Innovator Programme is to have more scientists with disruptive new ideas working alongside businesses to solve industry challenges. It is open to scientists from public research organisation who demonstrate a clever new idea and a willingness to work closely with industry as they develop a prototype. The KiwiNet Emerging Innovator Programme is available to early career researchers based at universities and Crown Research Institutes across New Zealand.

About the Kiwi Innovation Network (KiwiNet)

Since its inception, the Kiwi Innovation Network (KiwiNet) and the wider Commercialisation Partner Network have demonstrated the power of bringing together diverse players across the science & innovation ecosystem to work towards a collective vision for New Zealand: a globally-competitive technology sector that delivers significant economic growth and prosperity. KiwiNet partners are dedicated to creating growth for our country through a collaborative approach to research commercialisation. By leveraging the combined capability of NZ's research organisations and increasing the scale and impact of scientific and technology based innovation, KiwiNet is achieving greater commercial outcomes for New Zealand. KiwiNet partners are Plant & Food Research, Callaghan Innovation, AgResearch, Otago Innovation, Landcare Research, Lincoln University, University of Canterbury, Viclink, WaikatoLink, AUT Enterprises Ltd, Cawthron Institute, Environmental Science & Research, NIWA, Scion, GNS Science and Malaghan Institute. Principal support is also provided by the Ministry of Business, Innovation & Employment (MBIE).

About the Norman F B Barry Foundation

The Norman F B Barry Foundation, is a charitable trust registered under the Charities Act 2005. Norman Barry was an entrepreneur and a philanthropist who established the Quality Hotel Parnell. During his successful business career he mentored motel owners in Auckland who were new to the industry and helped various charitable organisations in the form of donations. Norman left his shareholding in Quality Hotel Parnell Limited to the Foundation, and the distributions from this Company to the Foundation are used for charitable donations. In addition, Quality Hotel Parnell Limited is also a registered charity in its own right and this company also makes donations to the community. More: http://www.theparnell.co.nz/charity

The recovery of precious metals from electronic waste

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Keywords: *gold extraction, biometallurgy, electronic waste*

Electronic waste (e-waste) represents one of the world's fastest growing waste streams. It is estimated that approximately 45 million tonnes of e-waste will be generated worldwide this year, of which New Zealand is responsible for the production of 95,000 tonnes.[1] The majority of this e-waste ends up in landfill; not only is this destructive to the environment,[2] it is a missed opportunity. The value of metals in New Zealand's annual e-waste, such as gold, palladium and copper, is worth over NZ $100 million. Furthermore, the extraction of precious metals from virgin ore is becoming an ever more challenging task as the quality of known ores decline. Demand for some metals is expected to outstrip their known global reserves.[3] These factors render alternative feedstocks, such as e-waste, worthy of further consideration.

Despite the value of this "urban ore", there are only a few specialised smelting facilities in Europe and Asia that are equipped to conduct the recovery process safely. Unfortunately, this means that e-waste is regularly shipped to developing nations to be processed in what is often an unregulated and unsafe fashion at a rudimentary scale. E-waste is a notoriously difficult feedstock to process, which contributes to why it consistently ends up in landfill. Mint Innovation (Fig. 1), a cleantech start-up company based at Auckland's Level Two innovation hub, has developed a unique biometallurgical approach to recover precious metals from e-waste. At present, the most cost-effective hydrometallurgical processes use cyanide as a ligand to extract and concentrate gold.[4] However, its inherent toxicity inhibits cyanide use within an operational plant in a metropolitan environment, where the majority of e-waste originates.

Driven to design a process that is both scalable to requirement and safe to operate in an urban centre, Mint's technology utilises a non-cyanide leaching chemistry to dissolve metals from finely ground electronic scrap material. At this stage the key component of the process, naturally isolated microorganisms, are employed to target certain dissolved metal ions for binding. The desired metal ions are reduced to their elemental form and are amassed in the periplasmic space within each cell.[5] In Mint's process, biomass that is now enriched with the

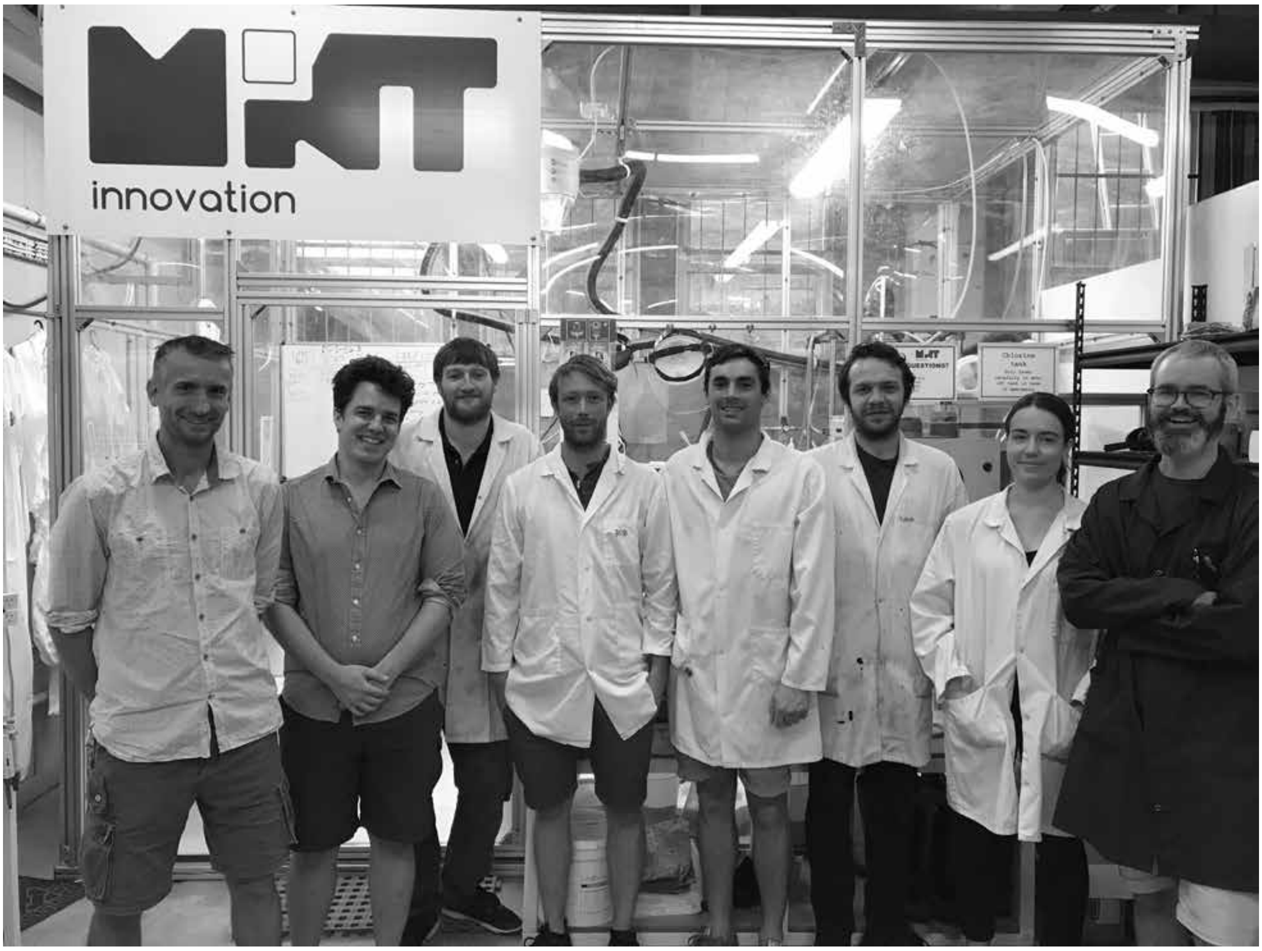

Fig. 1. The Mint Innovation team (left to right) – Will Barker, Jason Herbert, Reece Whitby, Robert Staniland, Nick Moleta, Ryan Smith, Danielle Maynard and Ollie Crush

target metal is collected. In the case of gold, the gold-rich biomass appears as a purple powder due to the nanoparticular nature of the bound gold. The significance of using microorganisms is that they allow for the selective concentration and collection of dissolved gold ions from very dilute solution, which otherwise remains a substantial challenge for non-cyanide chemical processes at a large scale.

Mint's system has been established to be effective and high yielding at a bench scale. The company's current efforts are now focused on scaling up this process. A pilot plant has been built in Parnell and has been operating this year, which is capable of processing kilograms of e-waste at a time. The next milestone is to construct a demonstration plant in Auckland that can process up to a tonne of e-waste per day, whilst recovering kilos of precious metals per year. The use of relatively benign chemicals and the high recyclability of many components in the process should allow for the construction of a plant which has a similar environmental footprint of a microbrewery. When Mint's process is compared to mining and extracting metals from virgin ores, recycling a tonne of e-waste (including collection, transport and processing) effectively offsets the creation of a tonne of carbon dioxide emissions by the mining of the equivalent raw materials.

After the construction and development of the demonstration plant, Mint's focus will shift to constructing their first commercial facility, designed to be capable of processing the e-waste produced from a large city. For example, a Mint plant in the state of Victoria, Australia, could be scaled to process 2,000 tonnes of e-waste per year while recovering 400 kg of gold and 400 tonnes of copper. From here, Mint plants will be rolled out around the world, each designed to a suitable scale for local market requirements. This will mark a shift from the current disposable culture of electronic devices, to a circular economy in which the major components of our electronic devices can find a second life.

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All that glitters is not gold: manuka honey and the issue of authenticity

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Keywords: *manuka, honey, authenticity, principle component*

Darren Saunders holds a BSc in chemistry from the University of Canterbury and an MSc in pharmacology from the University of Otago. He was the scientific officer for the Clinical Pharmacology department at the Christchurch School of Medicine for 10 years, being primarily involved in developing analytical methods for the analysis of drugs and endogenous compounds in clinical samples. For the last 20 years Darren has worked in the ESR Christchurch Science Centre Food Chemistry Laboratory conducting food forensics investigations and research for clients such as MPI involving analytical method development, particularly for analytes rarely assayed by the other main laboratories. He was promoted to senior scientist in November 2016. Darren has contributed a number of papers to *Chemistry in New Zealand*, ranging in subject matter from cyanide and mould toxins in foodstuffs to the authenticity of olive oil and fruit products and the history of chemistry.

Sarah Molyneux received a PhD in clinical chemistry from the University of Canterbury in 2006. Her PhD research, carried out at Canterbury Health Laboratories, involved analysis of coenzyme Q_{10} in human plasma and clinical trials with coenzyme Q_{10} supplementation. After completion of her PhD, this work was continued with the support of a Heart Foundation of New Zealand Research Fellowship. After a period of maternity leave Sarah worked part time as a scientific officer at Canterbury Health Laboratories. Sarah now works as a scientist in the Food Chemistry team at ESR in Christchurch.

Introduction

Honey is a completely natural product defined as the sweet substance produced by honey bees from nectar of blossoms or from secretions of living parts of plants or excretions of plant sucking insects on the living parts of plants which honey bees collect and store in honeycomb to ripen and mature.

Honey is primarily a highly concentrated solution of complex sugars (~80%, with water making up approximately 17%) and suspended particulate matter including (depending on degree of processing) particles of wax, pollen, yeasts, bacteria and fungal spores and hyphae. Non-sugar components include organic acids, enzymes, vitamins, acetylcholine, flavonoids, minerals and a wide variety of organic chemicals in trace amounts that give honey its taste and aroma. The sugars in honey are composed primarily of glucose and fructose (85-95% of total carbohydrate content) with slightly more fructose than glucose (average ratio 1.2:1). Sucrose comprises about 1.5% with the remainder being made up of other di- and oligosacharrides. Fructose is much more soluble than glucose, the latter is frequently present in honey at super-saturated levels which can lead to the formation of fine crystals that give many honeys their creamy appearance.[1]

Human use of honey can be traced back at least 8000 years courtesy of stone age paintings that depict ancient men climbing trees, smoking torch in hand, heads surrounded by a halo of angry bees. Prior to the discovery of a means of turning sugar cane juice into granulated crystals (India, 5th century CE) honey was the main sweetener in existence. According to the Greek historian Plutarch before man knew wine, he fermented honey (mead) as drink.[2] The ability of honey to preserve biological specimens was recognised quite early, with the body of Alexander the Great (356-323 BCE) thought to have been preserved in it.[3] Already well known by the time of soldier and historian, Xenophon (427-355 BCE) was the ability of bees to significantly concentrate the components of nectar derived from plants such as the rhododendron producing toxic honey that might be used to incapacitate enemies, or in dilute form as a medicine.[4] New Zealand has its own particular issue in this respect in the form of the toxin tutin, a poison derived from the tutu bush which is fed on by the passion vine hopper that produces a honeydew exudate that bees feed upon.

Honey is one of the oldest and most popular medicines. In addition to being employed to embalm the dead, it is described as a standard wound salve in the ancient Egyptian Smith papyrus dating from between 2600 and 2200 BCE and features as an ingredient in hundreds of medicinal recipes. Greek philosophers and physicians Aristotle, Hippocrates and Galen to name a few lauded its benefits for the treatment of almost every ailment imaginable from baldness and constipation to wound healing and eye disease. Honey also features strongly in Indian Ayurvedic tradition as a one of nature’s most remarkable gifts to humanity, a boon to good digestion, a treatment for coughs, skin disorders, cardiac pain and imbalances of the lungs.[5]

Antibacterial effects

Honey has been shown to be bactericidal to many pathogenic microorganisms in *in vitro* studies and when used topically (there is no evidence of efficacy when honey is taken orally). This antimicrobial activity is a result of osmotic (water drawing) effect, acidity, hydrogen peroxide and phytochemical factors, e.g. polyphenols. Honey is a supersaturated solution of sugars resulting in very little water being available for microorganisms. Free or biologically available water is measured as Water Activity (a_w, on a scale from 0 to 1.00). Pure water has an $a_w = 1.00$ while a saturated salt (NaCl) solution has an $a_w = 0.76$. A_w values for honey range between 0.562 and 0.62. Many species of bacteria are completely inhibited if water activity is in the range of 0.94 to 0.99.

Honey is also quite acidic with a pH of between 3.2 and 4.5, low enough to be inhibitory to many animal pathogens. Hence, in undiluted honey, acidity is a significant antibacterial factor.

Hydrogen peroxide (H_2O_2), a potent antiseptic, is produced enzymatically in honey. The glucose oxidase enzyme is secreted from the hypopharyngeal gland of the bee into nectar to assist in honey formation. The acidity and H_2O_2 are produced according to Eq. 1:

$$\text{Glucose} + H_2O + O_2 \rightarrow \text{Gluconic acid} + H_2O_2 \qquad \text{(Eq. 1)}$$

On dilution of honey, the H_2O_2 activity increases by a factor of 2500 to 50,000 and is the most significant contributor to antibacterial activity in most honeys.[6]

Phytochemical factors are complex phenols and organic acids frequently referred to as flavonoids. Flavonoids are also found in abundance in propolis, the mixture of plant resins, wax, essential oils and pollen used by bees as a sealant.[7]

Antibacterial activity is determined by the agar well diffusion method which measures the extent to which *Staphylococcus aureus* is inhibited with reference to a phenol standard. The antibacterial activity of honey is highly variable and depends on floral source, processing and storage conditions of the honey.[6]

Manuka - the uber honey

A small number of honey varieties show *in vitro* antibacterial activity above and beyond that conferred by the presence of hydrogen peroxide, i.e. antibacterial activity that remains after neutralisation of hydrogen peroxide. Such activity is commonly referred to as "non-peroxide activity" (NPA). Manuka honey, produced from *Leptospermum scoparium* found in New Zealand, is the most prominent of these honey varieties. Manuka is the common name used for the specific species *Leptospermum scoparium* in New Zealand. The Australian industry tends to use manuka to mean all species in the genus, but from a NZ perspective this is not valid and the name refers specifically to honey derived from *Leptospermum scoparium*. NPA has been used in various industry grading systems for manuka honey including the "Unique Manuka Factor" (UMF) a trademark registered by the UMF Honey Association (UMFHA) available to use under licence by producers of manuka honey in New Zealand.[6]

The compound methylglyoxal (MGO, Fig. 1) was subsequently found to be present at high concentrations (compared with non-manuka varieties) in manuka honeys that exhibited NPA and that the levels found correlated broadly to the UMF of the honey.[8] UMFHA now use MGO, dihydroxyacetone (DHA) and leptosperin to grade manuka honey. Interestingly, MGO in water has less than half the antibacterial activity than the same concentration in honey.[9] MGO reacts rapidly with arginine, lysine and cysteine amino acids in proteins to form advanced glycation products (AGEs) as well as amino-containing lipids and nucleic acids. There is clearly a synergy between MGO and other honey components to produce the NPA. When MGO is neutralised manuka honey still retains *in vitro* antibacterial activity due to several unknown factors.[8,10]

The nectar from manuka flowers does not contain MGO but does contain high levels of DHA (Fig. 2). The MGO in honey is created over time from the interaction of DHA with various proteins and amino acids in the honey.[8]

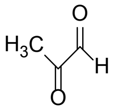

Fig. 1. Methylglyoxal

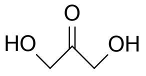

Fig. 2. Dihydroxyacetone

Manuka honey has many features that make it a promising treatment for wound care. Manuka honey can inhibit a diverse range of bacterial and yeast pathogens and is effective against multi-drug resistant bacteria and has also been found to prevent the formation of biofilms. Resistance to manuka honey has never been observed or induced in the laboratory.[11] Consequently, manuka honey is used not only as raw honey but in any number of other products including skincare, soaps and lotions, throat lozenges and cough medicines, food and beverages.

Liquid gold

New Zealand is the world's third largest honey exporter, with export revenue that grew at an annual rate of 23% between 2005 and 2015. This growth was primarily fuelled by manuka honey sales which accounted for between 75 and 80% of the value of honey exports. Total honey exports in 2015 were worth $285 million, of which manuka honey accounted for $221 million.[12] In 2016 the value of New Zealand honey exports rose to $315 million. In 2017 the value of light clover honey (i.e. the price paid to beekeepers for bulk honey) ranged from $10.00 – $14.00/kg, the value of manuka honey ranged from $10.80 – $127/kg. A total of 14,855 tonnes of honey was produced in New Zealand in 2017 (9,245 tonnes in the North Island, 5,610 tonnes in the South Island) of which 8,450 tonnes was exported.

In 2017, China was the largest export destination for New Zealand honey followed by the United Kingdom, Australia, Japan, the United States, Singapore, the EU, Hong Kong and the rest of the world in descending order.[13] Of course while manuka honey is the biggest earner due to its value compared with other varieties it makes up a relatively small percentage of the total mass of honey produced in New Zealand.

All that glitters is not gold

Honey is a valuable commodity and as such has been prone to adulteration in order to extend it. Adulteration of honey has been going on for thousands of years. Grape juice was added to honey in ancient Roman times as an extender and an Act passed in England in 1581 referred to the selling of 'deceitful mixtures' as honey. The degree of adulteration ranges from adding small amounts of water or sugar to honey to the sale of a totally artificial product.

The maximum content of water in honey permitted in the *Codex Alimentarius* is 21%. Many honeys contain less than 21% water leaving room to extend honey by the addition of water. Honey volumes can also be enlarged by addition of sugar or syrup either to the final product or as feed for bees with the addition of high fructose corn syrup being the most popular extender used in recent times. Such adulteration can frequently be detected by measuring isotopic ^{18}O:^{16}O, ^{2}H:^{1}H ratios (water) and ^{13}C:^{12}C ratios (added sugars).

In addition to extending honey other forms of adulteration may involve marketing heat treated honey as 'raw' or as originating from a particular botanical source when it does not, the latter being of particular concern in regards to manuka honey.

The temptation to extend or otherwise fake manuka honey is considerable given that the cost of the genuine product can be an order of magnitude higher than regular varieties.[1] New Zealand produces approximately 1700 tonnes of manuka honey annually. Historically accurate production figures are difficult to determine as neither MPI nor industry had an agreed definition of manuka honey and estimates of production vary considerably. Regardless, the annual global consumption was recorded as approximately 10,000 tonnes! The UK alone consumed New Zealand's official annual production.[14] Even taking into consideration the uncertainty in the production estimates, it appeared that substantially more manuka honey was being sold than produced.

One of the most commonly used means of determining honey floral source is the examination of pollen. Pollen grains from different types of plants have a distinctive morphology that allows the family, genus or often the individual species of plant to be identified… mostly.[1]

The microscopic pollen analysis of honeys (melissopalynology), has its limits in reference to authentication of manuka honey as manuka pollen and kanuka (*Kunzea ericiodes*) pollen appear identical. Manuka and kanuka have similar flowering periods and can be difficult to tell apart in the field, therefore, manuka honey may contain a proportion of kanuka nectar. In contrast to manuka honey, kanuka honey shows only weak *in vitro* anti-bacterial activity and can be up-graded to 'manuka' honey by the addition of MGO or its precursor, DHA, both of which can be purchased off the shelf relatively cheaply from chemical suppliers making determining MGO content in honey less than helpful as a marker of authenticity.[15]

The need to be able to authenticate manuka honey was manifest but pollen used to identify the floral source of many honeys could not be employed. This led to a search for other chemical markers that would enable the identification of manuka honey (whether mono- or multifloral) in order to reassure overseas regulators and consumers who desired a Government-backed definition to safeguard the authenticity of manuka honey products.

In search of manuka's unique chemical fingerprints

Pollen analysis may be problematic and DHA/MGO levels far from definitive in reference to fingerprinting manuka honey but honeys still contain many non-sugar components with the potential to act as authenticity markers including a multiplicity of phenolic and other compounds along with volatile components specific to various floral sources.

Leptosperin

Leptosperin (Fig. 3) was a compound thought to be a unique marker for manuka honey as it is present only in the flower of *Leptospermum scoparium* and some other *Leptospermum* species found in Australia. New Zealand manuka honey exhibits unique fluorescence signatures that distinguish it from other honey types. One marker is the MM1 fluorescence marker (λ_{ex} = 270 nm, λ_{ex} = 365 nm) which is due to the presence of leptosperin. Leptosperin is also present in the woody-fruited Australian *Leptospermum* species (at levels significantly higher than those found in New Zealand) and is also stable over prolonged storage at 37°C. These findings suggested fluorescence spectroscopy could offer a rapid screening method for identification of *Leptospermum* honeys. Indeed, a handheld fluorescence-based detector was launched commercially in 2015, developed by UMFHA in collaboration with Analytica Laboratories and Comvita. The device acts in a similar manner to a breathalyser detecting potential issues with a honey sample which can then be forwarded to a suitable laboratory for further analysis. Leptosperin, however, gives a similar fluorescence signal when added to clover or artificial honey varieties.[16]

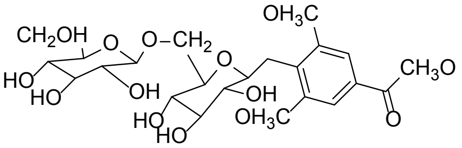

Fig. 3. Leptosperin

Well aware of the drawbacks of relying on MGO levels and pollen analysis as markers of manuka honey authenticity, between 2014 and 2016 MPI led a 3 year manuka honey science programme to develop criteria for identifying manuka honey from New Zealand.[17]

Many analytical techniques have been brought to bear in reference to honey authenticity determinations including chemical analysis of volatile and non-volatile components, Fourier transform infrared (FTIR) spectrometry and DNA analysis.[15,18-21]

Analysts often took a scatter-gun approach comparing GC or HPLC UV-VIS profiles of different honey varieties in an effort to tease out and identify compounds that might act as potential markers of authenticity.

Of particular interest in regards to our research (described briefly in the following section) were the papers of Daher and Gulacar[19] and Beitlich *et al.*,[15] the latter was especially fruitful as it examined not only manuka honey and kanuka for characteristic compounds of interest but also Australian jelly bush honey derived from a close relative of New Zealand manuka bush and often marketed as manuka honey. While the Australian industry is relatively small compared with New Zealand production (which is worth approximately 10 times more), there has been considerable resistance from Australian producers in regards to New Zealand producers' efforts to trade mark manuka honey.[22]

ESR Food Chemistry Laboratory Pioneer Project

Given the ongoing interest in manuka honey research our group applied for an ESR Pioneer Grant to investigate chemical markers of manuka honey authenticity.

***Aim*:** Our project sought to place the qualitative findings of previous researchers in reference to possible marker compounds on a firmer quantitative foundation in an effort to differentiate between manuka honey (derived from the species *Leptospemum scoparium*), blended manuka honey, non-manuka honey, kanuka and Australian "manuka" honeys (derived from various species in the genus *Leptospermum*). Primary standards of possible marker compounds were procured and their levels in a variety of honey samples determined.

***Samples*:** A total of 71 samples of honey were acquired for analysis: manuka (n=18), manuka blends (n=9), Australian sourced manuka honey (n=7), kanuka honey (n=4) and non-manuka varieties (n=33). Non-manuka honeys included: rata, clover, beechforest honeydew, thyme, kamahi, tawari, rewarewa, borage, pohutukawa varieties. All samples, manuka (mono- and multifloral) and non-manuka varieties, were purchased from local providers in Christchurch, ordered online from within New Zealand or imported from Australia through online vendors.

***Marker compounds*:** These were chosen because they are found in abundance in manuka honey or previous researchers had identified them as possible markers for manuka or other honey varieties of interest: *p*-anisaldehyde, 2'-hydroxyacetophenone, 4-hydroxyphenyllactic acid, 2-methoxybenzoic acid, 4-methoxybenzoic acid, 2-methoxyacetophenone, 2-methylbenzofuran, methyl-3,5-dimethoxybenzoate, methyl syringate, 3-phenyllactic acid, p-propylanisole and 3,4,5-triphenol.

Manuka (Australian and New Zealand produced), blended manuka and kanuka samples were also tested for MGO content by Ultra High-Performance Liquid Chromatography (UHPLC) with diode array detection (the non-manuka samples were not tested due to time and financial constraints).[23]

Method: (in brief) ~1.5 g of honey was accurately weighted into a 50 ml centrifuge tube and made up to 5 ml with 0.1M HCl. Samples were analysed using a Shimadzu Nexera X2 UHPLC equipped with diode array and fluorescence detectors using a gradient elution.

Column: 150 x 2.1 mm, 1.8µm Zorbax Eclipse Plus C18

Mobile phase: A = 0.1% v/v trifluoroacetic acid, B = 100% acetonitrile

Detection: UV @ 205 nm or fluorescence at ($\lambda_{ex}/\lambda_{em}$): 300/350, 250/340, 280/350 and 250/300 nm

Flow: 0.5 ml/min

Inj. vol: 10 µl

Standard curves comprised of mixed solutions of the compounds listed above were prepared in the following concentrations: 20, 10, 5, 2 and 1 mg/L.

Results and discussion

The MGO compositions of 38 pure and blended Manuka and pure kanuka sample are presented in Table 1. On average pure Manuka had higher MGO than either kanuka of blended Manuka. The range of NZ Manuka samples overlapped with the ranges of all the other samples.

***Table 1*.** GO concentrations (mg/kg) in kanuka and manuka honeys

Samples	MGO mean mg/kg (range)
Kanuka (NZ) (n = 4)	26 (3-41)
Manuka (NZ) (n = 18)	109 (19-415)
Manuka (Aust) (n = 7)	118 (70-208)
Manuka (NZ) blends (n = 9)	17 (4 – 47)

The results from analysis of the concentrations of the marker compounds in individual honey samples are summarised in Fig. 4.

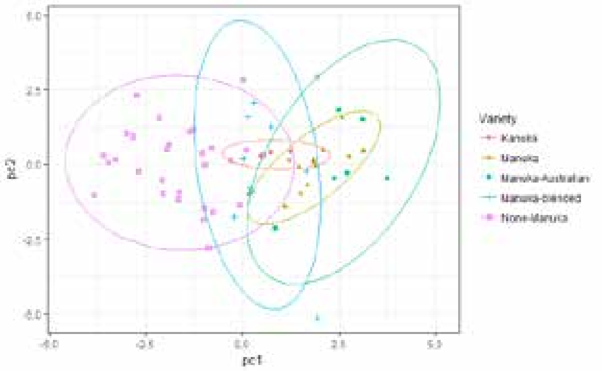

***Fig. 4*.** First two components of PCA from various varieties of honey

It is important to note in Fig. 4 that the ellipses, which represent the normal confidence interval, are not fully overlapping. They occupy different areas in the principal component space. This means that there is a possibility to differentiate honey varieties based on their composition.

It is encouraging to see that manuka-blended honey sits between manuka and none-manuka, as might be expected for a mixture. The fact that the manuka and none-manuka do overlap, at least in PC1-PC2 space, means that for some compositions of honey, there will be some uncertainty as to which variety of honey a sample belongs too. But no classification method is perfect.

The key variable that appears to differentiate manuka and non-manuka is PC1. The following six analytes load onto PC1:

2-MEB = 2-methoxybenzoic acid

2'-HA = 2'-hydroxyacetophenone

3-PL = 3-phenyllactic acid

4-MEB = 4-methoxybenzoic acid

Methyl-3,5- = methyl-3,5-dimethoxybenzoate

MS = methyl syringate

The results from the PCA gave enough confidence to take the analysis further.

Classification tree

A similar dataset to that employed in the principle component analysis was run through a classification tree. The overall correct classification rate was approximately 87%.

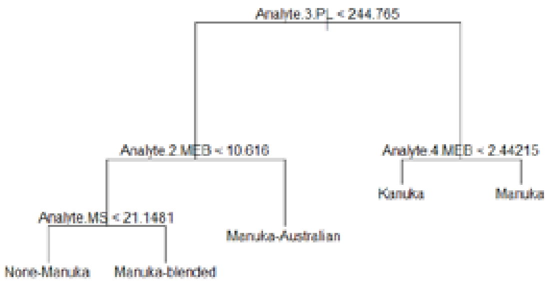

Fig. 5. Classification tree for honey varieties

Discussion

Approximately half way through our project MPI issued criteria defining manuka honey and manuka honey blends. The criteria involved quantitation of four key chemicals and analysis for the presence of manuka DNA.

MPI's work was based upon the analysis of some 800 samples representing over 20 different honey types from 16 different countries and has recently been published.[25]

Our project investigated only a very small number of samples but *may* point to a possible chemical means of discerning kanuka from manuka honeys and Australian manuka honey from the New Zealand variety based upon the concentrations of four compounds: 3-phenyllactic acid, 2-methoxybenzoic acid, 4-methoxybenzoic acid and methyl syringate. If further study were to be undertaken it would require ideally a much larger data set including more samples of kanuka honey and Australian manuka in comparison with the number of New Zealand manuka samples (mono- or multifloral) and non-manuka samples investigated.

Acknowledgements

The authors would like to thank ESR for the Pioneer Grant that made this investigation possible and ESR Statistician Dr David Wood for his analysis of our results. A huge thank is also be extended to Dr Claire McDonald, Senior Advisor, Ministry for Primary Industries, for her trenchant comments and advice regarding this paper.

Table 2. MPI criteria for monofloral manuka and multifloral manuka blends

Compound	**Manuka (monofloral)**	**Manuka (multifloral)**
3-phenyllactic acid	≥ 400 mg/kg	≥ 20 mg/kg < 400 mg/kg
2'-methoxyacetophenone	≥ 5 mg/kg	≥ 1 mg/kg*
2-methoxybenzoic acid	≥ 1 mg/kg	≥ 1 mg/kg
4-hydroxyphenyllactic acid	≥ 1 mg/kg	≥ 1 mg/kg
Manuka DNA	< 36 Cq value	< 36 Cq value

* The concentration of 2'-methoxyacetophenone was initially set at ≥ 5 mg/kg for multifloral manuka but was changed to ≥ 1 mg/kg. MPI was presented with new test results from industry and a testing laboratory showing the initial multifloral manuka definition was set too conservatively and could exclude legitimate multifloral honey.[24]

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The chemistry of gin and tonic

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Keywords: *chemistry teaching, gin and tonic, water chemistry, acid and base chemistry*

Introduction

Gin and tonic (G & T) is a wonderful concoction of plant alkaloids (including quinine and juniper berry extracts), fizzing aqueous carbon dioxide, ethanol, citric acid and ice. It is prepared by mixing gin (an ethanolic extract distillate of juniper and herbs) with tonic water (saturated CO_2 (aq) containing quinine and sucrose) in an approx. 1:2 ratio, and served over ice with a slice of lime (or lemon). It has a pronounced soothing effect and a moreish flavour.

I have used G & T to illustrate my 100-level chemistry lectures on water, acids, bases and buffers for some 5 years - much to the amusement and, I hope, learning of my students. In this article, I will set the infamous G & T in the context of 100-level chemistry teaching and learning. But before I do this, I will introduce the basic components of a G & T – gin and tonic water.

Gin

The origins of gin are uncertain, but it was mentioned as "genever" in *The Duke of Milan*, a play written in 1623 by Philip Massinger. It almost certainly goes back further than this; indeed it is reputed that the English troops who provided support to the Dutch against the Spanish in Antwerp in 1585 used it to calm their nerves before battle – hence the phrase Dutch courage. Still further back, there is a reference to genever in *Den Naturen Bloeme* (The Natures Floral) written *ca*. 1350 by Jacob van Maerlant. Genever was known in the English-speaking world as Dutch gin or Hollands, but now of course we simply call it gin.[1]

In a far-reaching (indeed literally universal) literary context, Douglas Adams in his novel, *The Restaurant at the End of the Universe* noted that '85% of all known worlds in the Galaxy, be they primitive or highly advanced, have invented a drink called jynnan tonnyx, or gee-N'N-T'N-ix, or jinond-o-nicks…".[2] Adams' gee-N'N-T'N-ix are quite different in composition to our worldly G & T, but the concept clearly spans galaxies.

Gin is manufactured by twice distilling malt spirit (ethanol produced by fermenting part-germinated wheat which enzymically liberates maltose from starch) with juniper (*Juniperus communis*) berry (actually modified cones) and herb mixtures; e.g., caraway (*Carum carvi*), coriander (*Corinadrum sativum*), anise (*Pimpinella anisum*) that give different gins their flavour characteristics. The predominant and very characteristic flavour and scent of gin is from the juniper berries which contain essential oils comprising α- and β-pinene, sabinene, terpinene-4-ol, borneol and geraniol (Fig. 1) all of which contribute to gin's flavour and aroma.

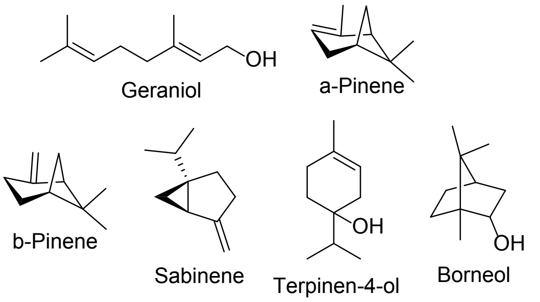

Fig. 1. The essential oil constituents from juniper berries responsible for gin's flavour and aroma

Interestingly the individual flavour components of juniper berries are also present in other coniferous trees. Pinene (as its name suggests) is a key component of pine and is responsible for the characteristic smell of a pine forest; geraniol is responsible in part for the sweet scent of roses; borneol is present in the spice galangal (*Alpinia officinarum*) and the anal sacks of the North American beaver (*Castor canadensis*) and is thought to play an important role in beaver scent recognition; sabinene is found in Norway spruce (*Picea abies*) and contributes to the evocative scent of Christmas trees; and terpinen-4-ol is found in nutmeg and tea tree (*Melaleuca alternifolia*) oil. It is the unique combination of these essential oils that adds up to the very characteristic aroma of juniper berries, and their solubility in ethanol accounts for the flavour and enticing aroma of gin.

Tonic water

The origins of tonic water lie in the malaria prophylactic use of its key component, quinine (Fig. 2), extracted from the bark of cinchona trees (e.g. *Cinchona officinalis*). The original tonic waters were used by the British stationed in Africa (and other tropical countries) to protect them from malaria parasites (e.g. *Plasmodium falciparum*) transmitted by mosquitos (e.g. *Anopheles gambiae*). These tonic waters contained high quinine concentrations which gave them a characteristic and very unpleasant bitter taste. A quinine dose of 10 mg/kg body weight every 8 h is necessary for effective malaria prophylaxis.[3] Therefore, for a 70 kg human a dose of 700 mg every 8 h would be required. Assuming approximately 200 mL of tonic water is used to make a G & T, this would mean that the quinine concentration in the tonic water would need to be 3.5 mg/mL and a G & T taken every 8 h for effective malaria control. A quinine concentration of 3.5 mg/mL is intensely bitter – the taste threshold for quinine is 0.008 mM,[4] which is equivalent to 1.14 mg/mL.

Tonic water was used as an essential malaria prophylactic by the British in the early days of the British Raj (1858-1947). The ingenuity of the early colonists led to the awful

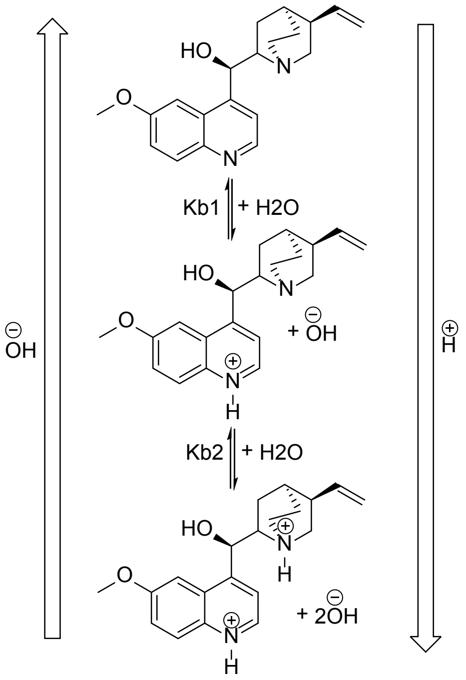

Fig. 2. Quinine is a weak base; K_{b1} = 3.3 x 10^{-6}, K_{b2} = 1.1 x 10^{-9} (K_bs calculated from http://www.science.uwaterloo.ca/~cchieh/cact/tools/pkb.html). Acid moves the equilibrium towards the protonated quinine ion, base moves the equilibrium toward neutral quinine. This is why quinine is absorbed well in the basic environment of the duodenum and small intestine.

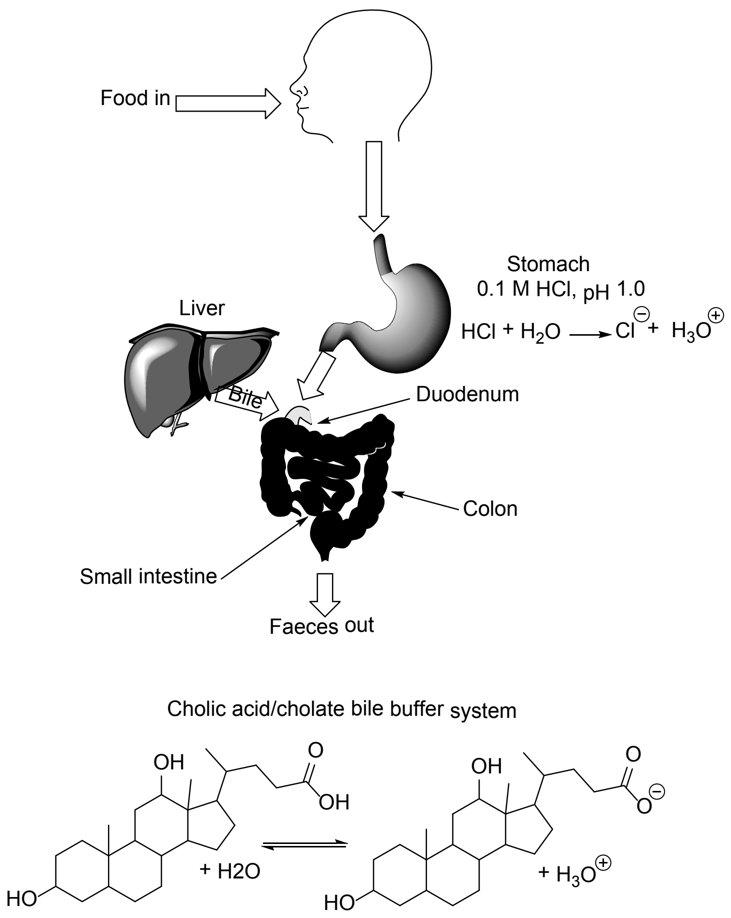

Fig. 3. Top: The human digestive system showing that HCl creates a very acidic (pH 1.0) environment in the stomach, and that bile produced in the liver passes along the common bile duct into the duodenum where is neutralises the acidic chyme from the stomach and buffers it to pH 7-8. Bottom: Bile is a complex mixture containing cholic acid and its derivatives (e.g. taurocholic acid) which with their conjugate bases mean that bile is a buffer and maintains the intestinal pH between 7 and 8.

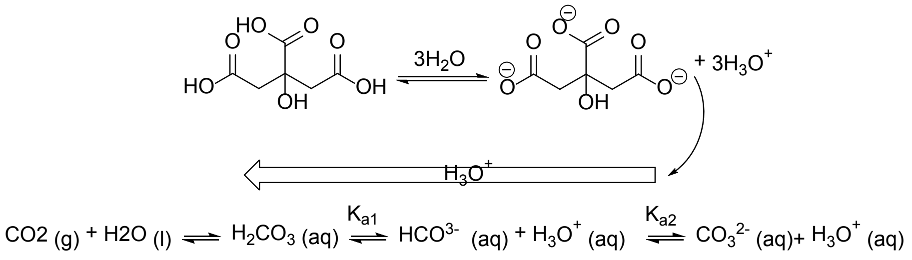

Fig. 4. Bottom: Reaction of carbon dioxide (CO_2) with water (H_2O) to form carbonic acid (H_2CO_3) which dissociates to form hydrogen carbonate (HCO_3^-) and a hydronium ion (H_3O^+) where K_{a1} = 4.46 x 10^{-7}. The HCO_3^- further dissociates to liberate another H_3O^+ and carbonate (CO_3^{2-}) where K_{a2} = 4.68 x 10^{-11}. Top: triprotic citric acid dissociates to form citrate and three H_3O^+s where K_{a1} = 7.5 x 10^{-4}, K_{a2} = 1.7 x 10^{-5} and K_{a3} = 4.0 x 10^{-7}. The three H_3O^+s push the H_2CO_3 acid dissociation equilibrium to the left liberating CO_2 (g) which is why a G & T fizzes when lime or lemon is added.

taste of tonic water being made more palatable by mixing it with gin – the G & T was born!

As the G & T evolved, tonic waters were manufactured with lower quinine concentrations to reduce the intense and unacceptable bitterness to a pleasurable level. Indeed, the USA Food and Drug Administration now limits quinine in tonic water to 83 ppm on toxicological grounds.[5] This equates to 0.083 mg/mL and is the level that makes a G & T taste good too.

Where in the digestive system is quinine absorbed?

Quinine is a weak base and, therefore, exists as the dication in the acid conditions of the stomach (Fig. 3) and thus is not readily absorbed into gastric cells because it cannot readily traverse the hydrophobic lipid-based cell membrane. This means that quinine's uptake from the stomach is minimal. However, basification (and buffering) by bile of the stomach contents on release into the duodenum (Fig. 3) de-protonates quinine ions making the

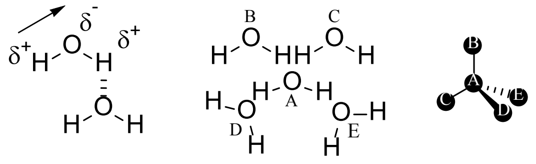

Fig. 5. Left: The electronegative oxygen in a water molecule leads to electron pull (→) which creates a polar molecule which leads to H-bond (≡) formation between water molecules. Middle: Crystal lattice of ice showing 4 water molecules (A-E) H-bonded to a single water molecule which forms a tetrahedral arrangement (right) which is the basic unit of the ice crystal lattice.

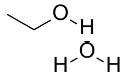

Fig. 6. Hydrogen bonds (≡) between water and ethanol molecules reduces the number of water-water hydrogen bond interactions thus depressing the freezing point of water-ethanol mixtures by disrupting the formation of the ice crystal lattice.

neutral quinine well absorbed in the small intestine.[6] Bile contains a complex mixture of liver metabolites including bilirubin, cholesterol, fatty acids, inorganic salts and cholic acid and its derivatives (e.g. taurocholic acid) and their conjugate bases which are responsible for bile's acid neutralising and buffering properties - the pH of the duodenal and the upper small intestine contents is 7-8; this deprotonates quinine, removing its positive charge and facilitating absorption across the duodenal and upper intestinal mucosa.

Why does G & T fizz?

The fizz of tonic water is made by pressure-assisted solubility of carbon dioxide in an aqueous solution of sucrose and quinine. Carbon dioxide forms carbonic acid in aqueous solution which is a diprotic acid and dissociates to produce a hydrogen carbonate (bicarbonate) ion which further dissociates to form a carbonate ion (Fig. 4). When lime or lemon juice containing citric acid (a triprotic acid) is squirted into a G & T, or a slice of lime or lemon is dropped in, the drink fizzes because the hydrogen ions introduced into the solution when the citric acid deprotonates push the carbonic acid/hydrogen carbonate/carbonate equilibrium to the left which releases carbon dioxide gas (Fig. 4).

Why does ice float on a G & T?

Water molecules are polar due to the electronegativity of oxygen and form intermolecular hydrogen bonds (H-bonds) between the δ- oxygen of one water molecule and a δ+ hydrogen of another water molecule (Fig. 5). The three states of water are determined by the degree of hydrogen bonding between water molecules. In solid water (ice; </= 0°C, at p = 1 bar) the maximum number of H-bonds holding the water molecules together creates a crystal lattice (Fig. 5); this open array lattice means that the water molecules are slightly further apart than they might be in liquid water where there is no crystal lattice and so the water molecules can pack together optimally (i.e. more water molecules per unit volume). In liquid water (>0°C-<100°C) there are fewer hydrogen bonds and greater kinetic energy than ice – as the temperature rises kinetic energy increases and the number of H-bonds decreases; in water vapour (=/>100°C) there are very few if any H-bonds and high kinetic energy. As a result of this, the density of ice is 0.92 g/mL at 0°C and the density of liquid water at 4°C is 1 g/mL which means that ice floats on water.

The situation in a G & T is different because the liquid is ethanol (aq.) not water. Gin contains approx. 35-40% (aq.) ethanol,[7] and a good G & T contains approx. 30% v/v gin; this means that a G & T is approx. 13% ethanol. The density of 13% ethanol (aq.) is 0.98 g/mL at 20°C[8] and since the density of ice is 0.92 g/mL it still floats on a G & T.

Why does G & T freeze below 0 °C?

Ethanol forms H-bonds with water molecules (Fig. 6) and between ethanol molecules which disrupts water-water H-bonds. This means that the freezing point of ethanol (aq.) is lower than the freezing point of water; indeed gin (40% v/v ethanol (aq.)) freezes at approx. -30°C[9] and 13% v/v ethanol (aq.) (= 10.3% w/v based on ethanol density = 0.789 g/mL; i.e. the concentration of ethanol in G & T) freezes at -5°C. Ethanol depresses the freezing point of water because it interferes with water-water hydrogen bond formation so inhibiting the formation of the ice crystal lattice.

In conclusion

The simple G & T is a cornucopia of chemistry including hydrogen bonding between water molecules and the interference of ethanol, acid base chemistry of quinine and carbonic acid/hydrogen carbonate/carbonate systems and triprotic citric acid. It is this chemistry that underpins the pH-dependent absorption of quinine in the digestive system, the enticing fizz when a slice of lime or lemon is added to a G & T, and the lip-cooling ice floating on the surface. And all of this makes a nice story for this quirky academic to enhance his teaching of 100-level acids, bases, buffers and water chemistry…cheers!

Acknowledgements

I thank Professor Bryce Williamson for his G & T enthusiasm which added significantly to the content of this article, and I offer my heartfelt thanks to those students who came to my CHEM 111 lectures at the University of Canterbury over the last 5 years – I raise a glass to you all!

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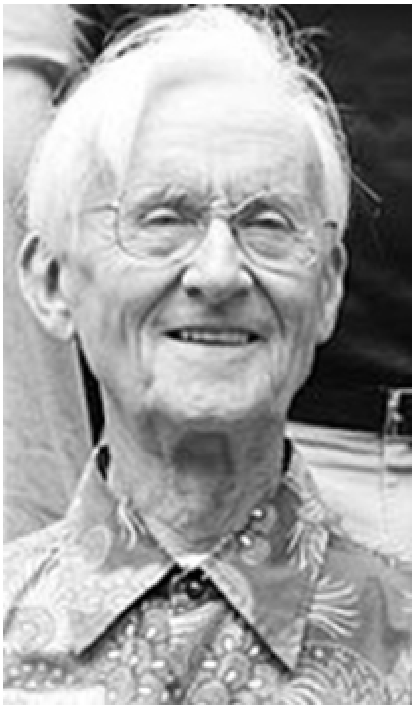
Vincent Richard Gray, FNZIC, 1922 – 2018



Vincent (Vince) Richard Gray passed away on Thursday 14 June 2018 in Wellington aged 96. He was a key figure in New Zealand's scientific community and was known (and respected) for his controversial views on climate change. Vince was the first Director of the Building Research Association of New Zealand (BRANZ) and Chief Scientist at the Coal Research Association of NZ during the 1970s and 1980s respectively.

Vince was born in London and educated at Cambridge University (Emmanuel College). He held professional positions in France, Canada and the UK before making the move to New Zealand in 1970. As the first Director of BRANZ, he brought other talented scientists to New Zealand to work there. One was Rob Whitney, who arrived as a Materials Research Scientist and continued there for 15 years, as Head of Materials and ultimately as Deputy Director of Research. Dr Whitney remembers that Vince left BRANZ in 1973 over his reluctance to endorse single skin blockwork for residential use.

After BRANZ, Vince worked at the Technical Correspondence Institute for a short time before moving to DSIR Forensics until 1982. He was then appointed as Chief Scientist at Coal Research. After retiring from Coal Research, Vince took up a professorship in China where his wife was teaching English. Rob Whitney, then Director of Coal Research, appreciated that he kept in touch with the organisation. When he returned from China he was contracted by Coal Research for specific projects, primarily taking a critical look at the science behind climate change. He was well regarded by Coal Research staff.

In 2004, Vince authored *The Greenhouse Delusion: A Critique of Climate Change 2001*, which challenged the Intergovernmental Panel on Climate Change (IPCC) report. He regularly submitted comments on draft IPCC reports – including 1,898 for the Working Group 1 volume of the Fourth Assessment Report (2007), 16% of the total! David Wratt, who was a review editor for some IPCC report chapters and disagreed with many of Dr Gray's opinions about climate change, said authors found this a bit overwhelming. Nonetheless, this was a valuable contribution, since it helped ensure that statements in assessment chapters were expressed clearly and unambiguously and were well supported by references to underlying scientific publications.

A regular attendee at Wellington Branch NZIC meetings for many years, Vince would sit at the front and ask penetrating questions of the speakers. He would often be accompanied by his wife Mary. They were valued members of the Institute and the science scene in Wellington. Vince also often attended public talks on climate matters. Here too, he would sit up near the front of the audience, his face clearly expressing his disagreement with any implications that humans were significantly affecting the climate. He would follow this up with a rather long question or two into which he managed to inject many of his own views!

Vince maintained a wide range of interests and activities into his late eighties and early nineties, especially in music, travel, and science. He maintained a passion for music, continuing his great interest and skill in jazz, developed in France, by playing in the Valley Stompers band for many years. They performed at his funeral.

Fellow scientists valued that Vince was able to separate scientific criticism from personal criticism and to maintain friendships with people he disagreed with on scientific matters. He was widely regarded as a scientist with an amazing grasp of a wide range of detailed facts and figures. He will be missed.

Vincent's wife Mary died just fifteen days after her husband. An article about Vince and his wife Mary was published in the Dominion Post in July: *https://www.stuff.co.nz/life-style/105746754/mary-and-vincent-gray--couple-die-15-days-apart*

Contributed by Joanne Harvey and Rob Whitney with input from Brian Halton, David Wratt and Trevor Matheson

Structure prediction for bottom-up graphene nanoribbon assembly

Daniel M. Packwood

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Keywords: *structure prediction, machine learning, Monte carlo, graphene nanoribbon, self-assembly*

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Daniel Packwood received his BSc (Hons) degree in 2007 and PhD in 2010 from the Department of Chemistry at the University of Canterbury. His postgraduate studies were supervised by Prof. Leon Phillips, where he developed a theory of atom-liquid surface collisions. From 2010-2012 he was a JSPS Postdoctoral Fellow in the group of Prof. Yoshitaka Tanimura in the Department of Chemistry, Graduate School of Science, Kyoto University, where he worked on a stochastic theory of phase decoherence in 2D-IR spectroscopy. From 2012-2016, he was an Assistant Professor in the Mathematical Sciences Group at the Advanced Institute for Materials Research (AIMR), Tohoku University, where he developed mathematical models for a variety of topics in materials science. Since 2016 he has been a Senior Lecturer (with tenure) and Principal Investigator at the Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University, where he is mainly focusing on structure prediction for organic materials on metal surfaces. He has been the recipient of several competitive research grants, including a PRESTO grant from the Japan Science and Technology Agency in 2014. He was awarded the 5th Fujiwara Hiroshi Prize in Mathematical Science in 2016 and was a TEDx speaker in 2017.

Towards theory-driven materials science

Since the launch of the Materials Genome Initiative in the United States in 2011, an enormous effort has been made to introduce state-of-the-art mathematical, machine learning, and data science techniques into materials science.[2,3] These efforts are partly motivated by a vision of a 'theory-driven materials science', in which theoretical methods and database screening are used to predict new materials with desired properties, as well as their synthetic routes. By integrating theory to guide experiment in this manner, it is expected that the time required to discover new materials or optimise existing ones would be significantly shortened. Thanks to the strong support for this approach in the United States and elsewhere, the theoretical materials community has diversified dramatically over the last few years through the inclusion of applied mathematicians and data scientists, and the theoretical breakthroughs needed to realise this vision have been identified.[4,5] In a small number of cases, new materials obtained by the integration of theory and database screening have even been reported.[6,7] While the vision of 'theory-driven materials science' is on its way to being realised, continued support for this approach by both scientists and funding agencies is essential to ensure concrete outcomes which benefit society.

Shortly after the launch of the Materials Genome Project, funding agencies in Japan started to show an interest in 'theory-driven materials science' as well. In fact, it is probably due to this support that I have survived in academia so far. In January 2012, I had just entered the final year of a postdoctoral fellowship at Kyoto University and was quite worried about whether I would be able to find an academic position. As a theoretical chemist who double-majored in mathematical statistics, I obsessed over model simplicity and analytical rigor. Most theoretical chemists, on the other hand, were more interested in calculation accuracy and computational times. My postdoctoral supervisor, Yoshitaka Tanimura, recommended that I look for a position in a mathematics department, however this did not look particularly easy either. And yet in March 2012, just as I was putting together a game plan to find an academic post, the Advanced Institute for Materials Research (AIMR) at Tohoku University announced three assistant professor positions in the field of 'mathematical materials science'. These positions had opened as part of a fund-securing strategy and were intended to further integrate theoretical research into AIMR's world-leading experimental materials research. AIMR already had a strong team of computational physicists, and therefore in their announcement for these new positions they specifically asked for chemists and physicists with mathematical, rather than computational, backgrounds. It looked like divine luck, and so I put together the best CV that I could and landed one of the positions. During my time as assistant professor, I worked out mathematical theories for a variety of different materials, including nanoporous metals,[8] molecular magnetism,[9,10] organic semiconductors,[11] and oxide thin films,[12] and in some cases predicted things which were useful to my experimental colleagues. While it remains to be seen whether these particular studies will help realise a 'theory-driven materials science', Japanese funding agencies are still enthusiastically supporting such work, and the pressure to deliver an exciting result *via* such approaches remains strong.

Having worked in materials science for a few years now, it has become abundantly clear that we need reliable methods for predicting a material's atom-scale structure from a knowledge of chemical composition. Such methods, if available, would tell experimentalists what chemical composition they should use in order to create a material with desired structure. While the situation is improving particularly for bulk atomic solids and molecular crystals,[13,14] our ability to predict material structure is generally quite feeble.[15] Prediction of a material's structure is far too complicated for pen-and-paper mathematics alone, and computational methods are absolutely necessary. Most commercial quantum chemistry software has the ability to 'optimise' the structure of a material or molecule starting with an initial guess. However, these optimisations are based upon local potential gradients. Consequently, they are almost guaranteed to predict metastable structures rather than the true structure of the material (unless the initial guess was chosen extremely well). The optimisation routines found in commercial software are therefore unable to predict material structure at present. The situation gets even worse when we realise that it is actually the free energy, rather than the energy, which should be minimised during a structure prediction calculation. At present, it is very difficult to incorporate free energy into a structure prediction calculation, and moreover the qualitative effects of the entropy term on atomic-scale structure are not even well understood at present. In short, computational methods that can predict the free energy-minimising structure (or structures) of a material must be developed in order to enable a 'theory-driven materials science'.

At this point, the reader may be wondering whether mathematical methods would be useful at all for predicting material structure, especially given the necessity of computational methods for tacking this problem. Actually, the development of a new computational method requires a great deal of mathematical work, as mathematics is needed to prove that the computational method is correct and efficient. It is for this reason that the interaction between mathematics and computation is considered crucial for achieving a 'theory-driven materials science'. Upon appreciating this point about three years ago, I decided to change the flavour of my research: instead of using mathematical approaches to analyse simple physical models of materials, I would use mathematical approaches to develop new computational methods for predicting material structure. The purpose of this article is to summarise some of our recent efforts in this area. We focus on materials formed *via* so-called surface-assisted molecular self-assembly processes. 'Surface-assisted molecular self-assembly' refers to the spontaneous assembly of surface-adsorbed molecules into a larger supramolecular structure. In turn, these supramolecular structures can be used as synthetic intermediates for low-dimensional materials such as graphene nanoribbon. Working in close collaboration with scanning tunneling microscopy experts Patrick Han and Taro Hitosugi (ex-Tohoku University colleagues), we succeeded in creating a method which can predict the outcome of the molecular self-assembly process, and hence predict the supramolecular structures described above.[16,17] This method is an example of one which can predict structure from chemical composition. Moreover, by virtue of the mathematical analysis used to develop this method, we obtained a formula which explains how entropy affects the outcome of the self-assembly process. For clarity, we will introduce our method within the specific context of graphene nanoribbon fabrication. However, it should be noted that the method can be applied to other types of systems with little modification.

Bottom-up graphene nanoribbon synthesis

Graphene nanoribbon (GNR) can be loosely visualised as a narrow strip of width 1 – 10 nm cut out from ordinary graphene sheet (Fig. 1A). GNR, like ordinary graphene sheet, has remarkable electrical properties, including electron mobilities over 100 times that of silicon.[18] However, unlike ordinary graphene sheet, GNR has a non-zero band gap, which means that it could be used as a tiny

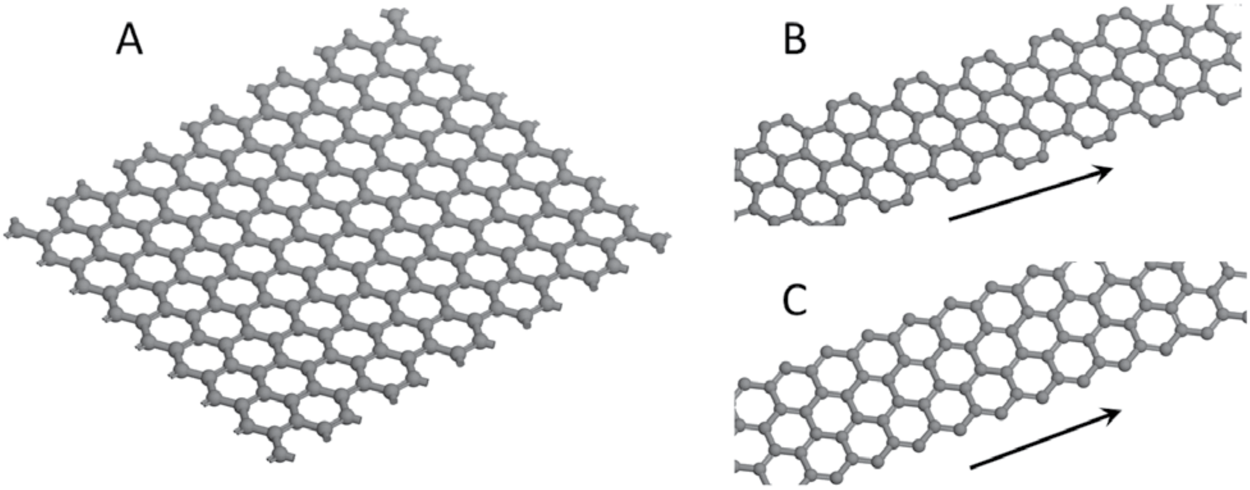

Fig. 1. Some types of graphene nanoribbon. (A) Ordinary graphene sheet, (B) graphene nanoribbon with armchair edges and (C) graphene nanoribbon with zig-zag edges. The arrows indicate the direction in which the edges run. Hydrogen atoms have been omitted for clarity. Grey spheres = carbon atoms.

semiconducting channel for device applications.[19] Two examples of GNR, showing armchair and zig-zag edge configurations, are shown in Figs. 1B and 1C respectively.

At present, there are two ways in which GNR is synthesised. One way is the top-down approach, in which GNR is cut from a graphene sheet using electron beam lithography or related techniques.[20] However, even with the most precise top-down techniques, it remains extremely difficult to prepare narrow GNR without creating any atomic defects. Unfortunately, the electronic properties of GNR are very sensitive to atomic defects, and defective GNR is not particularly useful for device applications. The other method of synthesising GNR is the bottom-up method. In this method, organic precursor molecules adsorbed to a substrate undergo self-assembly to form a chain-like supramolecular structure (Figs. 2A & 2B). Upon heating, a chemical reaction occurs between the precursor molecules, and the supramolecular structure transforms into graphene nanoribbon (Fig. 2C). This approach was used by collaborators Patrick Han and Taro Hitosugi, who selected 10,10'-dibromo-9,9'-bianthracene (Br_2BA) as the precursor molecule and copper(111) (Cu(111)) as the surface, and succeeded in creating a novel kind of GNR (Fig. 2C).[21-23] Other groups have successfully created pure armchair and zig-zag edge GNR by using a gold (111) (Au(111)) surface in place of Cu(111) as well.[24,25]

Scanning tunneling microscopy (STM) has been the major experimental tool for examining the GNR formation mechanism. Using STM, Han and co-workers showed that the length and shape of the supramolecular structure determines the shape of the resulting GNR structure.[26] In particular, supramolecular structures which contained a 'bend' were shown to result in 'bent' GNR. These observations strongly suggest that the supramolecular structure can be regarded as an intermediate in the synthesis of GNR; once the supramolecular structure is set, the GNR structure is then determined. If we could therefore predict the supramolecular structures resulting from a specific type of precursor molecule and substrate temperature, then it may become possible to control the widths and shapes of GNR that emerge from the bottom-up approach. Unfortunately, it is extremely difficult to derive predictive rules from STM data alone.

The chain-shaped supramolecular structures described above are held together by weak van der Waals forces. As a result, it may be expected that these structures fall apart at high temperatures. However, STM imaging showed that these structures persisted at temperatures even of the order of 400°C, without showing a clear change to a disordered state. In order to explain this result, a method with predicts both structure and accounts for temperature, and hence entropy, is required.

Theoretical method for predicting supramolecular structures

Having been inspired by the experimental results described above, we set out to create a theoretical method which can predict the formation of chain-shaped supramolecular structures that result from Br_2BA self-assembly on Cu(111). More specifically, we wanted a computational method which could predict the free energy-minimising arrangement of molecules on the surface. As mentioned in the introduction, it is generally not possible to make such predictions using off-the-shelf first-principles or molecular dynamics software. In the current situation, the following two difficulties arise in particular.

The intermolecular interactions and molecule-surface interactions involved in such systems are very complex, and there is no easy model or formula available for calculating the energy of the system. The energy of the system can only reasonably be calculated from first principles, however the large number of atoms involved in these systems (at least in the order of 1000) demand unreasonable computational times. Such large computational

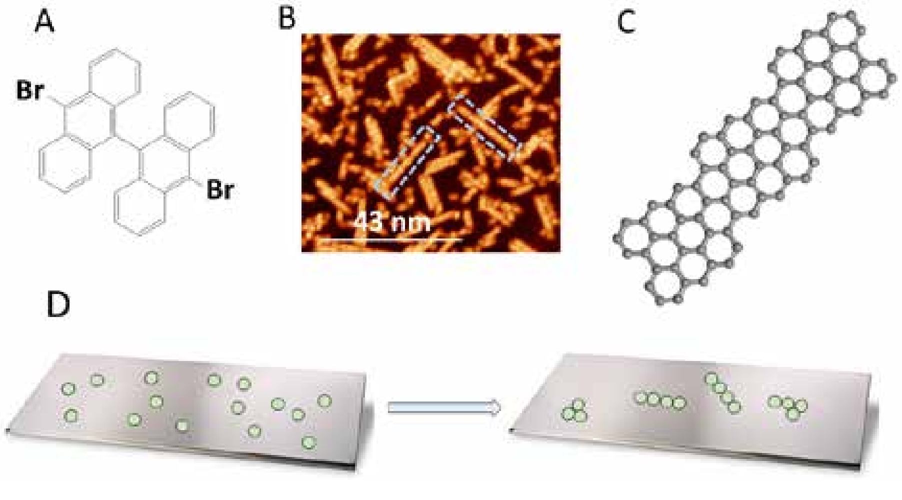

Fig. 2. Bottom-up graphene nanoribbon fabrication. (A) Chemical structure of 10,10'-dibromo-9,9'-bianthracene ("Br_2BA"), which is used as the organic precursor. (B) Scanning tunneling microscope (STM) image of a copper(111) (Cu(111)) surface after deposition of Br_2BA. The formation of chain-shaped supramolecular structures (indicated by the blue boxes) is evident. (C) Structure of a (3,1)-chiral edge graphene nanoribbon ((3,1)-GNR). The chain-shaped supramolecular structures in (B) transform into (3,1)-GNR upon annealing the Cu(111) substrate at high temperatures.[16] (D) Cartoon of the surface-assisted molecular self-assembly process. The green circles represent molecules. Initially, the molecules are distributed randomly on the surface (left). However, as a result of intermolecular interactions and other factors, they go on to form supramolecular structures (right). STM image courtesy of Patrick Han and Taro Hitosugi.

costs for the energy calculations will dramatically slow down any attempt to search for the optimal arrangement of molecules on the surface.

Experimentally, the molecular self-assembly process takes place over long, microsecond-exceeding time-scales. Only at these long time scales does the system reach thermodynamic equilibrium and the free energy minimising arrangement of molecules on the surface can be identified. Unfortunately, these long time scales are extremely difficult to access with molecular dynamics simulation or conventional structure optimisation methods at present.

Following a lot of hard work, we came up with a new method which overcomes difficulties 1 and 2 described above. Our method, which we named the GAMMA (= Generalized block AsseMbly equivalence class Machine leArning) method, overcomes these difficulties by combining machine learning techniques with a new kind of Monte Carlo sampling.[16]

Fig. 3 briefly explains how the GAMMA model overcomes difficulty 1. Firstly, a database of around 2000 distinct, pairwise intermolecular interactions was compiled, and the energy for each interaction was computed from first principles. This database is relatively small, considering that around 3 x 10^8 different intermolecular interactions are possible for a Cu(111) surface containing 50 x 50 unit cells. Around 2 weeks were required to compile this database using our computational resources. Following this, the database was analysed using a machine learning method for pattern recognition, which essentially figures out how pairwise intermolecular interactions (a pattern) are correlated with interaction energies (a number). Having trained our computer to correlate intermolecular interactions with energies, it could then determine the total energy of the system by simply identifying all pairwise interactions in the system, predicting their interaction energies, and them summing the result (the contribution of the surface-molecule interaction is also accounted for, however details are omitted here). Using this method, it became possible to compute the total energy of the system within 0.1 – 3 s, depending upon the number of molecules in the system. On the other hand, such a calculation would require at least weeks of computing time if standard first principles calculations were employed.

Difficulty 2 was overcome by developing a new Monte Carlo sampling method called equivalence class sampling (ECS). To explain the ECS method, consider a box full of balls, and imagine that each ball contains one specific supramolecular structure that might emerge from the molecular self-assembly process. In the ECS algorithm, the following process is repeated a large number of times: a ball from the box is 'randomly' chosen, the energy of the supramolecular structure contained inside is computed, and the ball is put back inside the box. At each iteration, a record is kept of which structure was contained inside the ball, as well as its energy. We write 'randomly' in inverted commas, because the algorithm is set up in a special way so that balls containing structures with low free energy tend to be selected more frequently than the others. Providing that the ECS algorithm is run for a sufficiently long length of time, we can find the free energy-minimizing supramolecular structure by simply identifying the ball which was selected most frequently. Because this algorithm specifically targets structures with low free energy, it directly probes the system at thermodynamic equilibrium and does not have to deal with the long time-scales of the self-assembly process.

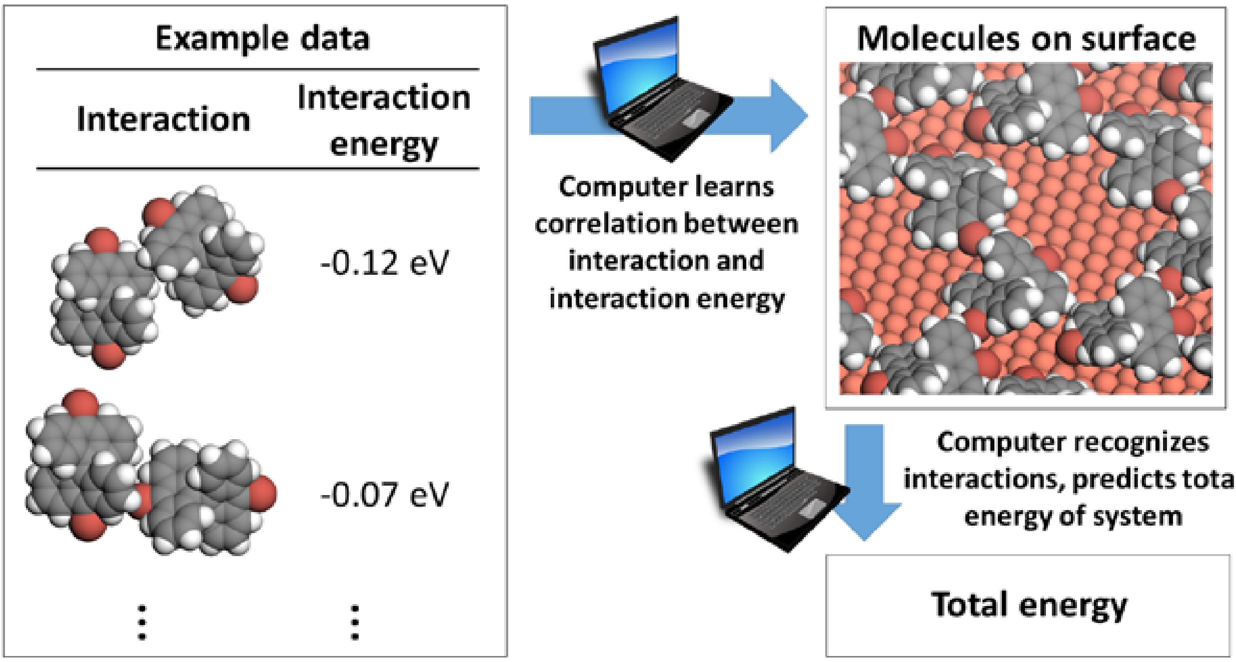

Fig. 3. Summary of the machine learning method for calculating energies. First, a small database is compiled containing a sample of intermolecular interactions and their interaction energies. Secondly, a machine learning algorithm learns the correlation between interaction and interaction energy. Finally, given a group of molecules arranged on a surface, the computer identifies all of the intermolecular interactions taking place on the surface, predicts the interaction energy for each case, and then sums the result to obtain the total energy of the system. Grey spheres = carbon atoms, white spheres = hydrogen atoms, red-brown spheres = bromine atoms, pale orange spheres = copper atoms.

Fig. 4 shows a free energy-minimising supramolecular structure identified by the GAMMA model for the case of Br_2BA self-assembly on Cu(111). We can see that this method correctly predicts the formation of chain-shaped structures. The relatively modest image in Fig. 4 was very exciting for us, as it showed that it is indeed possible to predict supramolecular structures which emerge from molecular self-assembly processes. This approach makes no assumptions about the interaction between molecules, and hence there is no way that our chemical intuition could have biased the results. In other work, we have also explored how supramolecular structure is affected by choice of functional group on the bianthracene unit (Br in the case of Br_2BA), which produced some additional predictions, some of which have been experimentally confirmed[16,17]. As described above, such predictions are plainly impossible with the conventional tools of computational chemistry at present.

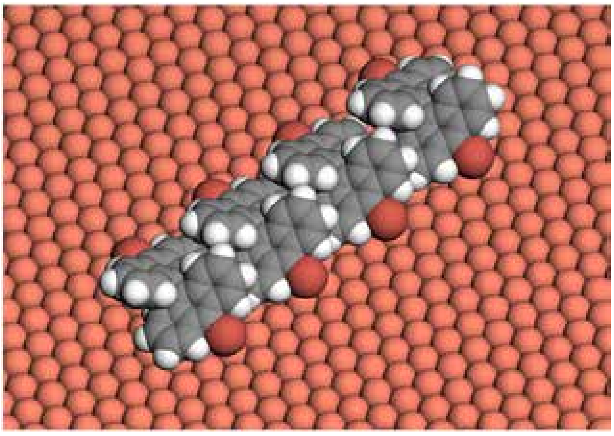

Fig. 4. Prediction from the GAMMA method: a free energy minimising supramolecular structure formed from Br_2BA self-assembly on Cu(111) at 200 K. These calculations assumed 10 molecules and a low surface coverage. While the structure shown above contains 4 molecules, it actually occurs in combination with another chain-shaped structure containing 6 molecules in our calculations (not shown). Grey spheres = carbon atoms, white spheres = hydrogen atoms, red-brown spheres = bromine atoms, pale orange spheres = copper atoms.

While the GAMMA method must be simulated on a computer, its development required some interesting mathematical work. The mathematics involved in the machine learning part is not so new. Rather, it consists of a combination of methods which I learned about during a three month stay at the Institute for Pure and Applied Mathematics at the University of California, Los Angeles, in 2013. During this stay, I heard some presentations describing early applications of machine learning in materials science, and became quite inspired by what I saw. On the other hand, in order to develop the ECS technique, a fiddly analysis of 'Markov chains on quotient spaces' was required.[27] Roughly speaking, this amounts to considering a random walk hopping between points in a discrete space, but with the complicating feature that certain groups of points are 'indistinguishable' from one another in some sense. Details are omitted here, however as a by-product of this analysis we obtained a deep physical insight into the role of entropy in the present system, as described in the following section.

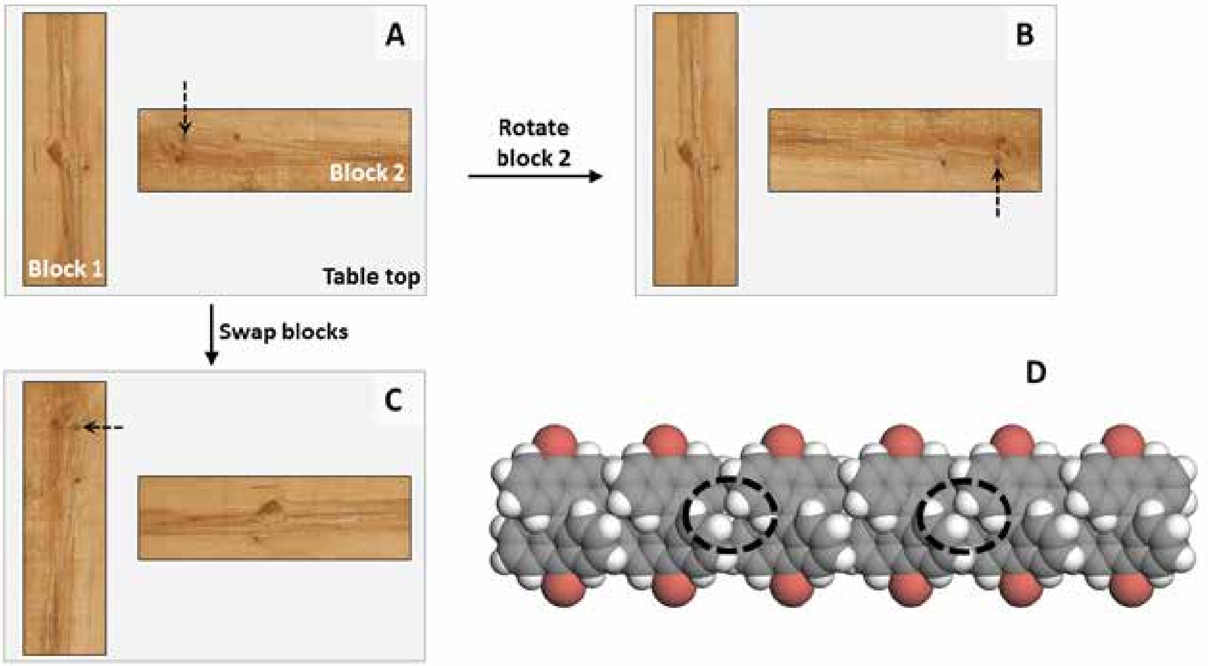

Fig. 5. Low symmetry principle and configurational entropy. (A) Two wooden blocks placed on a table top. (B) Obtained from (A) by rotating block 2. (C) Obtained from (A) by swapping blocks 1 and 2 around. The dotted arrow is a guide for the eye, and points to a defect on the surface of block 2. If the defects and wood patterns on the surface of the blocks are ignored, then the images in (A), (B) and (C) would be indistinguishable, and the system would have low configurational entropy. However, if the defects and patterns are not ignored, then (A), (B), and (C) are fully distinguishable from one another, and the system would have a relatively high configurational entropy. (D). A chain-shaped supramolecular structure predicted by our calculations. The dotted circles show that the spacing between neighboring molecules in the structure is not regular, which means that these structures lack two-fold rotational symmetry. The chain-shaped supramolecular structure therefore contributes relatively large configurational entropy to the system, despite its superficial appearance of having order.

Role of entropy

In the above paragraphs, we emphasised that the supramolecular structure which minimises free energy, rather than energy, is the one which has a high likelihood of appearing from the molecular self-assembly process. In the current context, we are referring to the Helmholtz free energy, which is defined as $A = E - TS$, where E is the energy of the system, T is the temperature of the surface, and S is the entropy of the system. According to this formula, in order for a specific supramolecular structure to appear on the surface at nonzero temperatures, the energy of the system should be low (large and negative), and the entropy of the system should be high. The chain-shaped structure shown in Fig. 4 certainly results in a low system energy, due to energetically stabilizing π-stacking interactions between neighboring chains. On the other hand, with its molecules lined up in such a beautiful manner, the structure in Fig. 4 superficially looks like it should have a low entropy. However, experimentally and in our calculation, this chain-shaped structure remains relatively stable even at higher temperatures. This is an unexpected result, given that an apparently ordered structure should become less thermodynamically favorable at higher temperatures.

To get to the bottom of this mystery, we considered the so-called configurational entropy. Roughly speaking, the configurational entropy measures the number of ways a set of supramolecular structures can be placed on the surface without affecting the total energy of the system. While configurational entropy is just one of several types of entropy which contribute to the S term in the free energy, its contribution is expected to be relatively large in the present case. As a by-product of the mathematical analysis mentioned at the end of the previous section, we obtained an analytic formula for the configurational entropy. By visual inspection of this formula, we could then deduce the following: A set of supramolecular structures on a surface can have high configurational entropy, providing that a kind of 'low-symmetry principle' is obeyed.

This low-symmetry principle is briefly explained in Fig. 5, which shows two rectangular wooden blocks placed on a table. Firstly, let us ignore the wood grain or scratches on the surface of the blocks. By ignoring these features, the blocks become indistinguishable from one another. In particular, in-plane rotation of either block or swapping the blocks around will not alter the appearance of the table. This is a low configurational entropy situation, because the number of distinct ways in which the blocks can be placed on the table is reduced by symmetry. Now, let us take full account of the wood grain and scratches on the surface of the blocks. In this case, the appearance of the table changes when the blocks are exchanged or rotated in-plane. This is a high configurational entropy situation, because the number of distinct ways in which the blocks can be placed on the table is relatively large. Each of Figs. 5A – C show distinct ways in which the wooden blocks can be placed on the table due to exchange of blocks or in-place rotations.

At first glance, the low-symmetry principle does not seem to apply to chain-shaped supramolecular structures on a surface, due to the superficial presence of rotational symmetry in the chains. However, a closer inspection unveils that the spacing between molecules in the chains is not constant; some neighboring molecules are closer together than others (Fig. 5D). This irregular spacing slightly increases the energy of the chain, because it forces some pairs of molecules be away from the ideal interaction distance. On the other hand, this irregular spacing also eliminates in-plane rotational symmetry in the chain. In other words, at the cost of a little energetic stability, chain-shaped supramolecular structures can boost their entropy by having irregular spacings between neighboring molecules. This provides one explanation of why chain-shaped supramolecular structures appear from Br_2BA self-assembly on Cu(111) even at relatively high temperatures, and in fact such irregular spacing can be observed in high-resolution STM data as well.

Conclusions

Theoretical methods which can predict a material's atomic-scale structure from a knowledge of chemical composition are a prerequisite for making 'theory-driven materials science' a reality. As mentioned in the introduction, such methods would tell experimentalists what chemical composition they should use in order to create a material with desired structure and properties. In this article we have summarized the GAMMA method, which applies specifically to materials fabricated bottom-up on solid substrates. With this method, we can predict the supramolecular structures which form from the self-assembly of precursor molecules at a given substrate temperature. In turn, these supramolecular structures can be used as intermediates to form low-dimensional nanomaterials such as graphene nanoribbon. As the next step of our research, we are trying to integrate this theory into experiment, and hope to see it accelerate the discovery of new supramolecular structures with desired shapes and properties. If we can succeed at this challenge, then we will have made 'theory-driven materials science' a reality in the case of bottom-up materials fabrication.

Acknowledgements

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Book review: *Energy, Entropy and the flow of nature*

Sherman, T.F. *Energy, Entropy, and the Flow of Energy*. Oxford University Press: Oxford, 2018

The announcement of the publication of *Energy, Entropy, and the Flow of Nature* included the attribute: "offers the fascinating life histories of scientists such as Michael Faraday, whose discoveries contributed greatly to the understanding of electromagnetism".[1] The first chemistry book I owned as a teenager included a striking image of the youthful Michael Faraday (Fig. 1) in its chapter on 'Electrolysis',[2] and so part of the potential appeal of Professor Sherman's book for me was the publisher's assertion on the book's rear cover that it will "provide a careful consideration of the historical roots of the ideas involved". The opening chapter – Origins of the Idea of Energy and its Conservation – certainly does that, introducing the concepts to be developed later in the book in a simple way, generally through mechanical rather than chemical examples, while subtly introducing other aspects of the 'origins of the idea of energy and its conservation' – the theme of the chapter. The interaction between electricity and chemistry, demonstrated by the section featuring Michael Faraday, is perhaps the best presented of the scientists that Professor Sherman profiles, but all are readable and interesting.

Fig. 1. The youthful Michael Faraday, 1791-1867: "Chemists honour him particularly for the discovery of the laws of electrolysis and for his studies on the liquefaction of gases. Physicists honour him for his investigations in electricity and magnetism, which led to the modern electrical industry" (image and text in reference 2) [Image: https://www.theiet.org/resources/library/archives/exhibition/faraday/intro.cfm]

The content and pace of the second chapter (Measurement, Dimensions, and Energy) is tedious, by comparison with the first chapter. It also stands in marked contrast to Chapter 3 – The Laws of Energy, in which the examples of what happens when a car battery and a heating coil are used to heat a room (pp. 73-74):

"Clearly a battery is a source of free energy. But after heating the room, the discharged battery and the warmer room can do nothing whatever because the warmth produced by the battery and electric coil has been evenly dispersed about the room, and there are no longer any gradients – chemical, electrical or thermal. All the energy has become equipotential (Brönsted) or bound (Helmholtz). The chemical gradient inside the battery has been destroyed and no new gradient has taken its place. … no matter how long we wait, the warm room will never recharge the battery for us. Uniformity can never create gradients, nor bound energy convert itself to free."

… and, as a prelude to a discussion on osmotic pressure, the story of the shepherd attempting to cool milk in a stream (pp.82-83):

"At some time in the dawn of agriculture, a shepherd probably put a bladder of fresh milk into a mountain brook to keep it cool and was astonished to see it swell and burst open. … water has a greater free energy when it is concentrated, and it tends to diffuse from high concentrations to low. When other substances such as proteins, sugars and salts are mixed with water (as in milk), the water's concentration is decreased and so is its free energy. If such a solution is placed in contact with pure water, pure water will diffuse into the region containing solutes, and solutes will diffuse toward the pure water. But suppose that a membrane (such as a bladder) is permeable to the water but not to the solutes. Then water will diffuse into the bag, but the solutes are prevented from diffusing out. The bag will swell….”

… are so much more readable than the timeworn and traditional approach: “Suppose that we have 1 mole of an ideal gas in a closed cylinder, but with a piston that can slide in or out at one end of the cylinder.” In fact, most of us don’t have such a cylinder – and are probably not disappointed by the fact! In places this chapter becomes bogged down in the minutiae of ideal gases and thermodynamic variables, detracting from the overall progress of the book.

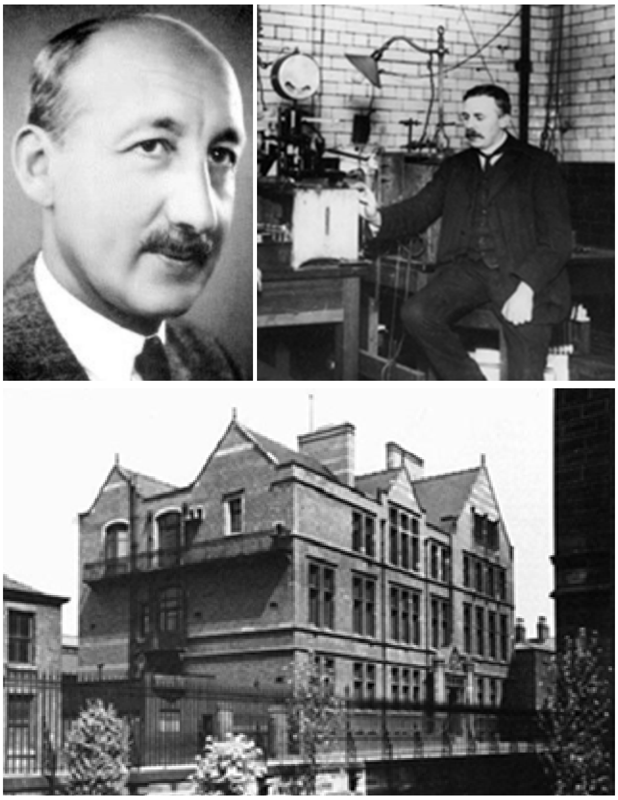

Fig. 2. A New Zealand connection. *Upper left:* George Hevesy undertook his Nobel prize-winning research on radioactive tracers in the Physics Laboratory at the University of Manchester (*below*, dated 1908), initially working with New Zealander Ernest Rutherford (*right*). [Image of Hevesy from: https://www.google.co.nz/search?q=george+hevesy&source=lnms&tbm=isch&sa=X&ved=0ahUKEwiJxLPsgZjcAhUrBjQIHfNzDqUQ_AUICigB&biw=1893&bih=920#imgrc=ZT0qThtaqjj_EM. Images of Manchester and Rutherford from: https://www.manchester.ac.uk/discover/history-heritage/history/buildings/rutherford/

I anticipated that the next chapter (Chapter 4 – Thermal Energy, Temperature, and Entropy) might suffer similarly by relying too much on ideal gases, but it proved to be surprisingly readable. Even so, the quotation from Hans Fuch’s book offers a future scholar an opportunity for a new look at the topic of entropy (p. 109):[3]

“It is almost impossible to recognise the true nature of a quantity [viz., ‘entropy’] which is introduced on purely formal grounds and led onto the stage through the back entrance only. If we were to teach basic electricity in a manner analogous to that found in the chapters on thermodynamics of our introductory texts, we would never realize that there is a quantity with the properties of electric charge.”

In this chapter the use of Hevesy’s experiment demonstrating the interchange of lead between radioactive lead chloride (Pb-210) and non-radioactive lead nitrate in contact with a solution saturated with lead as a demonstration of Le Chatelier’s principle (pp. 121-122)[4] may resonate with New Zealand readers, since the experiment was originally undertaken in Ernest Rutherford’s laboratory – albeit in Manchester (Fig. 2). Similarly in the following chapter (Chapter 5 – Energy and Entropy in Heat Engines and Heat Pumps), modern-day readers are more likely to identify with the heat pump (pp. 142-143) or refrigerator than the hypothetical Carnot heat engine.

The sixth chapter – Brownian Motion and Diffusion – has fewer equations (see Table 1) and is more readable than some of the earlier chapters because of its well-chosen examples of the concepts being described. Of particular note is the analogy between Brownian motion and the expanding universe (p. 163):

“Although all nature ultimately is interrelated, one would not wish to claim a direct connection between the large-scale cosmological forces that cause our universe to expand and the microscopic thermal forces that sustain

Table 1. The influence of mathematical equations, chemical reactions and diagrams in chapters of *Energy, Entropy, and the Flow of Nature*

Chapter		P*	Reading complexity†			Reading relief‡	
			NM	NC	C	D	R
1	Origins of the Idea of Energy and its Conservation	36	11	0	0.31	0	0
2	Measurement, Dimensions, and Energy	17	18	0	1.06	0	0
3	The Laws of Energy	31	25	0	0.81	1	0.03
4	Thermal Energy, Temperature, and Entropy	38	34	0	0.89	0	0
5	Energy and Entropy in Heat Engines and Heat Pumps	18	16	0	0.89	0	0
6	Brownian Motion and Diffusion	18	9	0	0.50	0	0
7	Chemical Energy	42	45	13	1.38	3	0.07
8	Biological Energy	39	10	15	0.64	12	0.31

**P* is number of pages in chapter

†*NM* is the number of mathematical equations in the chapter; *NC* is the number of chemical reactions in the chapter that are presented as equations. A measure of ‘reading complexity’ attributed to a greater proportion of equations in the text, *C*, is $(NM + NC) / P$

‡ *D* is the number of diagrams in the chapter. A measure of ‘reading relief, attributed to the presence of diagrams, *R*, is D/P

Brownian motion and diffusion. Yet the analogy should not be discussed two lightly, for both phenomena portray a fundamental asymmetry relating to time, pronouncing that the past gives way to the future – that time has direction as well as duration. … Galaxies disperse with time and so do molecules."

The author's linking of diffusion to entropy, and his observation in this chapter that "Diffusion is a model for all natural processes for whenever anything happens in nature, a gradient of some kind is involved, and that gradient is diminished by the activity it drives" is actually implicit throughout the book, but moves him to conclude the chapter in a philosophical tone (p. 164):

"In science, as in life more generally, we can look at ultimate meaning in any way we wish. But if one person insists that nature is running downhill and burning itself out, it is perfectly reasonable for another to point out that without the random motion seen by Brown [i.e., 'Brownian motion"] and the diffusion that can accompany it, no life as we know it could exist on our Earth."

The seventh chapter – Chemical Energy – returns to 'traditional' explanations of enthalpy, free energy, equilibrium and rate constants. As in earlier chapters, sometimes the author introduces unnecessary details (e.g., the potentiometer, p. 199), or unwittingly introduces confusion. As an example of this, the equilibrium constant for the dissolution of water, given on p. 193 as $K_{eq} = 10^{-14}$, suddenly and without explanation becomes the 'ionization constant' and the 'ionization coefficient' two pages later: surely bewildering to a neophyte of physical chemistry. This chapter progresses to ideas of 'electrical flow' and

Fig. 3. Julia Hamilton describes her piece of art, crafted in 2014, as wanting "to capture the mesmerizing experience of watching new waters flowing to shore, the ancient rhythm of the sea. To quote Heraclitus (535 BC - 475 BC), 'You can never step twice in the same stream, for new waters are ever flowing in upon you.' It seems incredible that someone who lived so long ago could say something that resonates with people today." [Image used with permission: Julia Hamilton, 'New Waters', 2014: https://www.artbyjuliahamilton.com/]

'chemical energy flows', and once again concludes in a lyrical tone, which foreshadows the closing chapter (pp. 205-206):

"Chemical energy flows through the landscape of our lives, uniting the wind with the waters and the earth with fire. It has been one of the great feats of human thought, drawing upon the genius of Lavoisier, Hess, Faraday, Carnot, Mayer, Helmholtz, Joule, Clausius, Gibbs [all of whom are at least mentioned in this book] and many others to see into the nature of this flow. These chemical rivers run ultimately into the sea of time, but in their passage through Earth give rise to the miracles of living organisms, and to that we shall turn in the concluding chapter."

The final chapter – BIOLOGICAL ENERGY – is the highlight of the book. The chapter includes simple representations of closed and open systems, likening the latter to "a river that is always flowing but that remains a constancy of its basic characteristics", drawing on the assertion of the Greek philosopher Heraclitus that "you can never step twice in the same stream for the stream's water is constantly flowing in and out, and the water of one moment is not that of the next" (Fig. 3). The clearly presented concepts related to the steady state ideas (which includes reference to "No man is an island, entire in itself", recalling this quotation from John Donne,[5] used much earlier in the book) These are summed up as "interlocking open systems of living nature" and followed by an over-arching statement:

"To a very close approximation, if we could write a chemical equation for each activity of every living organism on Earth and were able to sum up the whole scheme, the result would be zero, for everything produced in one equation would be consumed in some other. In terms of material change, life all adds up to nothing. Does that mean that life is the 'sound of fury signifying nothing?'[6] Or does it mean that it is the grandest example of how much can be had for so little?"

The later sections of this chapter explain the energetics of reaction coupling whereby, for example, "the cell can couple the oxidation of nutrients such as glucose to the formation of the higher energy ATP [adenosine triphosphate] from the lower energy ADP [adenosine diphosphate]", and hence the "ATP-ADT transformations form a coupling device between the downhill oxidation of glucose and the uphill formation of polysaccharide from glucose, demonstrating this by changes in the free energy associated with the relevant reactions. This is one of the few chapters that includes diagrams (see Table 1), and it is pleasing to see the energetics of a coupling process (diagram on p. 228) associated with a mechanical analogue – the 'ancient undershot waterwheel pump (p. 229). The chapter continues with a discussion of 'vectorial chemistry' as applied to biological reactions – a concept whose introduction is assisted with the use of diagrams; revisits aspects of membrane chemistry, and touches on photochemistry.

After reading this chapter and reflecting on the book as a whole, the description of the author on the book's rear cover as "a student of physical chemistry and as a professor and researcher in biochemistry, physiology and general biology" seems appropriate. Although Professor Sherman's book provides students of physical chemistry with a highly readable introduction to the energetics of biological systems, the learning needs of biology students seeking an introduction to thermodynamics may not be quite as well met. For a wider non-student audience, the book introduces a large range of topics and their underpinning theories, many of which are set in a historic context, and some of which have encourage the author to traverse wider scientific and philosophical implications.

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5. John Donne's "No man is an island …" is from the 1624 Meditation 17, from *Devotions Upon Emergent Occasions.*
6. Sherman does not give the source of this quote, perhaps considering it would be well enough known. It is from Act 5, Scene 5 of William Shakespeare's *Macbeth* and is part of a longer verse: *"Life's but a walking shadow, a poor player | That struts and frets this hour upon the stage | And then is heard no more: it is a tale | Told by an idiot, full of sound and fury, | Signifying nothing."*

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Some Unremembered Chemists

This is the last of a series of articles by this author that explores the lives and work of selected chemists who have made a significant contribution to the advancement of the discipline, the profession and well-being of mankind, yet who are little remembered. If you are interested in continuing the series, please contact the editor.

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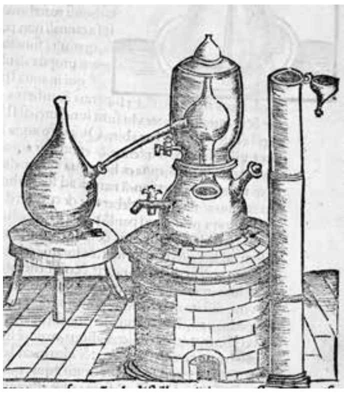
Women pioneers

Historically, chemistry is a woman's science — more than any other is. The first known chemists were women whose names were inscribed on the cuneiform tablets of ancient Mesopotamia some 4000 years ago. They were concocters and purveyors of perfume, a vital commodity in the age before personal hygiene. From then until the time of the Enlightenment in the 16th century, the secrets of medicines, cosmetics and perfumes passed from mother to daughter through the generations. Although the act of formally writing down and debating scientific knowledge only took hold of mainstream aristocracy in the 17th century, Mary the Jewess (Mary Phrophetissima aka Mary the Prophetess) was an alchemist who lived between the first and third centuries AD. She was one of the first writers and the first true alchemist of the Western world.[1] The subject of chemistry and all sciences became male dominated from the Enlightenment. Nonetheless, Mary is credited with the invention of apparatus that includes the the bain-marie and the first true distillation still that consisted of copper tubing, ceramic pottery and metal.



An alchemical *bain Marie* (or Maria's bath), from *Coelum philosophorum*, 1528 by Philippus Ulstadius

According to Wellington *et al.*,[2] the first PhD was awarded in Paris in ca. 1150 but it was not until the early nineteenth century, following university practice in Germany, that the term PhD acquired its modern meaning as the highest academic doctoral degree. The earliest record of a woman gaining an advanced degree came in the early 17th century with Spaniard Juliana Morell the first female to receive the degree for study on Aristotle.[3-5] She received her doctorate in Canonic Law in Avignon, France, in 1608. Her public defence was in the papal palace of the vice-legate before a distinguished audience. Later that year she entered the convent of Sainte-Praxède at Avignon. Then in 1678, Elena Cornaro,[6] an Italian philosopher of noble descent gained her PhD degree from the University of Padua and this is often cited as the first to a woman. Because of her gender, Gregorio Cardinal Barbarigo, the Bishop of Padua, had refused to allow her to submit for a theology degree. However, he did permit a degree in philosophy and, after brilliant study, she received the doctoral degree and took up a lectureship in mathematics at the University that same year. Elena was an expert musician in addition to mastering almost the entire body of knowledge. She was proficient with the harp, harpsichord, clavichord, and the violin, and demonstrated her skills from the music she composed in her lifetime. She was a member of various academies and esteemed throughout Europe for her attainments and virtues.

The earliest acknowledgement of a women chemist that this author has found came from the early 17th century with Martine Bertereau, Baroness de Beausolei (1590-1643), a French mining engineer and mineralogist. Together with her husband, Jean de Chastelet, they travelled extensively in Hungary, Germany and South America in search of mineral deposits using divining rods and the like.[7] In 1626, they were commissioned by King Henry IV to survey France for possible mine locations and revive the French mining industry. They surveyed hundreds, subsequently in the service of Henry IV's son, King Louis XIII. However, religious and financial concerns led the government to move against them, bringing charges of witchcraft. Both husband and wife (together with their daughter) were separately imprisoned (the Bastille and Vincennes) where they died.

In 1656, the first chemistry book by a woman, *La Chymie Charitable et Facile, en Faveur des Dames* (*Useful and Easy Chemistry, for the Benefit of Ladies)* was authored by Marie Meurdrac. She is likely the most important female chemist and alchemist never heard of. Her tome discussed instrumentation (vessels, lutes, furnaces, weights), how to make medicine from plants (especially by purifying through distillation), as well as animals, metallurgy and compound chemistry.[8] The final component addressed the female audience and covered methods of preserving and increasing beauty. Irrespective of whether her work is chemistry, alchemy or medical cookery, Meurdrac directly contributed in print a means that allowed for collaborations, as well as scrutiny, and it later defined the field of modern chemistry and science as a whole. This book appeared in 1656, five years before Boyle's *The Sceptical Chymist*.

The first woman to gain a PhD degree in science was Laura Maria Caterina Bassi (1711-1778),[9] who holds a unique place in science history and education. She gained her PhD in physics in 1732 from the University of Bologna and that same year became the first woman to accept an official, salaried teaching position there. This was when, generally, women could not pursue studies and intellectual professions. Throughout her academic career, Bassi led a relentless struggle to achieve equal conditions in teaching, while making a name for herself in the world of academia, a world that then in Italy and worldwide was exclusively male. She also had a pivotal role in spreading Newtonian physics in Italy and in pioneering research on electricity. In Bologna, she presented dissertations on subjects such as gravity, refrangibility, mechanics, and hydraulics. With her husband, Giuseppe Veratti, she made Bologna a centre for experimental research in electricity. Despite numerous public appearances, most of Bassi's teaching and research took place in her home, where from 1749 until her death, she and her husband established a laboratory, taught classes in experimental physics and natural philosophy, and presided over a lively scientific "salon." In 1776, she accepted the chair of experimental physics at the Bologna Academy of Sciences, with her husband as her assistant and intellectual partner. He took it over in 1778 when she died.

Bassi's graduation was followed in Germany by the award of PhD degrees in medicine to women and by a second physics PhD from Bologna to Italian Cristina Roccati in 1751; she then taught physics at the Scientific Institute of Rovigo for 27 years. The woman chemist received no further recognition until after these events and into the last quarter of the 18th century. This came from the work of Marie-Anne Pierrette Paulze. Married at age 13 to Antoine Lavoisier, Marie-Anne began to assist her husband and, as her interest evolved, two of her husband's assistants, Bucquet and Gingembre tutored her. The Lavoisiers spent most of their time together in the laboratory, working as a team on many aspects of research, she as his assistant and translating chemical papers from English to French for her husband. Lavoisier, regarded as the father of chemistry, published the first accepted chemistry textbook in 1789, *Traité Élémentaire de Chimie* (*Treatise of Elementary Chemistry*) this some 120 years after the book by Meurdrac. After Lavoisier's death in 1794, Marie-Anne subsequently married Benjamin Thompson, Count Rumford, one of the most noted physicists of the era.

In 1794, some six months before Lavoisier's death, Mrs Elizabeth Fulhame published a book: *An essay on combustion: with a view to a new art of dying and painting*. This woman is another whose chemistry did not gain the recognition it deserved.[10] Married to Thomas Fulhame, an Irish-born physician who had attended the University of Edinburgh and studied chemistry, little is known about her other than that she appears to have been Scottish. She began her chemistry with an interest in finding ways of staining cloth with heavy metals under the influence of light. She was encouraged to publish an account of her fourteen years of research after a meeting with Sir Joseph Priestley in 1793. She had studied the reduction of metallic salts in a variety of states (aqueous, dry, in ether and in alcohol) by exposing them to the action of various reducing agents, employing hydrogen, phosphorus, potassium sulfide, hydrogen sulfide, phosphine, charcoal, gas, and light. She discovered a number of reactions in which salts reduced to pure metals. Likely, her most important discovery was that of aqueous chemical reduction at room temperature, rather than from smelting at high temperatures.

Her theoretical work on catalysis was a major step in the history of chemistry, predating both Berzelius and Buchner, but for which she was given little recognition. She proposed, and demonstrated, that many oxidation reactions occur only in the presence of water, involve water, and that it is regenerated and detectable at the end of the reaction. Furthermore, she proposed modern mechanisms for the reactions, and may have been the first scientist to do so. The role of oxygen, as she describes it, differed significantly from other theories of the time. Thus, she disagreed with some of the conclusions of Lavoisier and the phlogiston theories that he analysed. Her research was a precursor to the work of Berzelius, although she focused on water rather than heavy metals. Fulhame's work on silver chemistry is a landmark in the birth and early history of photography and that on the role of light sensitive silver salts on fabric (photoreduction) predates Wedgwood's more famous photogram trials of 1801. Mrs. Fulhame was appointed a corresponding member of the Chemical Society of Philadelphia in 1810 which stated: *Mrs Fulhame has now laid such bold claims to chemistry that we can no longer deny the sex the privilege of participating in this science also*.

Some 12 years after the Fulhame book, likely the first chemistry textbook appeared, the amazingly popular *Conversations on Chemistry* was published appearing anonymously in 1806. Its authorship was not revealed as Jane Marcet (1769-1858) until the 12th edition in 1832.[11] Her book (in two volumes) served as a model of successful "popular science" writing despite its subject matter and was one of the first elementary science texts. It appeared in seventeen British and two dozen American editions, and numerous translations; 20,000 copies had sold in England by 1865. Humphrey Davy helped popularise it in his Royal Institution lectures and Michael Faraday gained his grounding in chemistry from it. Jane Marcet, the daughter of a London banker, had married Alexander John Gaspard Marcet, a doctor and subsequent lecturer at Guy's Hospital in 1799. He set up a home laboratory where his wife gained her chemical knowledge.[12] The book takes the form of conversations between two young female pupils, Caroline and Emily, and their teacher Mrs Bryant. The younger Caroline asks flippant questions that move the dialogue along, while the more controlled Emily is somewhat reflective. The maternal Mrs. Bryant is a mentoring figure who leads them to question and examine their ideas.[13]

Just two years later in 1808, Anna Sundström (1785-1871), the daughter of a farmer and born Anna Christina Persdotter who took the name later, became housekeeper and assistant to the famed Jöns Jacob Berzelius. From simply a housekeeper, she began to assist Berzelius and over a period of 28 years gained her chemical knowledge from working alongside him. She became an effective assistant and co-worker acquiring a vast knowledge of chemistry. Berzelius stated *"She is used to all my equipment and their names to such a degree that I could without hesitation make her distil hydrochloric acid"*. She maintained the laboratory and supervised his students, and was termed affectionately *strict Anna* by them. Her employment ended in 1836 after 56-year old Berzelius married Elisabeth Poppius some 32 years his junior. Sundström is immortalised in an annual award of the Swedish Chemical Society's inorganic chemistry division for the best Swedish PhD thesis - the Anna Sundström Award.

What is undoubtedly the first PhD degree in chemistry awarded to a woman was still half a century away. Between 1837 and 1857 the education of women advanced significantly with co-educational and single sex schools opening throughout much of the northern hemisphere, Egypt and Chile.[3] Bedford College opened in London in 1849 as the first higher education college for women in the United Kingdom while, in 1855, the University of Iowa became the first US university to become co-educational. In the late 1860s Anna Fedorovna Volkova gained chemical knowledge from lectures at St Petersburg University and became the first woman to publish research in a chemistry journal (from work at the St Petersburg Technological Institute) having two papers on sulfonic acids published in 1870;[14] and working predominantly with amides. She became the first woman member of the Russian Chemical Society. Volkova was also the first to prepare *p*-tricresol phosphate from *p-cresol*, the *o*-analogue of which is an important plasticiser.

The universities in Switzerland were the first in modern-era Europe to admit female students. Lydia Sesemann (Lidiia Zesemann) from Vyborg in Finland was the first woman to study chemistry in the Faculty of Natural Sciences in Zurich (1869-1874).[15,16] She defended her dissertation in organic chemistry *Über Dibenzylessigsäaure und eine neue Synthese der Homotoluylsäure* (On dibenzylacetic acid and a new synthesis of homotoluic acid) and was awarded her degree in May 1874 (see Fig.1) for work under Victor Merz and Wilhelm Weith. She was the first woman to graduate in science at the university, but she never practised the profession, which likely accounts for her absence in much documented history. Many of the references to the early PhD graduates accord Stefania Wolicka as the first woman PhD graduate but this is not so. Her university of Zurich matriculation document No. 3798 (the equivalent of Fig. 1) gives the date of submission (November 5, 1874) and award (March 6, 1875),[17] which are clearly after those for Sesemann. The first woman to study and graduate PhD from Zurich was Russian Nadzhda Suslova who gained her degree in medicine in 1867 and was the first in Europe in the modern era.[18] The Russian Iuliia (Julia) Vsevolodovna Lermontova was the second PhD chemist. The University of Göttingen granted her degree in the autumn of 1874 from studies with Bunsen in Heidelberg and Hofmann in Berlin at about the same time as her friend and compatriot Sofia Kovalevskaia (1850-1891) obtained her doctorate, the first woman PhD in mathematics. Göttingen accepted these women for advanced degrees whereas neither Heidelberg nor Berlin would. Lermontova subsequently worked in Markovnikov's Moscow laboratory on aliphatic hydrocarbons from which she published alone (as J. Lermontoff) the synthesis of 1,3-dibromopropane (1876) and 2,4,4-trimethylpent-2-ene (1879),[19] prior to working with Butlerov[20] in St Petersburg. On returning to Moscow, she became likely the first woman to work on petroleum chemistry (Caucasian) with Markovnikov.

A year after Sesemann graduated in Switzerland, Lovisa (Louise) Katarina Hammarström (1849–1917) became the first formally trained female chemist in Sweden. Her father, a medically trained priest, was widowed when Louise was young and she grew up at an Ironworks in Dalarna (central Sweden). There she became interested in chemistry from the city chemists she met. She was a student at Konstfack (now the University of Arts, Crafts and Design in Stockholm), then the Handicraft School, and studied chemistry by private lessons, though she

Universität Zürich

Matrikeledition

Sesemann (Frl.) Lydia (Maria)

Matrikelnummer	3617
Fakultät	philos.
Semester	Wintersemester
Immatrikulationsjahr	1869
Geburtsdatum	
Geschlecht	weiblich
Herkunftsort bzw. CH-Bürgerort	Wiborg
Herkunftsort bzw. CH-Kanton	Finnland
Herkunftsland	russ.Reich
Angaben zur Vorbildung	unklar ob Stuttgart (= ev. Wohnort d.Eltern) od.Priv.unterr. in Finnland ?
Weggang von der Universität	ab mit Zgn.24.04.1874, (prom.15.05.1874)
Informationen über die Eltern	E. majorenn
Zusatzinformationen	* 1846, Dr.phil.II (StAZ U 110 e.1 = 1.Promotion einer Frau in Zürich an die- s Diss."Üb.Dibenzylessigsäure und eine neue Synthese der Homo- toluylsäure" (' S.34; MB

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Fig. 1. Lydia Sesemann (left) and a copy of her matriculation record (http://www.matrikel.uzh.ch/).Right: Julia Lermontova

never gained a formal qualification. From 1875-1881 she was employed as an assistant in the engineering laboratory of Werner Cronquist in Stockholm, performing arsenic analyses. She then joined the Ironworks at Bångbro (1881–87) as a mineral chemist, then the Fagersta Bruk (1887–91) that produced carbon steel wire and rod, and finally at Schisshyttan (1891–93). In 1893, she opened her own Bergchemical laboratory in Kopparberg and focused on minerals and geological studies.

Nadezhda Olimpievria Ziber-Shumova (1856-1914) was another of the Russian women to be educated in Switzerland in the early 1870s. However, she was there together with her husband Nokoli Ziber (an early Marxist economist) and never enrolled for a degree in Zurich. When the Russian women were ordered out of the city by the Russian government in 1873, she transferred to Bern. By 1877, she was working with Polish chemist/biochemist, Professor Marceli Nencki, but she was still without qualification. When Nencki transferred to Moscow in 1891 to head the newly established, and first, Russian biochemistry laboratory (the chemical laboratory of the Imperial Institute of Experimental Medicine, the first research medical-biological centre) Ziber-Shumova transferred with him. She continued to act as his assistant making significant advances to the biological studies. When Nencki died in 1901, Ziber-Shumova headed the Laboratory where she continued developing the science proposed by Nencki. In 1912 Ziber-Shumova was appointed a Head of the Chemical Laboratory with the rights of an actual Member of Imperial Institute (equal to a full Professor) and devoted 25 years of her life to the development of biochemistry there. Her publications with Nencki and coworkers dealt with the formation of urea in the organism and role of liver in this process; the chemical composition and biological properties of pepsin; the analogy in chemical structure of haemoglobin and chlorophyll; the processes of oxidation, putrefaction, and fermentation of carbohydrates amongst other studies. Nadezhda O. Ziber-Shumova was the first woman professor of biochemistry in Russia and she made a vital contribution to the formation and development of the science there. Of the early female chemists, she published what is most likely more papers in the chemical literature than any other woman before 1901.[14] In 1909 Ziber-Shumova donated to the Polish Society of Biological Investigations 50,000 rubles (roubles) for the foundation of the Nencki research institution, which was opened in Warsaw in 1918 (the Nencki Institute of Experimental Biology).

The last of the Russian women worthy of inclusion is Vera Yevstafievna Popova (née Bogdanovskaya), 1867-1896. Born in St Petersburg, she spent four years from age 11 taking the Bestuzhev Courses, an institution founded in 1878 in St Petersburg to encourage Russian women to stay in Russia to study. It was the largest and most prominent women's higher education facility in Imperial Russia, and included amongst its distinguished lecturing staff Alexander Borodin.[21] She then worked in the Academy of Sciences and Military Surgical Laboratories for two years prior to doctoral study at the University of Geneva. Her research there was with Karl Gräbe on dibenzylketone and she gained her PhD in 1892. She returned home and taught at the Bestuzhev Courses giving the first course on stereochemistry. It was there that she wrote her first book, a text on basic chemistry and the first by a Russian woman. It gained a favourable widespread reputation.[22] In 1895 she took a marriage of convenience with the older Jacob Popov, director of a military steel plant, and moved to Izhevskii Zavod, a town in the Western Ural Mountains dedicated to weapons manufacture. One condition of the marriage was that Jacob build his wife a laboratory where she could continue her chemical research. Here she returned to the synthesis of the prussic acid analogue methylidenephosphane ($\text{P}\equiv\text{C-H}$), a topic that Gräbe had dissuaded her from for PhD study because of the perceived difficulty. It is an analogue of hydrogen cyanide in which the nitrogen atom is replaced by phosphorus. The first communication on its synthesis appeared only in 1950 and its structure established unambiguously a decade later.[23] This attractive derivative is easily self-ignited and combusts in air even at low temperatures. Sadly, Vera Popova's life was ended on May 8, 1896 following an explosion involving PCH in her laboratory.[24] She was just 28 years old.

Despite the significant influence of Russian women in chemistry in Zurich, they were not the only female students there. Rachel Holloway Lloyd (1839–1900) was a pupil of organic chemist August Viktor Merz, became the first American female chemist to gain a doctorate, and

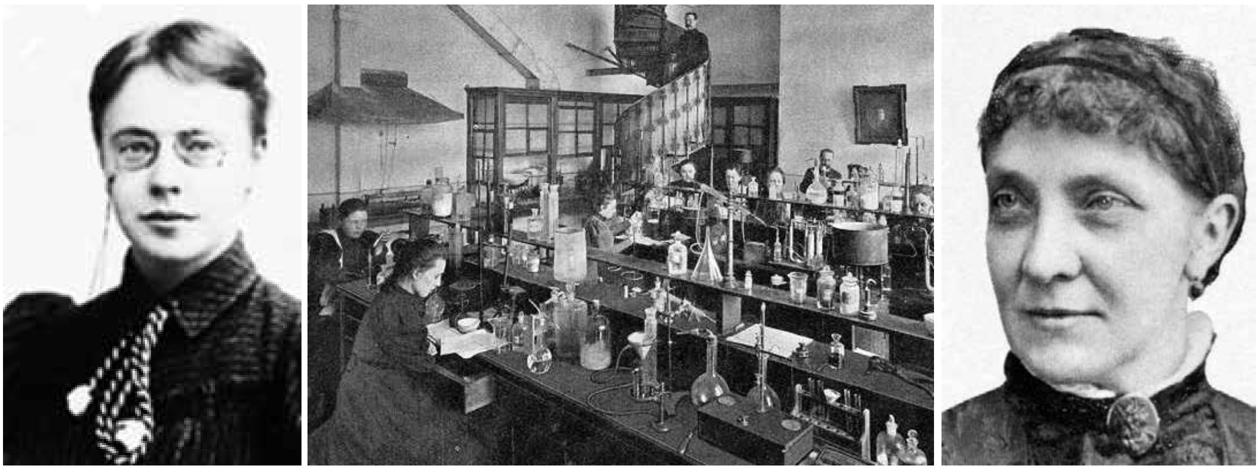
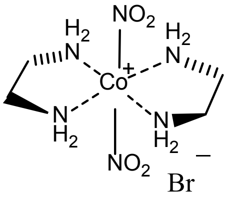


Fig. 2. Left: Vera Yevstafievna Popova (née Bogdanovskaya) and the Laboratory of the Bestuzhev Courses. Right: Rachel Lloyd

was, in 1891, the first female admitted to the American Chemical Society. She is best known for her work on the chemistry and agriculture of sugar beets. She studied at the Harvard Summer School before receiving her doctorate from the University of Zurich in 1887 for her thesis *On the conversion of some of the homologues of benzol-phenol into primary and secondary amines*. More than a century later in 2014, the ACS designated her research and professional contributions to chemistry a National Historic Chemical Landmark at the University of Nebraska—Lincoln. Another woman of note at Zurich was the British inorganic chemist Edith Ellen Humphrey (1875–1978), who carried out pioneering work in co-ordination chemistry as assistant to Alfred Werner. Her Zurich PhD was granted in November 1901. Her siblings were educated to degree level and she attended Camden School for Girls, then from 1891, North London Collegiate School, one of the first girls' schools in the UK to include science in the curriculum. Between 1893 and 1897, Humphrey studied chemistry (and physics) at Bedford College, London, prior to moving to Zurich to study under Werner. She became the first of his students to prepare the first new series of geometrically isomeric cobalt complexes, a class of compounds crucial in Werner's development and proof of co-ordination theory. One of these compounds, the *cis*-bisethylenediaminedinitrocobalt(III) bromide, was the first synthesis of a chiral octahedral cobalt complex.[25] In 1991, the Swiss Committee on Chemistry donated Humphrey's chiral crystals to the Royal Society of Chemistry, where they are held in Burlington House, London. However, later study has cast doubt on the quality of the sample,[25] but Humphrey's status as a pioneer woman scientist remains significant. Her doctoral thesis: *On the binding of compounds to metals and on dinitroethylenediaminecobalt salts* was accepted by the University of Zurich in 1901and she became the first British woman to obtain a doctorate in chemistry.



cis-bisethylenediamine-dinitrocobalt(III) bromide

The first Swedish woman PhD chemist (second among all disciplines) was Astrid M. Cleve von Euler (1875-1968). She was a Swedish botanist, geologist, chemist and researcher at Uppsala University. Her PhD was awarded in 1898 at Uppsala University for study of the germinating time and the juvenile stage of some Swedish plants. Astrid's father was the noted Per Teodor Cleve who discovered holmium and thulium. After graduating with a bachelor's degree in 1894, she became an assistant chemistry professor at the progressive Stockholm University. While working there she met the German-Swedish biochemist and subsequent (1929) Nobel laureate Hans von Euler-Chelpin. They married in 1902 and she became Astrid Cleve von Euler, had five children prior to the marriage ending in 1912, and taught in Anna Sandström's women teacher's seminary in Stockholm until 1917. She had published 16 papers with her husband on nitrogenous organics after her papers on lanthanum and selenium appeared from Stockholm. She continued her research at the forestry laboratory at Värmland where she was head.

The beginning of the 20th century saw Germany award its first PhD degree to a woman. Clara Immerwahr (1870-1915) graduated PhD from the University of Breslau in 1900 from study under Richard Abegg. Her thesis was *Contributions to the Solubility of Slightly Soluble Salts of Mercury, Copper, Lead, Cadmium, and Zinc*. Born of Jewish parents, her father a chemist, she converted to Christianity and married like convert Fritz Haber in 1902. He became the 1918 Nobel Laureate awarded for the Haber-Bosch process, who directed the German use of chlorine in WWI. Clara's work after her marriage was that of assisting her husband. She committed suicide in 1914, some say because of her husband's political views.

Astrid Cleve von Euler and Clara Immerwahr

Postgraduate study in the USA started at Yale University and the first three PhD students graduated there in 1861. Of these, Arthur Williams Wright was its first science graduate with a degree in physics. Perhaps surprisingly, in 1876, Edward Alexander Bouchet became the first African American to gain a PhD (physics, calculus, chemistry, and mineralogy; awarded in physics). By comparison, Marie Maynard Daly (1921–2003), a biochemist, was the first African-American woman to earn a PhD in chemistry, but only in 1947 and from Columbia University. The first seven women Yale PhD students graduated in 1894. Despite this, and because graduate study is (and was) specialised, it was relatively easy for the professors then to avoid teaching female graduate students if they so wished. Admitting women as graduate students, a Yale professor assured the *Times* in March 1892, would not "commit the members of either the academic or scientific departments of the university to coeducation in any sense". Of the women pioneers, Charlotte Fitch Roberts (1859-1917) was a chemist. She received her bachelor's degree in 1880 from Wellesley College (near Boston), which made her a graduate assistant in 1881and an instructor in 1882. She spent the year of 1885–1886 as the equivalent of a postdoctoral fellow in Cambridge, England, working with Sir James Dewar. In 1896, she published her book *The Development and Present Aspects of Stereochemistry*[26] with her Yale professor Frank Gooch calling it *the clearest exposition of which we have knowledge of the principles and conditions of stereochemistry*" adding, *there is nothing in English that covers similar* *ground so broadly and so lucidly.* Roberts became a full professor at Wellesley in 1896, chair of her department, and eventually, a fellow of the American Association for the Advancement of Science.

Charlotte Fitch Roberts and Mary Pennington

Charlotte Roberts was followed a year later in 1895 by Mary Engle Pennington (1872-1952), an analytical chemist, who earned her PhD under Edgar Fahs Smith at the University of Pennsylvania. Pennington's postgraduate work led her to the field of bacteriological chemistry and ultimately to refrigeration engineering. Her work there earned us our confidence in the safe handling, storage, and transportation of foods.

Naturally, there were other women pioneers who did not graduate with a PhD degree but these are too numerus to outline here. The reader may wish to explore: Agnes Luise Wilhelmine Pockels (1862–1935),[27] a German whose work was fundamental in establishing surface science; Josephine Silone Yates (1852 –1912), the first African American woman to hold a full professorship at any US college or university; Laura Alberta Linton (1853–1915)[28] who, as an undergraduate, analysed mineral specimens collected by her professors that they named *Lintonite*, a rare zeolite mineral; Ellen Gleditsch (1879–1968),[29] Norway's second female professor and a radiochemist and second woman to be elected to Oslo's Academy of Science in 1917.

Acknowledgements

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Letter to the Editor

Re: Economic versus social imperatives as the final arbiter of environmental air quality

John Hoare, Association for Independent Research (AIR), Christchurch

Having experienced in Leeds during the severe UK winter of 1962/63 similar extreme air pollution, I can relate personally to Alec Smith's account of the earlier (1952) London event published in the June 2017 issue of *Air Quality and Climate Change* (AQ&CC).[1] Also, given the contentious nature of urban air pollution and its control, I suspect Alec's scepticism regarding "……*how so many figures which quote deaths, premature deaths due to air pollution, cost to GNP and such disturbing figures are arrived at*…" is shared by other people having similar educative and work experience backgrounds.

Regarding such matters, surely the perception of environmental air quality including measurement and/or quantification in terms of its impact on human affairs is crucially dependent upon what, exactly, one is discussing or referring to! Thus we have as one attempt at clarification:[2]

> ***Ambient air quality criteria*** or standards are concentrations of pollutants in the air (usually outdoor air but sometimes indoor air) specified for a variety of reasons including for the protection of human health, buildings, crops, vegetation, ecosystems, etc. as well as for planning and other purposes. There is no internationally accepted definition but usually "standards" have some legal or enforcement aspect, whereas "guidelines" may not be backed by laws. "Criteria" can be used as a generic term to cover standards and guidelines. Various organisations have proposed such criteria, e.g. WHO, EU and the US EPA. They are often similar - but not always - even if they are proposed for the same purpose such as the protection of human health.

To the uninitiated, such explanations are welcome providing as they do an insight into a complex matter. However, at the same time, they offer clues as to why modern air quality science frequently lacks consistency, objectivity, accuracy, etc. and hence may not always justify being described as intrinsically scientific,[3] at least as understood by those trained in the relevant disciplines.[4-6]

In New Zealand, regulation of air quality can be seen, broadly speaking, as coming under the aegis of:

1) Workplace exposure standards (WES) cf. obligations and rights under the Health And Safety at Work Act 2015 (HSWA) and the associated Health and Safety at Work (General Risk And Workplace Management) Regulations.[7]

2) General exposure standards or (ambient) guidelines (NESAQ[8]/AAQG[9]) cf. the Resource Management Act (RMA) 1991[10] requiring that that natural resources should be "…..managed……in a way, or at a rate, which enables people and communities to provide for their social, economic, and cultural wellbeing and for their health and safety".

While regulation of general exposures undoubtedly normally requires monitoring of the air found outdoors (reflecting the historically important emissions to air from industry, motor vehicles, home fires and natural sources and because the sampling involved is usually more convenient or less intrusive when organised in this manner),[8, 11] the fact remains we spend on average 80-90% of our lives indoors.[12] Crucially, the fact that the specific risk factors comprising the NESAQ and AAQG are outdoor-based means that threats to human health from exposure to unhealthy air and related environments located indoors [13] are effectively ignored.

Consequently, the setting (under the NESAQ) of arbitrarily-decided (low), legally-enforceable limits for particulate matter (PM) characteristic of the emissions from solid-fuelled domestic fires employed for space heating whereby the use of such technology is banned or otherwise discouraged seems likely to be counterproductive, at least in some situations.[5] Furthermore, because the health risks associated with hypothermia are plain to most health professionals, one might be excused perhaps for thinking that such stringency may well have been devised as a means of conflating public health with other, not necessarily compatible, policy commitments i.e. under the RMA

In theory, the NESAQ, AAQG and WES all involve control of specific substances in the interests of public health. In practice, however, several important points of difference emerge.

In the case of the WES, given the workplace is the intended main focus, economic considerations involving a great variety of industries and, hence, specific substances and/or exposures are very much to the fore. Also, as a means of mitigating the potentially harmful effects, the importance of exposure variations and/or interludes are taken into account allowing the daily exposure (8 hours time-weighted average) limits to be maximised.

Concerning the NESAQ and AAQG - designed, one would have to say, to cater to modern relatively low exposure scenarios - the following rules of thumb apply:

i) the projected effects of the pollution and/or consequences of its reduction typically are estimated – presumably for reasons of convenience and/or expediency – commonly using particulate matter PM10 (or the subfraction PM2.5) alone as a surrogate for whatever may, actually, be responsible i.e. for the alleged effects

ii) no account is taken of the fact that particulate matter (e.g. PM10/2.5) is defined in generic terms (mass/volume) without any reference to its chemical composition

iii) PM10/PM2.5 are assumed to be toxic at any level

Table 1. NZ exposure limits for some common air pollutants

Pollutant	**Limit**
Respirable coal dust (≤ 3.5 μm)	WES: 3,000 μg m^{-3}
Carbon black	WES: 3,000 μg m^{-3}
Diesel particulate matter (DPM) as elemental carbon (EC)	WES: 100 μg m^{-3} Equivalent to 500 μg m^{-3} minimum PM2.5 assuming aerodynamic diameter is ≤ 2.5 μm and EC content is ≤ 20%[20]
Particulate matter as PM10	Currently under review NESAQ: 50 μg m^{-3} 24 hr av. allowing ≤ 1 exceedance/yr; AAQG: 50 μg m^{-3} 24 hr av.; 20 μg m^{-3} annual av. Equivalent PM2.5 values are calculated assuming PM10 is 70% w/w PM2.5. Such values can be contrasted with a) the current EU standard of 50 μg m^{-3} 24 hr av. allowing ≤ 35 exceedances/yr; 40 μg m^{-3} annual av. b) the current EU standard for PM 2.5 (exposure) of 20 μg m^{-3} annual av. c) NZ PM2.5 annual av. 4-12 currently.[21]
Sulfur dioxide	WES: 5,200 μg m^{-3} NESAQ: 350 μg m^{-3} 1 hr av. allowing ≤ 9 exceedances/yr); 570 μg m^{-3} 1 hr av. not to be exceeded; AAQG: 350 μg m^{-3} 1 hr; 120 μg m^{-3} 24 hr av.
Nitrogen dioxide	WES: 5,600 μg m^{-3} NESAQ is 200 μg m^{-3} 1 hr av. with ≤ 9 exceedances/yr; AAQG is 200 μg m^{-3} 1 hr; 100 μg m^{-3} 24 hr. av.
Carbon monoxide	WES: 29,000 μg m^{-3} NESAQ: 10,000 μg m^{-3} 8 hr av.; AAQG: 30,000 μg m^{-3} 1 hr av.; 10,000 μg m^{-3} 24 hr av.
Ozone	WES: 200 μg m^{-3} NESAQ: 150 μg m^{-3} 1 hr av.; AAQG:150 μg m^{-3} 1 hr av; 100 μg m^{-3} 8 hr av.
Hydrogen sulfide	No NESAQ limit; AAQG: 7 μg m^{-3} 1 hr av. (odour annoyance).
Benzene	WES (skin): 3,200 μg m^{-3} No NESAQ limit; AAQG: 3.6 μg m^{-3} annual av.

notwithstanding that the harmful effects of poisonous substances ordinarily are dose-dependent above a given minimum.[14]

iv) no account is taken of the fact that the mere presence of air pollution outdoors does not mean, automatically, that public unhealthiness results or is prevalent or, putting this another way, that benefits to public health would necessarily accrue in the absence (or lower levels) of such pollution.[15]

In New Zealand, emissions of concern normally consist of those attributable to motor vehicles, industry and natural sources (PM) etc. augmented occasionally, such as during winter, by domestic fire emissions. To this extent the relevant airsheds presumably reflect day-to-day emission patterns not greatly different from those of the ordinary workplace environment, i.e. pollution peaks followed by troughs of somewhat longer duration typically involving other (different) types of pollution and/or exposures. As the pollution from motor vehicles occurs at or near ground level all year round, the relevant exposures while commuting or through residing close by busy roads or thoroughfares are conceivably intrinsically more harmful, potentially, than those attributable to domestic fire emissions occurring higher up and at a time when people are mainly indoors.

To summarise, as confirmed by the data provided in Table 1 and given:

a) the generally more relaxed standards involving the so-called criteria pollutants as WES i.e. compared to the same substances as embodied in the NESAQ and AAQG

b) that an aged population is more expensive to cater to than a younger (healthier) one

c) regulations of the NESAQ and AAQG type although nominally for the purpose of protecting or enhancing public health aimed at saving lives seem likely to have the opposite effect[5] insofar as the most vulnerable members of the population are concerned, the three sets of air quality regulations, i.e. NESAQ, AAQG and WES, would each appear likely to engender economic growth either by facilitating (cf. b and c above) the lowering by a small amount of the average life expectancy affecting mainly the elderly or by exploiting to the maximum (cf. a above) the natural resilience and bullet-proof mentality of the average (male) employee tasked with working in a potentially "risky" environment.[16]

Meantime, given the apparent deterioration in various social and/or public health norms occurring currently[15] coupled with the perceived threats presented by climate change,[17] an adjustment of priorities may well be called for. Also if, as a consequence of such awareness, a "new normal" emerges giving a higher priority to substantive criteria of public health rather than, as favoured currently, hypothetical outcomes based on prospective mortality construed from statistically-contrived epidemiology[18] seemingly in the interests of economic growth assisted by an "inclusive" approach,[19] then who is to say that this does not represent real progress?

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reflecting, necessarily, those of any individual referred to or implied thereby.

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Dates of note

OCTOBER

21 ***Alfred Nobel*** was born this day in October 1833.

22 ***Stephen Moulton Babcock,*** the American agricultural chemist often called the father of scientific dairying because of his development of the 1890 Babcock test (a simple method of measuring the butterfat content of milk), was born in 1843.

Chester R Carlson demonstrated xerography for the first time this day 80 years ago.

23 ***William Coolidge***, the American physicist, engineer and physical chemist whose improvement of tungsten filaments was essential in the development of the incandescent lamp bulb and the X-ray tube, was born in 1873.

John Dalton presented his essay in 1803 on the absorption of gases by water, at the conclusion of which he gave the atomic weights for 21 elements.

27 ***Lise Meitner***, the Austrian-Swedish physicist who shared the Enrico Fermi Award in 1966 (with Hahn and Strassmann) for their research that led to the discovery of uranium fission, died 50 years ago today in 1968. She was born on November 7, 1878.

Isidor Traub, the German physical chemist who founded capillary chemistry, died in 1943.

Du Pont announced its new synthetic fibre yarn *nylon* on this day in 1938.

It is 290 years ago that ***James Cook*** was born.

28 Sir ***Christopher Kelk Ingold,*** the British chemist famed for developing mechanistic chemistry, was born in 1893.

Marie Maynard Daly, the first African-American woman to receive a PhD in Chemistry (Columbia University, 1947) died in 2003.

John Backus, the American computer scientist who invented the FORTRAN computer programming language, died in 1988.

29 ***Carl Djerassi,*** the Austrian-American chemist, novelist, and playwright, best known for his contribution to the development of oral contraceptive pills, was born in 1923.

31 ***George Eugene Uhlenbeck,*** the Dutch-American physicist who with Goudsmit proposed the concept of electron spin in January 1925, died in 1988.

This day in 1888 saw pneumatic bicycle tyres patented by ***John Boyd Dunlop***.

NOVEMBER

1 ***Robert Kennedy Duncan***, the Canadian industrial chemist, teacher and populariser of science who advocated partnering scientific research and industry to create new and better consumer products, was born this day 150 years ago in 1868.

Severo Ochoa, the Spanish-American biochemist and molecular biologist who shared the 1959 Nobel Prize for Physiology or Medicine (with Kornberg) for the discovery of the mechanisms in the biological synthesis of ribonucleic acid and deoxyribonucleic acid, died in 1993.

This day also marks the 170th anniversary of the opening of the Boston Female Medical School to 12 students; it was the first medical school in the world exclusively for women.

3 ***Carl Dietrich Harries***, the German chemist, industrialist and leading scientist in the elastomer field at the turn of the 20th century, died in 1923.

5 ***Georges Urbain,*** the French chemist who first isolated the last of the stable rare earths, lutetium, died in 1938.

7 **Sir *Chandrasekltara Venkata Raman,*** the recipient of the 1930 Nobel Prize for Physics for the 1928 discovery of Raman scattering, was born in 1888.

On this day in 1908, ***Ernest Rutherford*** announced that he had isolated a single atom of matter in London.

10 ***Ernst Otto Fischer,*** the German theoretical chemist and co-recipient (with Wilkinson) of the 1973 Nobel Prize for Chemistry for his identification of the structure of ferrocene and sandwich compounds, was born 100 years ago today.

11 ***Arttwillmari Virtanen,*** the Finnish biochemist who improved the production and storage of protein-rich green fodder by the AIV method (named after him and vitally important to regions characterised by long, severe winters), which earned him the 1945 Nobel Prize for Chemistry, died in 1973.

13 ***Edward A. Daisy,*** the American biochemist who shared the 1943 Nobel Prize (with Darn) for Physiology or Medicine for his isolation and synthesis of vitamin K, was born this day in 1893.

14 ***Leo Hendrik Baekeland,*** the Belgian-American industrial chemist who invented Bakelite, the first thermosetting plastic that did not soften when heated, was born in 1868 (see *This Journal*, **2016**, *80*, 148-153).

It is 80 years today that ***Hans Christian Jaclyn Grant,*** the Danish pharmacologist and pathologist who invented the Gram stain, died.

16 ***James W.Mitchell,*** the American chemist best known for advancing the accuracy of trace element analyses by pioneering X-ray fluorescence methods for part per billion (ppb) trace element determinations, has his 75th birthday today.

21 In 1783, ***Jean Francois Pilatre de Rozier,*** a professor of physics and chemistry, and the Marquis Francois Laurant d'Arlandes, became the first men to fly by lifting their hot-air balloon off from La Muettte, a royal palace in the Bois de Boulogne, Paris, and flying nearly nine kilometres in 25 minutes. That same year on December 1, they rose to about 600 metres in their balloon, and landed 43 kilometres away after two hours in the air.

22 ***Wolfgang Ostwald,*** the second child of 1909 Nobel Laureate Friedrich Wilhelm Ostwald and one of the founders of colloid chemistry, died this day 75 years ago in 1943.

This day in 1903 saw the formation of the American Leather Chemists Association by nine founding members.

26 ***Karl Ziegler,*** the German chemist who shared the 1963 Nobel Prize (with Natta) for discoveries in the chemistry and technology of polymers (the Zeigler-Natta catalyst is named after them), was born in 1898.

27 ***Lars Onsager,*** the Norwegian-born American chemist whose development of a general theory of irreversible chemical processes gained him the 1968 Nobel Prize for Chemistry, was born in 1903.

In 1963, the first flight of a space vehicle powered by a liquid hydrogen and liquid oxygen fuel combination was made *by* the *Centaur II*.

28 Baronet Sir ***Robert Abbott Hadfield,*** the English metallurgist who developed manganese steel, was born in 1858.

It is also the day in 1828 that the Bakerian Lecture at the Royal Society was presented by ***William Hyde Wollaston***, in which he described the method of powder metallurgy he had devised to produce platinum from its ore.

29 ***Christian Doppler,*** the Austrian physicist of Doppler Effect fame was born in 1803.

200 years ago, Nicolas Clement, announced iodine as a new substance at the French Institute in the name of its discoverer, ***Bernard Courtois.***

DECEMBER

1 ***Martin Heinrich Klaproth,*** the German chemist and a founder of analytical chemistry who discovered uranium (1789), zirconium (1789) and cerium (1803), was born in 1743, 275 years ago.

3 ***Paul Crutzen,*** the Dutch chemist who won the 1995 Nobel Prize for Chemistry for showing that chemical compounds of nitrogen oxide accelerate the destruction of stratospheric ozone, has his 85th birthday today.

Carl Zeiss, the German industrialist and entrepreneur who gained a worldwide reputation as a manufacturer of fine optical instruments, died in 1888.

6 ***Charles Martin Hall***, the US chemist who invented

the inexpensive electrolytic method of extracting aluminium from its ore by using non-aqueous molten cryolite (sodium aluminium fluoride) as solvent, was born in 1863. As a young chemist, he experimented in a woodshed, initially unsuccessful until he realised that a non-aqueous solvent for the aluminium oxide was needed during electrolysis.

Joseph Louis Gay-Lussac, the French chemist best known for his work on gases, was born this day in 1778.

7 ***Martin Rodbell,*** the American biochemist who discovered the natural signal transducers, G-proteins, and gained the 1994 Nobel Prize for Physiology or Medicine, died in 1998.

9 ***Fritz Haber,*** the German physical chemist and 1918 winner of the Nobel Prize for Chemistry for his synthesis of ammonia from nitrogen and hydrogen, was born 150 years ago today in 1868.

Claude Louis Berthollet, the French chemist who was the first to note that the completion of chemical reactions depends in part upon the masses of the reacting substances, was born in 1748.

It is 50 years ago today that the first demonstration of a computer mouse was given (at Stanford University).

11 ***Vincent du Vigneaud,*** the American biochemist awarded the Nobel Prize for Chemistry in 1955 for his biochemically important studies of sulfur compounds and especially the first synthesis of a polypeptide hormone, died in 1978.

Georges Friedel (son of Charles Friedel), the French crystallographer who formulated basic laws concerning the external morphology and internal structure of crystals, died in 1933.

14 This day in 1933, ***Ernest Rutherford*** suggested the names *diplogen* for the newly discovered heavy hydrogen isotope and *diplon* for its nucleus; it was named *deuterium* by its original discoverer, Henry Urey.

15 ***Wolfgang Pauli*** (of Pauli Exclusion Principle fame) died this day in 1958.

Sir ***Humphry Davy*** was born this day in 1778.

17 ***Willard Frank Libby,*** the American chemist who devised the technique for carbon-14 dating, was born in 1908.

Alfred Wolf, the Brookhaven National Laboratory chemist who made pioneering contributions in the field of organic radiochemistry over almost 50 years, died in 1998.

19 ***Thomas Andrews***, the Irish physical chemist who demonstrated the continuity of the gaseous and liquid states, was born in 1813.

Robert Andrews Millikan, the American physicist awarded the 1923 Nobel Prize for Physics for his work on the elementary charge of electricity and on the photoelectric effect, died in 1953.

This day in 1853 saw ***Frederick Walton*** submit a patent application for his invention of linoleum.

22 ***William Hyde Wollaston,*** the English chemist and physicist who discovered palladium (1803) and rhodium (1804), died in 1828 (see also November 28).

23 ***James Prescott Joule,*** the English physicist who established that the various forms of energy were interrelated, was born this day 200 years ago.

26 ***Clemens Alexander Winkler,*** the German chemist who discovered the element germanium, was born in 1838.

On this same day in 1898, ***Marie Sklodowska Curie*** discovered the radioactive element radium while experimenting with pitchblende. During the years between 1899 and 1902, she dissolved, filtered and repeatedly crystallised nearly three tons of pitchblende. The goal of that work was a refined sample of the element - the yield was about 0.1 gram. This was enough for spectroscopic examination, and measurement of the exact atomic weight of radium. This discovery, along with the element polonium, earned her a second Nobel Prize in 1911.

28 ***Carl Regimius Fresenius,*** the German analytical chemist who devised a method for systematic identification and separation of individual metal and nonmetal ions by selecting the most suitable reactions from the many that were known, was born this day 200 years ago.

William Draper Harkins, the American nuclear chemist and one of the first to investigate the structure and fusion reactions of the nucleus, was born in 1873.

29 ***Alexander Parkes,*** an expert in electroplating and able to silver-plate such diverse objects as a spider web and flowers, was born in 1813.

This is the day in 1913 that ***William David Coolidge*** patented a method for making ductile tungsten for use as filaments in electric lamps.

JANUARY

1 ***Heinrich Hertz,*** the German physicist who was the first to broadcast and receive radio waves, died in 1894.

The Montreal Protocol, an international agreement to reduce the use of ozone-depleting substances (adopted 16 September 1987), came into force in 1989.

2 ***Roger Adams,*** the noted American chemist (Adam's catalyst) and teacher who joined the faculty at the University of Illinois at Urbana in 1916, was born in 1889.

3 This day 100 years ago saw ***Emest Rutherford*** succeed in splitting the atom by bombarding nitrogen atoms with alpha particles.

4 ***Norman Heatley,*** the English biochemist who solved problems in the extraction of penicillin from its mould, and paved the way for mass production, died in 2004.

5 ***Edmund Ruffin,*** the father of soil chemistry in the US, was born 225 years ago in 1794.

7 ***Eilhardt Mitscherlic***, the German chemist who promulgated the theory of isomorphism, was born in 1794.

The day also marks the 180th anniversary of ***Louis Daguerre***'s first announcement of his photographic system at the Academie des Sciences in Paris. The daguerreotype photo process needed only a few seconds, whereas earlier processes needed hours.

11 The first samples of alizarin, synthetically prepared by ***Carl Graebe*** and ***Carl Lieberman,*** were presented to the Berlin Chemical Society in 1869, 150 years ago.

12 ***Paul Hermann Miiller***, the Swiss chemist who received the Nobel Prize for Physiology or Medicine in 1948 for discovering the potent toxic effects of DDT on insects, was born in 1899.

13 ***Paul Urich Villard,*** the French physicist and chemist who identified a third kind of natural radiation in 1900, later called gamma rays, died in 1934.

This is the day in 1404 (during the reign of Henry IV) when English alchemists were forbidden to use their knowledge to create precious metals.

19 125 years ago, ***James Dewar*** exhibited several properties of liquid air and produced solid air at the meeting of the Royal Institution in London.

22 In 1939, the uranium atom was split for the first time using the cyclotron at Columbia University.

22 ***Richard August Carl Emil Erlenmeyer*** (of flask fame) died in 1909.

23 ***John Polanyi,*** the German-Canadian chemist and educator who shared the 1986 Nobel Prize for Chemistry (with Herschbach and Lee) for contributions to the development of reaction dynamics as a new field of research, has his 90th birthday today.

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