NZIC Chemistry IN NEW ZEALAND

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Articles and features

Other columns

Comment from the President

In the April issue I mentioned how well we do in New Zealand at attracting international attendees to conferences held here, and highlighting how New Zaland chemistry is playing a vigorous role on the world stage. Unfortunately we won't get the chance to host the IUPAC 2023 World Congress and General Assembly in Auckland. Our bid was considered at the 2017 Congress in Sao Paulo, Brazil, in July, but we lost out to the Netherlands.

We have a high profile at IUPAC – Richard Hartshorn (Canterbury) is the IUPAC Secretary General, Margaret Brimble (Auckland) is President of the Organic and Biomolecular Division, Gregory Russell (Canterbury) is President of the Polymer Division and Suzanne Boniface (Wellington) serves on the Committee on Chemistry Education. Margaret Brimble was presented with an award at the Sao Paulo Congress for outstanding service to IUPAC in the advancement of chemistry worldwide.

The NZIC is also involved in several other international chemistry organisations and consortia. Another area where we do well is our representation by Mark Waterland (Massey) on the Pacifichem organising committee. We are one of seven Pacific Basin chemical societies which co-sponsor the large Pacifichem conferences held in Hawaii every five years. As a sponsoring society we receive a share of the returns, resulting in a significant boost to the NZIC coffers after each conference. The division of returns amongst the sponsoring societies was recently renegotiated and Mark was successful in securing a larger slice for the smaller societies (like NZIC) than was formerly the case.

Another regional consortium to which we belong is FACS, the Federation of Asian Chemical Societies. The Asian Chemical Congress (ACC) meetings are organised under the auspices of FACS; the most recent ACC meeting was held in conjunction with the RACI Centenary Congress in Melbourne in August 2017. I attended the FACS General Assembly meeting in Melbourne as the NZIC representative. We have had a low profile within this organisation and we could do better. Its members range from large chemical societies in well-developed countries to much smaller societies in developing countries, and is an important forum for contributions to regional development of the discipline of chemistry.

The Asian Chemical Editorial Society (ACES) also held a meeting at the RACI Centenary Congress in July. ACES is an organisation of 13 major chemical societies in the Asia-Pacific region, of which NZIC is one, and publishes three journals, *Chemistry – An Asian Journal*, *Asian Journal of Organic Chemistry*, and *ChemNanoMat*. Past President Paul Plieger represented NZIC at this meeting, and reported that again our profile is low in this society and we could play a more active role.

Finally, closer to home, we are one of around 50 Constituent Member Organisations of the Royal Society Te Apārangi (RSNZ). We have the opportunity to contribute

to RSNZ through its Physical Sciences, Mathematical Sciences, Technology and Engineering discipline-based forum, which the President or other nominee from NZIC is invited to attend. Our engagement with the RSNZ has also been low.

On looking at all these relationships, we have the highest profile and the best outcomes for NZIC where we have continuity of representation, and the same person or people have attended on behalf of NZIC over a number of years, as occurs with IUPAC and Pacifichem. We have rotated the representation on FACS, ACES and RSNZ, and despite the willingness of the NZIC attendees at meetings and forums, the lack of continuity has meant our overall engagement has been lower, less rewarding and less productive. An important move for the future, as we move in 2019 to two-year terms for the NZIC President, will be to also consider more stable, longer-term representation on these bodies and a heightened commitment to our national and international role as New Zealand's chemical society.

Penny Brothers
University of Auckland
NZIC President 2017

New Zealand Institute of Chemistry

supporting chemical sciences

October News

NZIC Archives

A professional archivist has been looking at the boxes of NZIC historical material. From an archivist's point of view, important items are the minutes of meetings.

He was expecting to find a minutes book (or books) dating back to the start of NZIC, but so far we have not found anything. If any member has information that might help trace these, or any other archival material, please contact the Honorary General Secretary, Richard Rendle: rendle@xtra.co.nz or phone 03 359 7275.

AUCKLAND

The University of Auckland

Welcome to new staff

Welcome to *Sally* ***Hsieh***, our new analytical teaching laboratory technician. Sally did a great job for the School of Chemical Sciences as technical support at Grafton laboratories, and we now look forward to working with her on the city campus.

Welcome also to *Hayley* ***Benton-Hilder*** who joins us as a faculty assistant/receptionist, fronting the Plaza information desk for certain hours of the day and assisting the facilities team in the 302-Level 6 west office.

Farewell

Farewell to *Glenn* ***Boyes***, who has been with the Department and then School since 1978. Glenn was very reliable in his role as analytical teaching laboratory technician. Ahead of the semester, or prior to a particular laboratory session, he would have his check list at hand and know exactly what still needed to be done, and he has taken great pride in ensuring the laboratories run well. For many years he directly taught undergraduate students atomic absorption spectroscopy and gas chromatography, and more recently has instructed the graduate teaching assistants on how to demonstrate those experiments. He has managed to keep our analytical teaching instrumentation (some of which was older than the students using it) running over the years, with the help of *Vern* ***Rule***, *Ron* ***Bryant***, and more recently *Roger* ***van Ryn***. Glenn has also been a good friend to many people around the School, and we wish him well in his retirement.

Passing

We note with sadness the death of *Stephen* ***Rothman*** on 6 July 2017. Stephen was the School's manager about 12 years ago, and will be remembered for his confident competence and his wonderful sense of humour.

Events

Incredible science

More than 370 students and 55 teachers from 13 schools over Auckland spent a day immersed in science at the University of Auckland's *Incredible Science* day on Wednesday 5 July. The event is designed for students in Years 7-8 and aims to encourage them to think about future study in a field of science and to think about science as a career.

On the day, students learned what happens in an archaeological dig, the magic of mathematical patterns using origami and flexahexagons, saw a miniature tornado, as well as volcanoes and earthquakes, and practiced making slime and analysing fingerprints. Drones, a real-time analysis of Auckland Transport buses and glowing fluorescent proteins were also included in the science extravaganza.

The ever popular chemistry science Magic Show hosted by "Fred Dagg" aka *Gordon* ***Miskelly***, Head of School, School of Chemical Sciences, drew

"oohs" and "aahs" from his young audience. “Fred” and his sidekick, Nina, turned clear liquid into rainbows, exploded hydrogen balloons and demonstrated Oobleck - a non-Newtonian fluid - among many other "tricks".

The school groups were guided through the experience by University of Auckland science students, many of whom had their interest in science piqued at one of these days when they were at school.

Official opening of Building 302

27 July was the official opening of Building 302 – the newest addition to the faculty’s state-of-the-art Science Centre. The celebration included the science-specific segment of the University of Auckland’s *Campaign for all our futures*, featuring four questions we have set ourselves the challenge of answering, with support from distinguished friends and alumni of the University:

Can we uncover the mysteries of the human brain?

Can we build an economy based on what we know, not just what we grow?

Can we reveal the secrets of our world using modern instruments?

Can we bring back the dawn chorus?

Following a formal welcome by faculty kaiārahi Michael Steedman, Dr *Erin* ***Leitao*** from the School of Chemical Sciences acted as MC for the evening and welcomed speeches by Dean of Science Professor John Hosking, Vice-Chancellor Professor Stuart McCutcheon, Science Scholar Jessica Patterson and Tuākana Science programme member Leilani Ioelu.

Prime Minister Bill English echoed the words of Her Majesty Queen Elizabeth, the Queen Mother (who, in 1966, opened Stage A of the Science building, now Building 301) when he officially declared the building open.

The opening was an opportunity to meet up with alumni and donors, including former members of staff Professor *Brian* ***Davis*** and Professor *Charmian* ***O’Connor***, who both featured in the timeline video prepared for the event. Charmian was our first female professor (in chemistry), and has endowed a prize that we give to the top female student from first year who continues on to take second year chemistry courses. Brian was Head of Department in 1995, and earlier than that was Professor *Margaret* ***Brimble***’s MSc supervisor. He was also the Department’s chemical magician.

Green chemistry conference

Green Chemistry New Zealand 2017 (see advertisement in this issue) is a green chemistry conference organised by the Centre for Green Chemical Science. It will be held 8-9 December 2017 at the Science Centre, University of Auckland. This conference will bring together scientists from New Zealand, Australia and Asia-Pacific who work in the areas of green and sustainable chemistry. We encourage oral and poster contributions from staff and students. The conference will cover different aspects of green and sustainable chemical science and technology, in particular those that tackle global issues and problems that impact on sustainability. Please visit the website for more information, including registration and abstract submission: http://greenchemistry.blogs.auckland.ac.nz

Congratulations

Congratulations to the following people:

All of our spring graduates – the science ceremony was on 26 September. We had 97 graduates, including 15 PhD students and 9 MSc students who attended the ceremonies.

In recognition of her contributions, Distinguished Professor *Margaret* ***Brimble*** was presented with an award for *Outstanding service to IUPAC in the advancement of chemistry worldwide*. To receive the award, she went to the IUPAC General Assembly in Sao Paulo, Brazil. IUPAC has eight divisions, and Margaret is Chair of the Division of Organic and Biomolecular Chemistry. At the meeting, Margaret also took part in the Congress voting to approve the names of the four most recent additions to the Periodic Table: nihonium (Nh;

Top right: Building 302 official opening with (left to right): Simon Thrush, Director of the Institute of Marine Science, John Auld, George Mason Charitable Trust Chair, the Right Honourable Bill English, Prime Minister, Scott St John, Chancellor, John Hosking, Dean of Science, Professor Stuart McCutcheon, Vice-Chancellor. Top left: Erin Leitao acted as MC at the official opening of Building 302. Bottom: Dean of Science Professor John Hosking at the official opening of Building 302.

113), moscovium (Mc 115), tennessine (Ts 117), organesson (Og, 118). For further information (and the current rules on naming elements) see: https://iupac.org/iupac-is-naming-the-four-new-elements-nihonium-moscovium-tennessine-and-oganesson/ (see also Chemistry in New Zealand **80**, 57-59).

Dr *Geoff* ***Willmott*** and his collaborators (including Professor *Jadranka* ***Travas-Sejdic*** and Professor *David* ***Williams***) for gaining one of the Catalyst grants for overseas collaboration. This will allow student exchanges with some of the leading nanoelectrochemistry laboratories in the world.

Professor *Penny* ***Brothers*** has been appointed to chair the Physics, Chemistry and Biochemistry (PCB) panel of the Marsden Fund, and in that role she also joins Professors Juliet Gerrard and Gillian Dobbie from the Faculty of Science on the Marsden Fund Council. Penny has taken over from Professor David Williams, and her first activities in that role was overseeing the second round of the 2017 bids.

Distinguished Professor *Margaret* ***Brimble*** for gaining a contract for over $2M to develop novel peptide vaccines in cooperation with the Ferrier Research Institute at VUW.

The NZ Herald recently published an article on the agreement by the American drug development company BioMotiv to partner with the University on clinical trials of the vaccines developed by Sapvax (http://www.nzherald.co.nz/university-of-auckland/news/article.cfm?c_id=1503679&objectid=11895999). Sapvax is a start-up company making peptide-based vaccines based on research by *Margaret* ***Brimble***, *Geoff* ***Williams*** and *Rod* ***Dunbar***. It is great to see the success of companies such as Sapvax that are taking our discoveries into the wider world.

Associate Professor *Jonathan* ***Sperry*** and Dr *Paul* ***Hume*** have been awarded in this year's National Science Challenge Science for Technological Innovation (SfTI) SEED fund for a project entitled, *Mechano-chemical conversion of biomass into commodity chemicals*.

Fatemeh ***Mahmoodani***, a PhD student in Food Science, received the best paper award at the International Conference on Food Chemistry & Nutrition held in Vancouver, Canada, 24-26 July. Her paper was entitled, *Lipid oxidation and vitamin D3 degradation in dairy products as influenced by processing and storage*. Her research is supervised by Professor Conrad Perera and Dr Bruno Fedirizzi.

Chloe ***Cho***, a PhD student in the polymer lab of Dr Jianyong Jin for winning the best poster award about antimicrobial polymers at the 9th International Conference on Materials for Advanced Technologies, or more commonly known as ICMAT, which is a major biennial event organised by the Materials Research Society of Singapore (MRS-S), held from 18 – 23 June at Suntec Singapore and attracted 2,249 delegates from all over the world. The best poster award was presented by the journal *Biomacromolecules* and ACS publications. The prize was a certificate and $200 SGD.

PhD students who have published in very high impact papers:

Samuel ***Davidson***, PhD student with *David* ***Barker*** for his publication in Angewandte Chemie: *The first total synthesis of ovafolinin A and B: unique polycyclic benzoxepin lignans via a cascade cyclization*; Samuel J. Davidson and David Barker (DOI: 10.1002/anie.201705575).

Hans ***Choi***, PhD student with *Margaret* ***Brimble*** for his publication in Angewandte Chemie: Unexpected direct synthesis of *N*-vinyl amides through vinyl azide–enolate [3+2] cycloaddition; Hans Choi, Harry J. Shirley, Paul A. Hume, Margaret A. Brimble and Daniel P. Furkert (DOI: 10.1002/anie.201702727).

James ***Wood*****,** PhD student with *Margaret* ***Brimble*** for his article in Journal of Natural Products, marking the **500th** research article that Margaret has published: *Total synthesis and stereochemical revision of the 2-formylpyrrole alkaloid hemerocallisamine*; James M. Wood, Daniel P. Furkert and Margaret A. Brimble (DOI: 10.1021/acs.jnatprod.7b00314).

PhD candidates who successfully presented and defended their PhD theses:

Lakshika ***Perera***: *The good without the bad: selective chelators for beryllium encapsulation* (supervisors: Professor *Penny* ***Brothers*** and Dr *David* ***Ware***; funded by a Marsden grant).

Freda Li: *Total synthesis of gonytolide C* (supervisor: Professor *Margaret* ***Brimble***).

Rayomand Shahlori: *In-situ characterisation of the early stages of bio-mimetic calcium phosphate and calcium carbonate mineralisation* (supervisor: Associate Professor *Duncan* ***McGillivray***).

Leandro Dias Araujo: *Drivers of sauvignon blanc aroma at harvest: C6 compounds, antioxidants, and sulfur* (supervisor: Professor *Paul* ***Kilmartin***).

Harry ***Aitken***: *Synthetic studies towards the marine toxin portimine* (supervisor: Professor *Margaret* ***Brimble***).

Ashley ***Lindsay***: *Total synthesis of iheyamine A* (supervisor: Associate Professor *Jonathan* ***Sperry***).

Sandhya ***Badrinarayanan***: *Total synthesis and stereochemical revision of pestalospirane B* (supervisor: Professor *Margaret* ***Brimble***).

Rachelle Quach: *Total synthesis of citreoviranol* (supervisor: Professor *Margaret* ***Brimble***).

Thomas Kerr-Phillips: *Electrospun conducting polymer rubber fibres: synthesis and applications* (supervisor: Professor *Jadranka* ***Travas-Sejdic***).

CANTERBURY

NZIC Events

On 6 June visiting Erskine Professor, *Mark* ***Turnball***, Professor of Chemistry at Clark University (Worcester, Mass., USA), presented *The magic of chemistry*, a series of chemical demonstrations highlighting many aspects of chemistry and materials. Assisted by an ensemble of NZIC committee members, he produced changing colours, minor explosions and fire completely enrapturing a crowd of young people and their parents.

Mark has been a visitor to the University since 1995. His research focuses on the design, synthesis and study of low-dimensional antiferromagnets and is done in collaboration with Chris Landee (Clark, physics) and a variety of international collaborators including *Jan* ***Wikaira*** (chief assistant – see photos) and *Matt* ***Polson*** at UC.

Book launch

Scientific sleuthing: chemical discoveries made in New Zealand (16 tales of scientific success, illustrated in full colour) was proudly launched by the Canterbury Branch to a packed room at the Ilam Homestead on 11 August. Keynote speakers were Professor *Gary* ***Evans*** (Ferrier Research Institute, Victoria University of Wellington) and Adjunct Professor *William* ***Swallow*** (Department of Chemistry, University of Canterbury). With numerous contributors, the book boasts a list of compelling chapter titles including: *Toxic honey*, *Hoki to nanotechnology: a marine by-products story, Crime scene to court room: science for justice, A quarter century of sugary science success, Targeting cancer: the story of Auckland Cancer Society Research Centre.* The book is the sequel to *New Zealand is different* (1997) and has been has been beautifully co-edited by *Rebecca* ***Hurrell***, showcasing uniquely New Zealand chemical success stories.

The book is available for purchase and can be ordered directly from clerestory@xtra.co.nz for $49.95 including P&P within NZ (RRP $59.95).

University of Canterbury

Outreach

Sarah ***Masters*** and *Samantha* ***Bodman*** went to St Margaret's College recently to do some ice cream outreach with the Year 2 students. This was part of their technology unit, looking at processes and procedural writing. The girls learnt how to make ice cream three ways, and about sublimation and changes of state. They were very engaged in the process (which is not surprising given that the reward was ice cream at the end!) and have taken the topic to new levels, designing their own ice cream flavours, undertaking surveys to find out the preferences of others, and designing advertising for their product.

Congratulations

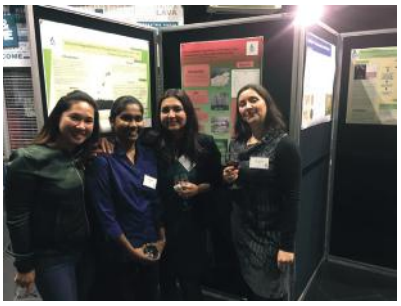
Professor *Ian* ***Shaw*** has been invited to be the food toxicologist on the Chief Scientist (Sir *Peter* ***Gluckman***)'s Folate & Pregnancy Panel. The Panel (set up by the Royal Society of New Zealand) will review the risks and benefits of fortifying the NZ diet with folate (to prevent spina bifida) to inform government decision making.

Ara Institute of Canterbury

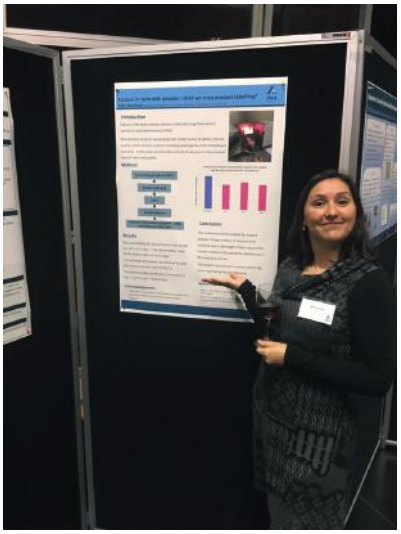
Graduate Diploma in Laboratory Technology students have taken part in industry work placements at Tumblar Products (contract chemical manufacturing), Meadow Fresh, Lincoln University, Hill Laboratories, Aoraki Salmon, Gribbles Veterinary, Southern Community Laboratories and Tegel Foods. Students complete 260 hours of industry work placement in their final semester of study toward their Graduate Diploma in Laboratory Technology from Ara Institute of Canterbury. The work

placement is highly valued by students and employers, as it provides the opportunity for great practical hands-on experience and can lead to a strong industry reference to help graduates with their job applications post study. For further information on the Graduate Diploma in Laboratory Technology please contact isis.carter@ara.ac.nz

Dr *Grant* ***Bennet***, in collaboration with Associate Professor *Craig* ***Bunt*** (Lincoln University), has been investigating how fats in foods can stabilise probiotic bacteria viability during storage. Their findings have been published in *Microorganisms.*



Graduate Diploma in Laboratory Technology students Mirdyn Englis, Melissa Tresa, Katherine McClelland and Sally Morrison present research posters at the Ara Industrial Science Symposium



Sally Morrison presenting her poster looking at the calcium content in New Zealand milk products

MANAWATU

NZIC President's Visit

The members of the Manawatu Branch were delighted to welcome Professor *Penny* ***Brothers***, from the University of Auckland, to Palmerston North on 21 June. Penny gave a public lecture at the Te Manawa Museum of Art, Science and History that evening. About 30 people attended to hear Penny discuss her recent achievements in her research into boron complexes of porphyrins and corroles and how to tune their properties. Penny also gave a stimulating presentation on her plans for her NZIC Presidency.

Massey University News

Holly ***Flay*** received the 300-level chemistry prize that was sponsored by NZIC.

Sam ***Brooke*** (*Characterisation and functionalisation of mechanically fractured graphene nanoribbons*) and *Ewan* ***Fisher*** (*Surface enhanced infrared absorption spectroscopy of functionalised graphene nanomaterials*) completed their MSc degrees with *Mark* ***Waterland***.

Haidee ***Dykstra*** (*At the cutting edge: structural analysis and chemical modification of the edges of mechanically cleaved graphene nanoribbons*) completed her PhD and passed without emendations, placing her in the top 5% of Massey doctoral candidates.

A new imaging spectrograph was recently installed in the IFS Raman lab at Massey University. The imaging spectroscopy provides high throughout and aberration-free imaging of Raman scattered light collected from the home-built Raman microscope.

Shane ***Telfer*** is the lead investigator on a $1.5M grant to work on *Disruptive technologies from metal-organic frameworks*. The research will involve the synthesis of new porous materials (MOFs) and their application in areas such as carbon dioxide capture and nitrous oxide reduction. This was one of only three projects funded under a Catalyst Fund call for New Zealand-Australia research collaborations. The research will be done in conjunction with scientists from CSIRO in Australia, and a number of chemists from other NZ universities including *Geoff* ***Waterhouse*** (University of Auckland), *Paul* ***Kruger*** (University of Canterbury), *Lyall* ***Hanton*** (University of Otago) and *Carla* ***Meledandri*** (University of Otago).

Gareth ***Rowland***'s group farewelled Manuela van Borselen as she returned to the Netherlands after spending nine months here as part of her undergraduate degree.

As part of a short leave trip in February 2017, *Dave* ***Harding*** delivered four presentations. The first was at the University of Sharjah, College of Dentistry, UAE entitled, *Tissue engineering with nanocellulose*. This presentation was repeated at the

Holly Flay, winner of the NZIC sponsored 300-level chemistry prize.

University of Science and Technology, Zewail City, Cairo, Egypt. The third, *Oil spill impact on biodiversity at sea and on land* was delivered at the University of Sharjah, Department of Chemistry, UAE. The fourth, *The sustainability of applied organic chemistry* was delivered as the opening plenary speaker at the Annual Conference of the Egyptian Petroleum Research Centre, Cairo, Egypt. Massey University's connection with the University of Science and Technology, Zewail City, Cairo is directly related to a Massey PhD graduate. The connection with Egyptian Petroleum Research Centre, Cairo is related to the now director who enjoyed a short sabbatical on the Palmerston North campus some years ago.

Massey University welcomed several speakers:

- Associate Professor Deanna D'Alessandro from the University of Sydney presented her Alan Sargeson Award lecture on *Exploring charge transfer in electroactive coordination frameworks* on 1 June.
- Five 700 level chemistry students gave a presentation on their research projects for their postgraduate studies on 12 June.
- Dr Loic Hilliou from the Institute for Polymers and Composites in Portugal presented on *Hybrid carrageenans: extraction, chemical structure and gel properties* on 26 June.
- Associate Professor *Mathieu* ***Sellier*** from the University of Canterbury gave a presentation on *Self-propulsion in confined/unconfined droplets* on 28 June.
- A MacDiarmid Institute seminar entitled, *Can we use alchemy to make the perfect pn-junction* was given on 6 July by Professor *Roger* ***Reeves***.
- Dr *Catherine* ***Whitby*** from Massey University gave a MacDiarmid Institute seminar on *Controlling soft material destabilisation: a route to fabricating new materials for delivery applications* on 3 August.
- Dr *Erin M.* ***Leitao*** from the University of Auckland gave a talk titled, *A mechanistic tour in inorganic synthesis* on 23 August.

OTAGO

Following the success of last year's inaugural Chemistry Quiz, the Branch held its second on the evening of 8 August in the School of Pharmacy. Twelve teams entered with members from across the university, from undergraduates to staff. The overall winners were *Darwin's Beagles*, with *Barmy Pharmys* and the *Garden Gnomes* close behind. *Andrea* ***Vernall*** and *Siddharth* ***Matikonda*** are thanked for their hard work in planning what was an enjoyable night for all, supported by *Dave* ***McMorran*** as MC and quiz master.

The Aurora Otago Science and Technology Fair was held at the Otago Museum in early August. The Otago Branch maintained its tradition of supporting the event through student prizes. The branch chair, *Nigel* ***Lucas***, awarded prizes to ten students, a difficult job considering the high standard across the 264 entries from 27 local schools. The projects awarded prizes all had an underlying chemistry theme, and were: *Limestone erosion* (Hazel Ross), *Making coins shine* (Alexander Hayward), *Whatever floats your boat* (Rowan Mestreyeon, Oe Hayward), *Phantastic phoam* (Evie Holt), *Winter washing* (Alyssa Batt), *Acid attack* (Ruby Walpole), *Walking on water: what affects surface tension?* (Caleb Simpson), *Winter windscreens* (Kate Fahey), *Electrolytes* (Tarryn Roxburgh, Regan Roxburgh), and *Horopito: insecticidal properties and chemical structure analysis of a NZ native plant* (Corrie Anderson).

University of Otago, School of Pharmacy

Sameek ***Singh***, a PhD student working with *Andrea* ***Vernall*** and *Joel* ***Tyndall*** attended *High throughput chemistry and chemical biology*, a Gordon Research Conference and Gordon Research Seminar at Proctor Academy, Andover, NH, USA in June.

University of Otago, Department of Chemistry

Huge congratulations to *Sally* ***Brooker*** who has been made a Member of the NZ Order of Merit (MNZM) in the Queen's Birthday honours for services to science. Sally and her science are well known to most of us in the chemistry community in New Zealand; she has made significant contributions in inorganic chemistry over the course of her career, and, most importantly to Sally, has been a supervisor and mentor to many young researchers. Well done, Sally, we couldn't be prouder!

Fittingly, Sally was also awarded the 2017 Burrow's award for significant contribution to inorganic chemistry and presented an award lecture at the RACI Centenary Congress in Melbourne.

In more award-winning news, *Bill* ***Hawkins*** recently received one of the University's annual Early Career Awards for Distinction in Research, which is a well-deserved recognition of his extremely productive research efforts. Well done, Bill! *James* ***Crowley*** was also a finalist in the Otago University Student Association Supervisor of the Year Awards.

The Department has recently acquired a state-of-the-art spectrofluorometer to replace our 20 year old workhorse. The new FS5 instrument from Edinburgh Instruments is a huge step up from the retired Perkin-Elmer LS50B instrument and allows for rapid quantum yield, singlet state lifetime and fluorescence measurements. This new capability will add

Participants ponder quiz master Dave McMorran's last question during the 2017 NZIC Otago Branch Quiz Night.

impetus to research projects in the department, such as those conducted by *Sean* ***MacKay*** and *Brian* ***Kueh*** who are funded by 2016 MBIE grants to investigate technologies for drug delivery through the skin and to the brain, respectively, under the supervision of *Eng Wui* ***Tan***.

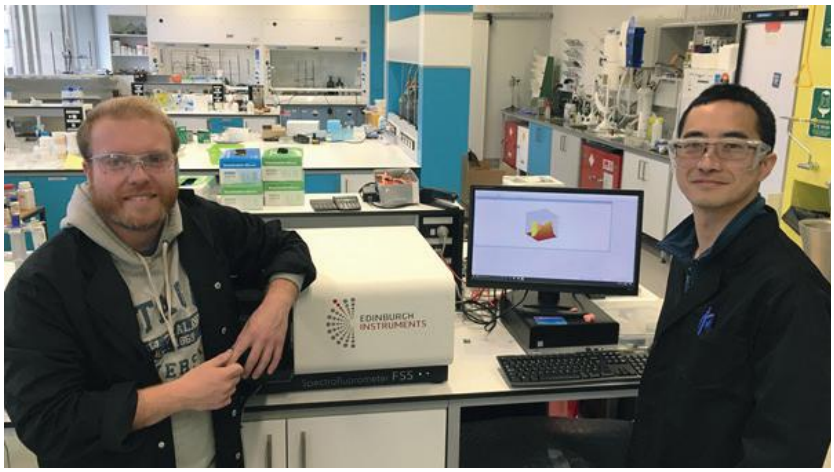
Jaydee ***Cabral*** gave an oral presentation titled, *In vitro adipogenic and osteogenic differentiation of bone-marrow derived mesenchymal stem cells using a chitosan/dextran-based hydrogel*" at the Secet Biosciences BioEngineering 2017: BioPrinting, Tissue Engineering and Synthetic Biology Conference in Boston, USA in March.

The Department of Chemistry was well represented at the RACI Centenary Congress in Melbourne in July; postgraduate students *Ross* ***Hogue***, *Joanna* ***Houlihan***, *Beth* ***Lippitt***, *Marina* ***Roxburgh***, *Brooke* ***Swaney***, *Mitchell* ***Clark***, *Richard* ***Lamb***, *Sinan* ***Gai***, *Quinn* ***van Hilst*** and researchers *Shailesh* ***Goswami***, *John* ***McAdam***, *Humphrey* ***Feltham***, *Sally* ***Brooker***, *Lyall* ***Hanton***, *Bill* ***Hawkins***, *Nigel* ***Lucas*** and *Dave* ***Larsen*** were in attendance. *Pauline* ***Bandeen*** and *Lisa* ***Bucke*** from the Campbell Microanalytical Microanalysis Laboratory also had a booth in the exhibition area to promote the facility.

In news from Waterworld and Centre for Trace Element Analysis, we said farewell to *Sylvia* ***Sander***, who has taken a new position at the International Atomic Energy Agency's Environment Laboratories in Monaco. Sylvia's PhD student, *Rebecca* ***Zitoun***, returned from a three-month research visit to Jacob's University in Bremen, Germany. There, she analysed Cu-speciation parameters of samples collected during the SONNE cruise SO253 in 2016/2017 to chemically characterise the hydrothermalism at the Kermadec Island Arc and its importance for elemental fluxes into the ocean. *Claudine* ***Stirling*** is an elected member of the Board of Directors of the international Geochemical Society and attended the Annual General Meeting in Paris on August 11. Several group members attended the Goldschidmt Conference in Paris in August with talks from *Claudine* ***Stirling*** (keynote), PhD student *Sophie* ***Gangl*** and former postdoctoral fellow (now at ETH Zurich) *Matthew* ***Clarkson***. Sophie is grateful to the New Zealand Federation of Graduate Women (NZFGW) for a $2500 travel grant.

PhD student *Matthew* ***Druce*** was awarded a prestigious fully-funded student internship to spend three months at Lawrence Livermore National Lab (LLNL) in the San Francisco Bay Area. Matthew's internship focuses on constraining the systematics of the molybdenum and zinc stable isotope systems, the latter forming part of his PhD project. PhD student *Kyyas* ***Seyitmuhamme-***

Sally Brooker receiving the Burrow's award from Phil Andrews, the Chair of the Inorganic Division of RACI.



Sean MacKay (left) and Brian Kueh with the new spectrofluorometer.

On board the research vessel RV SONNE, scientists uncover the secrets of the undersea volcanoes at the Kermadec Ridge.

dov spent three months at the Royal Netherlands Institute of Sea Research (NIOZ) from May to July 2017 analysing seawater samples from offshore Antarctica for their trace metal concentrations and receiving in-depth training in seawater pre-concentration techniques from his co-supervisor *Rob* ***Middag*** (formerly of Otago). *Ejin* ***George*** successfully defended his PhD thesis entitled, *Marine biogeochemical cycling of cadmium and its isotopes: studies of the South Pacific Ocean, Mediterranean Sea and Black Sea*. Ejin will shortly commence a two year appointment at the University of Otago.

As a member of the Scientific Committee on Oceanic Research working group, *Christina* ***McGraw*** attended a technical meeting at the International Atomic Energy Agency in Monaco in June. These meetings are used to develop a best practice guide for designing experiments to understand how marine biota will respond to a changing ocean. PhD student *Wayne* ***Dillon*** was awarded an IEEE Travel Grant to attend the Sensors Committee Summer School hosted by the University of Limerick, Ireland in June.

In news from the Plant Extracts Research Unit, *Nigel* ***Perry*** assisted Ed Morgan (Plant & Food Research) to coordinate a national research workshop focused on all things mānuka (6-7 July, Palmerston North). The workshop was attended by people from PFR, Scion, Landcare Research, Massey University and Waikato University. Forty researchers from a range of disciplines and organisations presented their science and themes included genetics and selection, physiology (flowering, nectar), microbiota including mycorrhiza, practical production, bioactives and pest and disease management (including Myrtle Rust). Nigel presented his team's work on *Mānuka bioactives*. The workshop served as a national 'stock take' to help guide and coordinate science strategy and investment, and assist with planning future mānuka-related research for Māori landowners, the honey industry and other interested groups. The workshop participants identified knowledge gaps and needs for mānuka research in New Zealand. A small team from the main research organisations have agreed to work together to analyse the gaps/opportunities and share their summary back out to the wider group. This team will also look at other native plant species beyond mānuka for further unique NZ product opportunities, and investigate partnering opportunities with Māori.

In news from the Gordon group, congratulations to *Joshua* ***Sutton*** and *Georgina* ***Shillito*** for giving talks at the recent International Conference on Advanced Vibrational Spectroscopy (ICAVS) meeting in Canada in early June. Joshua talked about his work on the use of low frequency Raman to investigate long range order in conducting polymers and how it is affected by polymer linearity and Georgina on donor-acceptor ligands in metal complexes. In addition, *Jono* ***Barnsley*** and *Jeremy* ***Rooney*** both presented posters. *Keith* ***Gordon*** also talked at ICAVS presenting a paper entitled, *Low-frequency Raman spectroscopy is suitable for quantitative analysis of multiple solid state forms of pharmaceuticals*. Georgina, Jono and Keith attended Applications of Photoactive Coordination Compounds (APCC) in St Andrews, Scotland (5-7 July). Jono and Georgina presented posters and Keith gave a talk on donor-acceptor systems with hexaazanaphthlenes complexes. Congratulations to Georgina who won a poster prize from RSC Dalton (poster title: *An investigation into the excited state behaviours of a series of [Re(L)(CO)3(diimine)] n+ complexes using spectroscopic and computational methods*). These three also attended the 22nd International Symposium on Photochemistry and Photophysics of Coordination Complexes in Oxford (9-14 July). Congratulations to Jono Barnsley for winning an RSC poster prize for his poster titled, *Spectroscopic and computational studies of ferrocene-Cu(I) complexes*. Georgina was the only PhD student to give a talk at the meeting and presented her work on rhenium(I) complexes with donor-acceptor ligands. Georgina also undertook a week long research visit to the Institute for Physical Chemistry in Jena, Germany for her ongoing collaboration with Dr Stephan Kupfer. Keith gave a plenary lecture at the Taiwan Association of Raman Spectroscopy (TARS) Summer Camp (29-30 June) and a plenary at the 5th Taiwan International Symposium on Raman Spectroscopy (TISRS 2017) (27-28 June). He also presented at the MacDiarmid Institute Energy meeting in Palmerston North on 22 June talking about *Spectroscopic studies on slinky and straight donor-acceptor polymers used in solar cells*. The following awards are gratefully acknowledged by the Gordon group: Jeremy Rooney – Science Division Travel Grant; Georgina – Claude McCarthy Fellowship, NZFGW(Otago) Travel Award, Division of Sciences travel grant; Jono – Brooker United Doctoral Travel Scholarship.

WAIKATO

Analytical Chemistry Competition

This annual event was held on 14 June. Invitations were sent to schools in the wider Waikato/Bay of Plenty region to send teams of four students to the University for the day to carry out an analysis. A total of 23 teams competed in the event.

The task was to analyse a sample of $ZnSO_4.nH_2O$ using a gravimetric procedure for SO_4^{2-} and a volumetric method for Zn^{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.

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: Tauranga Boys' High School (Daniel Bartley, Josh Bell, Anthony Fraser and Jack Wade)

2nd Prize: Aquinas College (Aileen Harwood, Alexander Hawkes, Jarod Schneebeli and Jamie Sutherland)

3rd Prize: Tauranga Girls' College

(Bianca Goyena, Dael Summerhays-Sunnex, Joanne Sutton and Geena Williams)

4th Prize: St Peter's School (Joseph Frengley, Tyla Grafas, Neeve Mckenzie and Nina Paripovich)

5th Prize: Pukekohe High School (Ben Allen, Paige Karanikolaou, Rose Lay and Finn O'Keefe)

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. Hill Laboratories and the Waikato Branch of the NZIC generously donated the prizes.

University of Waikato

We welcome Megan Grainger as a new lecturer in analytical chemistry. Megan completed her PhD at the University of Waikato on the kinetics of conversion of dihydroxyacetone to methylglyoxal in honey with Merilyn Manley-Harris in 2015 and has spent three years at Analytica Laboratories in Hamilton, firstly as a technologist in Environmental Chemistry and in the Food Division (as Honey Team Leader) and most recently as Operations Manager in the Foods Division.

Hannah Lowry has recommenced her Masters research following an area of interest in agriscience and Dylan McQuiston will soon take up employment in Auckland with Douglas Pharmaceuticals whilst completing his Masters research on pharmaceutical topics. Both students are working with *Michael* ***Mucalo***.

Michèle ***Prinsep*** attended the BioLive and ChemEd Conference which was held in Cambridge in July and gave a plenary address on her research on *Bioactive natural products from macro- and microorganisms* and also attended the Blue2Green, Marine Biotechnology Convention, held in Tauranga in August where she gave a keynote presentation on *Marine natural products research in New Zealand*.

WELLINGTON

Wellington Branch hosted the 2017 NZIC (Wellington Branch) Chemistry Quiz at Victoria University on 14 June. There were 145 Year 12 and 13 students from 19 Wellington region schools. Questions tested the students' knowledge of the NCEA chemistry curriculum as well as general chemistry and science. First prize was taken out by *Total Borons* from Wellington College with an impressive score of 72/81. Second place went to *Sieg* (also from Wellington College) and third to *OC Interpretive Dance Team Number 3* (from Onslow College). CoVFeFe (Cobalt, Vanadium, Iron, Iron) won the prize for best team name and The Cu's, fully dressed as a SWAT team, won best dressed. *Amanda* ***Berger*** treated the crowd to chemical demonstrations and there were lots of spot prizes – the most impressive being the student who recited the entire periodic table from memory, including the latest four elements to be added! Special thanks to the Branch student representatives *Garima* ***Dobhal***, *Amanda Berger* and *Alex* ***Gray*** who organised the event.

Prize winners: Tauranga Boys' High School's Jack Wade, Anthony Fraser, Josh Bell and Daniel Bartley were the winners of the 2017 NZIC Analytical Chemistry Competition with competition judge and chief organiser Associate Professor Michèle Prinsep (far left).

VUW

Three VUW students and NZIC members were awarded student travel funding to attend conferences. *Emma* ***Wrigglesworth*** attended the TechConnect conference in National Harbor, near Washington DC in May. Emma presented *A novel demonstration of the dichroic effect exhibited by gold nanoparticles and their incorporation into polymer* materials, a well-received oral presentation. The conference mixes academia, business and government so the talks covered a very broad range of topics which were interesting and of a very high quality. *Jim* ***Johnston***, Michelle Cook and Matilda Hayward also attended this conference. *Amira* ***Brackovic*** and *Sophie* ***Geyrhofer*** used their awards to attend the 18th Tetrahedron Symposium in Budapest in June. Amira presented *A scalable synthesis of peloruside A*, while Sophie presented *(-)-Zampanolide as an anti-cancer lead: towards the synthesis of analogues*. This conference highlighted the exciting advances in organic and bioorganic chemistry.

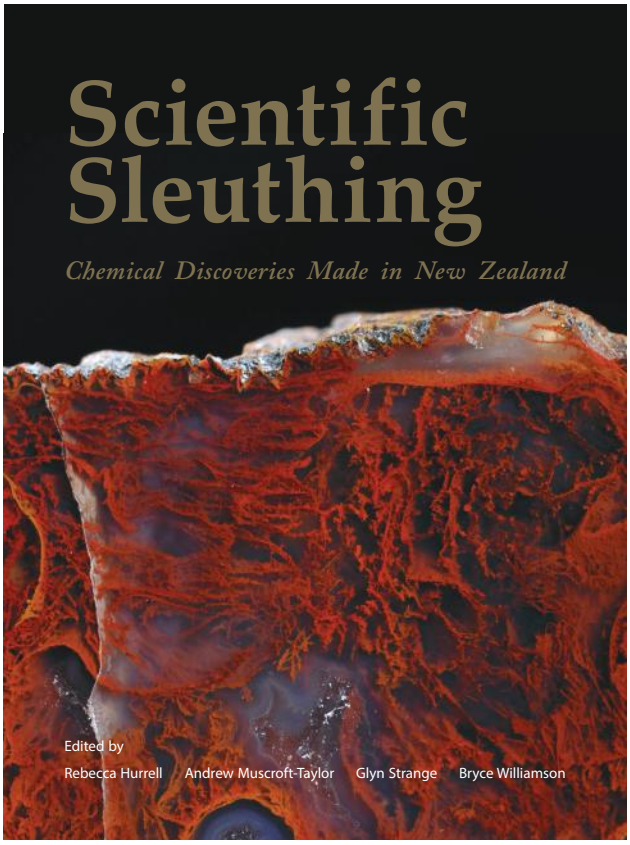
Graham ***Fairweather*** successfully defended his chemistry PhD thesis under the supervision of *Kate* ***McGrath*** in May.

The School of Chemical and Physical Sciences was treated to the following chemistry department seminars: *Peter* ***Schwerdtfeger*** (Massey Auckland) on graphene and three-dimensional variants, *Emily* ***Parker*** (now at VUW) on conformational changes in enzymes involved in biosynthesis of amino acids and a joint seminar by *Renée* ***Goreham*** and *Siobhan* ***Bradley*** (both VUW postdocs in *Thomas* ***Nann***'s group) on extracellular vesicles and storage technologies for renewable energy.

Ryan ***Schwamm***, a PhD student in *Martyn* ***Coles'*** group, has been selected as a finalist for the Reaxys PhD Prize in Chemistry. Ryan will travel to Shanghai to present his work which relates to the isolation of the first bismuth(II) radical to be stable in the solid state at the Reaxys Prize Symposium.

Scientific Sleuthing

Scientific Sleuthing - Chemical Discoveries Made in New Zealand (Rebecca Hurrell, Andrew Muscroft-Taylor, Glyn Strange & Bryce Williamson, eds), *New Zealand Institute of Chemistry*, Clerestory Press, Christchurch, New Zealand, 2017, pp. x, 270: ISBN: 978-0-9922517-7-2. $59.95



Scientific Sleuthing is a much needed sequel to the New Zealand Chemistry Institute's publication *Chemical Processes in New Zealand* that appeared in its second edition in 1998. The book comprises 16 contributions (chapters) by government agency scientists, academics and industrialists over 270 pages in a well-produced, high quality publication that is beautifully illustrated with scientific illustrations, personal photographs, and essential chemical detail. The book will appeal not only to chemists, biochemists and chemical biologists, but to all those with an interest in chemistry and the development of New Zealand. Those attracted to the recent evolution of the country from the actions of its entrepreneurs will find the book invaluable as it gives the country's chemists the rightful publicity they deserve. The sixteen chapters of the book are timely and appropriate, and can be grouped in a number of ways of which analytical chemistry (5), food chemistry (3), industrial chemistry (2) materials chemistry (3), and medicinal chemistry (3), is but one. Each chapter provides highlighted explanations, chemical and otherwise (in excess of 50) to assist the reader and each is completed with author profiles. The reader can dip in whenever she or he wishes.

The opening chapter on *toxic honey* is by Swallow, who has spent much of his career researching the topic. As one of the two major sources of food poisoning that have affected the New Zealand population, it details the identification of the toxins, the early animal testing, and the development of chemical analyses that now allow for accurate quantitative identification of these materials. The article on *spreadable butter* by Illingworth and Norris gives this forty-year-in-development innovation appropriate scientific exposure. The essential necessity was to control changes in the solid fat content between 5°C and 20°C and provide a product with the same composition as conventional butter, yet spreadable. Details of the trials and tribulations of this lengthy journey are appropriately documented and well-illustrated . The team of Hofman, Larsen and Tucker provide an account of *hoki to nanotechnology* that describes new and on-going research into innovative uses of the by-products from this country's most valuable off-shore fish species. Enhanced usage of hoki is current and looks promising from the New Zealand perspective. The article describes how the collagen from the fish is easily broken down to single strands at low temperatures, formerly commercialised as *Cfine* used in beer and wine fining. The use of collagen in the manufacture of proteins of specific molecular weight and the impact of biopolymers and their electrospinning in the nanotechnology industry is covered, the latter as potentially the most useful outcome. The solubility of the hoki skin collagen is stated as giving New Zealand advantage. Oils are now subject to innovation and targeted at omega-3 production for acceptable dosage. Use of the fish eye lens to provide self-assembled protein nanostructures, even from crude raw material, completes the article.

Hoki (photo credit: Neil Bagley, NIWA).

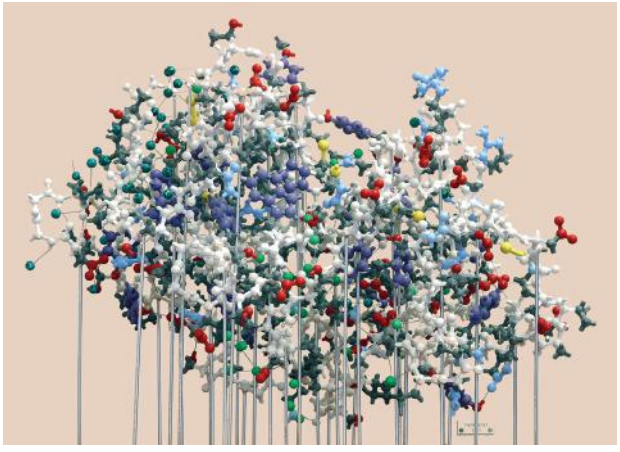
Hill laboratories: a commercial success by Hill, Robinson, and Hill is an inside account of the evolution of this analytical service company. From its origins in the basement of the Hamilton East Medical Centre to its 7000 m^2 dedicated facility in the former NZ Post building in Frankton, it now employs some 350 staff. It is New Zealand's largest privately owned commercial laboratory and this

personalised account of its growth and entrepreneurial leadership provides a welcome addition to the scientific literature. It explains the ethos of the company, its trials and tribulations and the way in which it has been able to develop and retain leadership of analytical services in New Zealand. The account takes the reader through the significant changes of scientific instrumentation and the difficult decisions of instrument purchase, company attention to detail, and the recognition it has gained from its accuracy and reliability. The developments, clearly based on chemistry, involve the company with tertiary education and in training of staff as well as students. This is an excellent contribution, easy to read, but has the minor disadvantage of not providing chemical structures for the organochlorine compounds it names. The second industrial essay by Smalley, Gooch, Walters, and Slinn is *the saga of a remarkable and challenging technology* and details changes in the paints industry over the past 60 years that now provide markedly more environmentally friendly products. The authors write from experience in different aspects of the industry with an authoritative account of the developments from the first NZ water-based paint product marketed in 1951 under the Resene brand name. The nature of the commercial product is described and the chemistry involved in moving to acrylic is appropriately covered and illustrated. The availability of a 100% acrylic product in the 1960s to the routine use of acrylic gloss and semi-gloss today is suitably detailed. Changes in consumer attitudes, the need to remove lead from paint and the difficulties associated with providing paint for application on corrugated iron sheeting (dominantly roofs) are covered, as are new products for road markings. Current emphasis of work on clean, green products, and recycling technologies completes the article.

The three medicinally-related essays entail *a quarter century of sugary science success* by Furneaux and Evans, about the country's sizeable carbohydrate group (now the Ferrier Institute), *targeting cancer: the story of the Auckland Cancer Society Research Laboratory* by Denny, and *visualising the molecules of life* by Baker. The first summarises the significant advances in carbohydrate chemistry from when Furneaux joined the Department of Scientific Research (DSIR) in 1980 to work with Miller studying seaweed polysaccharides. Furneaux's move to group leader and his emphasis on levoglucosenone (from 1985 with a staff of eight) and Tyler's use of it as a source of potential herbicide targets is covered. The move to iminosugar targets for anti-HIV activity that led to successful collaboration with ICI on the imino compound castanospermine is then described. The impact of the 1992 science reorganisation that had the carbohydrate team emerging as a thirteen strong natural products processing division of Industrial Research Ltd (IRL) follows with outlines of the search for cancer leads, pesticides and pharmaceuticals. A 1994 interaction with Schramm (Albert Einstein College of Medicine, New York) is shown to be pivotal in group growth as it led to the development of immucillin-H (ImmH), a potentially powerful inhibitor against purine nucleoside phosphorylase. The scale-up of facilities to small industrial production follows with BioCryst Pharmaceuticals and, in 2003, GlycoSyn (this spin-out, now part of Callaghan has a staff of 40) . There is an account of the contracts with New Zealand Pharmaceuticals. Despite industrial development, the Furneaux team remains focussed on academic research, which has led to advances in immuncillins, anti-malarial and anti-cancer targets and new antimicrobials – even 'green' paint in a collaboration with Resene.

Denny's contribution, *targeting cancer: the Auckland Cancer Society Research Centre*, details the growth of the Cancer Research Laboratory from its foundation with six staff in 1956 to the world renowned team of 85 today, of which he leads the Medicinal Chemistry Group. After initially cataloguing the plants and trees of New Zealand and gaining extracts to screen for anti-cancer activity, the laboratory moved to synthesising compounds in the 1970s; the chapter details this work. Initial quinolinium salts and DNA-binding drugs (compounds **4**-**8** are shown on P.88 and not P.78) led to molecular-targeted drugs in the 1980s and success with protein tyrosine kinases (PTK) enzyme inhibitors. Then the success of the vascular disrupting agents of this century with Valdemizan and hypoxia-targeting prodrugs (illustrated by the incorrectly named hydroxylamine **21**, P. 84) are covered. The final components outline the recent highly successful work of the laboratory and its commercial collaborations.

The last of what I have classified as medicinally related chemistry is the structural biology essay of Baker. Entitled *visualising the molecules of life* he takes the reader from the origin of X-ray crystallography, the foresight of Bernal, and Oxford and Cambridge work of the 1970s, to the involvement of New Zealand and the developments to today. Begun in NZ by Baker at Massey University in the early 1970s, structural molecular biology has been remarkably successful over the past 40 years. The chapter details earlier work that led to a solution for the kiwi fruit enzyme, actinidin, at a time when as few as ten protein structures were known. It then moves to the electron transfer protein structures of the late 1970s and the 1986 Baker group solution of the large lactoferrin molecule. The development of synchrotron sources for X-ray data collection from the 1990s that led to structure-based drug design for HIV-AIDS targets are covered. The country now has six groups actively involved in structural biology. It is a pity that there is no depiction of early kiwi fruit structure.



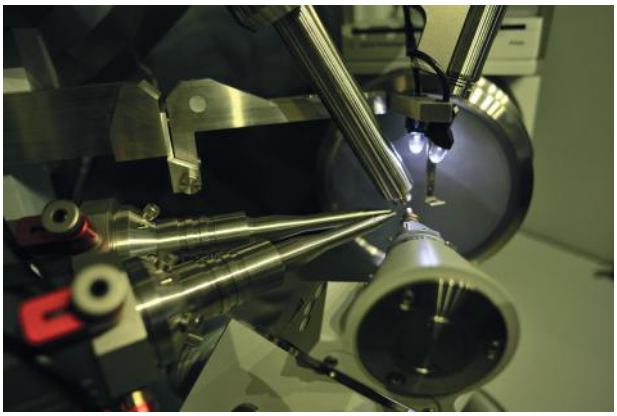
Actinidin from *visualising the molecules of life*.

Of the analytical chemistry components, two describe academic spin-out companies. The first, e*xtraterrestrial chemistry meets New Zealand industry*, is the story of Syft Technologies and the ***s***elected-***i***on ***f***low ***t***ube-mass spectrometer (SIFT). Written by McEwan and Prince, it takes the reader through the recognition of ion-molecule reactions in the ionosphere and the laboratory-based flowing-afterglow technique to study them, to the selected ion-flow tube of the mid-1970s. McEwan's involvement and the modification to couple SIFT with mass spectrometry (SIFT-MS) that has provided easy analysis of volatile organic compounds since 1996 are described, as is the Canterbury-built large SIFT spectrometer, "Big Bertha". The possibility of a markedly more user friendly and potentially commercial instrument led to Syft Technologies being formed as a spin-out company in 2002 , the subsequent modification of the Big Bertha design to provide a smaller instrument named Voice100®, which became commercial in 2004 follow. Instrument modifications from 2006 to provide an even smaller, more cost-effective model (Voice200®) at half the size and the 2014 Voice200*ultra*® are detailed. This last instrument is shown to operate with detection limits of more than an order of magnitude over its predecessor, and to provide for environmental monitoring in its various guises. Discussion of the SIFT-MS instruments which separate chemicals based on reactivity rather than physical interaction rapidly (within a minute) is included and the tolerance to almost any gas phase sample (unlike normal GS-MS) as well as simultaneous analysis for polar and non-polar compounds is described. Its provision of a dynamic range over 1000 times greater than before for concentrations ranging over six orders of magnitude are covered and examples of industrial uses included.

The second spin-out company, described by Summerfield, is titled *successful innovation takes time: the story of Canterbury Scientific.* This easily read article outlines the need for a haemoglobin A2 standard and covers the Carrell, Owen and Williamson preparation of three stable standards at the Christchurch Hospital clinical biochemistry laboratory through to the company of today. The standards became well recognised but with the Canterbury Hospital Board having little interest in a commercial enterprise, Canterbury Scientific emerged in 1985. The author outlines how its primary customer, Bio-Rad Munich, began to make its own standards and the company decision to continue to supply the Australasian market. The author describes how Owen became the senior researcher, the survival of the company through the Richardson changes to Health Boards in 1991, and Owen's creation of a control for haemoglobin A1c in early 1992. Involvement of Bayer's DCA 2000 instrument, and Owen's successful bid to supply Bayer with his control follow. The difficulties in gaining the needed equipment to produce the control in large volume are described, and the Kiwi tenacity and collaborations that led to 9000 samples being available and exported in 1997 nicely covered. From 2002 the company has had its own facilities with Owen there permanently. The company is reported as now having contracts valued in excess of $8 million, 16 full-time staff, and striving to upgrade its products.

The remaining analytically oriented contributions cover forensic science, X-ray crystallography and pulse radiolysis. *Crime scene to courtroom* is outlined by a team of seven working scientists and Keith Bedford, the forensic manager for the Institute of Environmental Science Research until his recent retirement. The essay includes crime scene examination and the physical evidence that it can provide. The more chemical aspects involve evidence which has to be sought; the use of luminol is covered. About one quarter of the essay is devoted to forensic biology and DNA profiling before moving to illicit drugs, P-labs, and party pills. Varying drug doses and their impact in coroner- and police-initiated analyses are described and there is a section on the well-known sleeping pill zopiclone. Overall the contribution is "what is done" rather than an explanation of the procedures involved, but it provides a welcome summary.

The second component details the emergence of X-ray analysis in New Zealand. Written by Gainsford and Wikaira, *a short history of the New Zealand pioneering X-ray laboratories*, gives just that. From the beginnings of NZ crystal structure analysis by F.J. Llewellyn in Auckland in 1947, the article covers the early structures solved there – potassium nitroacetate ($O_2NCH_2CO^{2-}K^+$) and formamidoxime ($H_2NCH{=}NOH$). It then moves to Canterbury University and DSIR involvement, the use of computers in the analyses, and the protein crystallography initiated at Massey University in the late 1960s, the time that automated data collection also arrived in this country. Instrument upgrades in the two main centres of activity (Auckland and Christchurch) that provided improved and faster analyses are covered, and the provision of the Canterbury data collection service, a major advance for New Zealand bench chemists, recorded. The impact of advances in computing capacity, instrument size and availability that led to the present state of crystallography here are appropriately discussed by the authors. This is a relevant and well-presented contribution.



A modern CCD diffractometer.

The final analytical essay is the account by Packer and Anderson on *radiation chemistry: radicals, reactions, rates and redox*. It provides an overview of the development of radiation chemistry in New Zealand from inception in 1956 at the DSIR's Dominion Physical Laboratory and the cobalt Co-60 source of 1959 (at the then Institute of Nuclear Sciences, INS). Having worked at INS for more than

a year, Packer built an equivalent source at Auckland University that also allowed for steady state radiolysis study. Maintenance of the Auckland source until it was replaced by a caesium Cs-137 unit in 2013 is covered. Beginning in the 1960s, NZ's use of pulse radiolysis, which required scientists to travel overseas until the Auckland purchase of a linear accelerator in 1993 (after its decommissioning and redesign in the UK) is described. The authors account for the accelerator providing absolute reaction rate measurements rather than the relative ones of earlier and they illustrate how the facility has been used extensively by the Auckland Cancer Society Research Centre in its drug development (see Denny, P. 77). Brief accounts of the people involved and their work are then provided. The highlighted components included here provide the essentials of radiolysis, the Auckland Dynaray 4 accelerator, and the techniques of radiolysis chain reactions and their commercial application in foods.

My final grouping covers the materials chemistry of advanced ceramics (Brown), cementing geothermal wells (Milestone), and high temperature superconductors (Tallon and Buckley). Brown's *advanced ceramics made in New Zealand* traces the impact of non-oxide ceramics since the 1980s and is written by NZ's foremost contributor. It outlines the basics of the materials and the importance of silicon nitride, before moving to the Sialon ceramics developed from the 1970s and their properties. New Zealand involvement by the IRL and forerunner DSIR team using X-ray diffraction and solid state NMR techniques to follow carbothermal reductions of local kaolinite and halloysite clays follow. The development of a silicothermal reduction process with no carbon monoxide emission is outlined prior to giving more detailed coverage of the Sialon ceramics. Here Sialon synthesis and oxidation of the materials are discussed and the minimised negative impact on high-performance cutting materials outlined. O-Sialons, in which the thickness of oxidised layer is reduced by two orders of magnitude and made without sintering aids, as well as the effect of nitrogen overpressure are described. The early commercialisation work of the late 1980s, the DSIR team's skill set and its facilities, which led to furnaces that allowed study of the ceramic chemistry at that time, follow. Collaboration with Pyrotek Products Ltd (from 1991) that provided the country's first advanced commercial ceramics production is dealt with, as are the further developments for O-Sialon ceramics. A new single step process to provide O-Sialon-SiC composites, easier to fabricate and at reduced cost, is included. The chapter concludes with the 2014 decision by Pyrotek to provide the country's first gas-overpressure furnace for ceramic production, which allows for improved quality and diversity in ceramics exports.

The challenge of cementing geothermal wells by Milestone outlines work underway to improve the cements used in casing the geothermal wells that provide wet steam (steam and water droplets) for geothermal electricity generation. After providing the history behind the Wairakei power station, the post-1980s growth in geothermal power generation, and well-drilling and cementing, the role of cement and the particular needs in well usage is discussed. The impact of cement on the developments at Ohaaki and Rotokawa that led to corroded steel casings, the need for research, study of the hydration reactions of cements, and the involvement of surrounding geothermal fluids is described. Grout formulations found to contain significant amounts of carbon dioxide from usage, the source of the gas, and the work of the DSIR/IRL team that led to much detailed information is given. The slowness of adequate improvements, as well as CO_2 sequestration and storage underground now add a new dimension to geothermal drilling. New cements may soon emerge.

The discovery and development of high-temperature superconductors provides a history of the internationally recognised ground-breaking work by Tallon and Buckley. These authors take the reader through the discovery of the superconductors in 1911 to the era of the high temperature (high *Tc*) superconductors and their 30+ years involvement in it. They provide details of the discoveries and the increases in operating temperature to the ~155 K of their 100 kbar pressurised Hg-1223 (plot, P. 206). This plot is erroneous in that only one entry is provided for Tl-2223, not the two stated (caption). Moreover, as the group also discovered Bi-2223 with a *Tc* of 110 K (P. 208), an entry has to be missing. The work of the (by then) IRL team that showed T_c to systematically increase across the lanthanide series and production of the third member of the BSCCO series with a T_c of 110 K, is described and the replacement of lead by bismuth is included. Following their exposition on discoveries, the authors turn attention to materials for testing, materials science and high performance wire. This last aspect covers commercialisation by the (now) Robinson Research Institute and its two spin-out companies HTS-110 and General Cable Superconductors. This is a timely contribution marred only by a few typographical infelicities.

Roebel cable. Photo credit: Robinson Research Institute.

Scientific Sleuthing does as its title implies. It provides clear accounts of the recent impressive advances made in chemical science in New Zealand. The New Zealand Institute of Chemistry is to be congratulated on publication of this elegant, informative, and timely book.

Brian Halton

Article

Extracellular vesicles: small particles with a big impact

Renee V. Goreham

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Keywords*:* nanobiotechnology, extracellular vesicles, drug delivery, detection

Renee Goreham completed her BSc (Hons) in nanotechnology at Flinders University, Australia and subsequently was accepted into a PhD program at the University of South Australia, which was completed in 2013 in the area of nanobiotechnology. Since 2014, she has had a post-doctoral position with Prof Thomas Nann at the MacDiarmid Institute, Victoria University of Wellington. Renee's research niche combines nano- and bio-materials, in particular detecting extracellular vesicles for disease diagnosis or using extracellular vesicles as bio-camouflage drug vehicles.

Introduction

Extracellular vesicles (EVs) are membrane bound vesicles released by most cells. Initially, they were described as artefacts or trash compartments discarded by cells, but it is now known that they play a vital role in cell function and cell-cell communication. EVs were discovered in the early 1990s, and are one of the many mechanisms used by cells to communicate with each other.[1] Cells release EVs to socialise and promote a specific cellular behaviour in response to the extracellular environment (such as stress). It was found that EVs are also released by healthy cells but more recently EVs have been found to play a vital role in everyday cellular activity. EVs are lipid bilayer liposomes released by cells and range in size from 30 nm to a few µm but each type has a different biogenesis pathway. EVs are released by prokaryotic and eukaryotic cells, thus they are an evolutionarily conserved method for intercellular communication. They are robust, efficient and an economically favourable way to exchange information between cells.[2] Although EVs are the broad name for any membrane bound liposomes released by cells, they are further defined by their cellular origin, size and biogenesis (how they are formed). The most interesting EV to date is the exosome, which is released by mammalian cells. Exosomes have shown massive potential as biomarkers for disease and EVs in general are viewed as biocompatible drug delivery vehicles.[3] Research in the area of outer membrane vesicles (OMVs), derived from gram negative bacteria, is also picking up momentum within the science community. This article will explore the many types of EVs but will pay closer attention to exosomes and OMVs.

Mammalian derived EVs

As mentioned before, EVs are defined by their size and biogenesis. There is a plethora of names for each type of vesicle, stimulated by the complexity within this area of research. Terms include (but are not limited to) exosomes, ectosomes, microvesicles, microparticles, prostasomes, tolerosomes (which induce immunological tolerance to dietary antigens), apoptotic bodies (released by apoptotic cells) and nanovesicles (see Table 1). Over the last decade, it has been found that cells deliver proteins and molecules between the intracellular organelles by membrane vesicles containing definite receptors to ensure traffic specificity. They are actively secreted by most cells and exist in most bodily fluids, including blood, saliva, breast milk and sperm. There are three main types: microparticles, microvesicles (100-1000 nm) and exosomes (20-100 nm).[4,5] Exosomes are bilayer membrane vesicles released from mammalian cells for intercellular communication. These unique vesicles are released by almost every cell and are unique to the cell of origin. For example, reports have demonstrated how exosomal release from cancer cells contributes to metastasis through intercellular communication. It is for this reason that interest has risen for using exosomes in theranostic applications, as exosomes have biomarkers specific to the diseased cell it was derived from.

Exosomes were first reported in 1983, when it was observed that blood reticulocytes matured into erythrocytes and transferrin receptors were released into the extracellular space via small 50 nm sized vesicles.[20,21] Later in 1987, they were named exosomes.[22] A Nobel prize was awarded in 2013 to Ames E. Rothman, Randy W. Schekman and Thomas C. Südhof for determining the mechanism of exosomal transport, thus exposing the potential of exosomes as promising biomarkers for diseases and treatment.[23] Prior to exosome discovery, it was known that mammalian cells transmitted information between cells indirectly, without being fully understood. Interest in the exosome area was not realised until 1996, when Raposo *et al.*[24] found that B lymphocytes secreted exosomes carrying membrane-bound molecules essential for the adaptive immune response. Another report showed how dendritic cells also secreted dexosomes (see Table 1) which carried functional immune agents that promoted antitumour responses in mice.[25] These results kick-started the hypothesis of the intercellular communication function of exosomes.[26]

Table 1. Summary of EVs from mammalian cells.

Name	Size	Origin	Comments	References
Microparticles & Ectosomes	0.1-2 µm	Formed from the cytoplasmic membrane		6,7
Microvesicles	0.03-1 µm	Plasma membrane	Sometimes used as a broad term to refer to exosomes and microparticles	4,4
Prostasomes	50-500 nm	Released from the prostate gland/epithelium to seminal fluid	Proposed to help regulate fertility	8-9
Exosomes	40-100 nm	See next section		10-11
Exosome-like Vesicles	30-100 nm			
Argosomes		Membrane fragments derived from Drosophilia	Membrane fragments on the run	12-14
Dexosomes		Released from Dendritic cells	Membrane contains sphingomyelin, CD9, CD 81, MHC class I and II	15-16
Epididymosomes		Derived from sperm	Cholesterol and phospholipid ratio high ~2	9,17
Tolerosomes		Intestinal epithelial cells	Carries MHC class II and antigenic peptides	18-19

Exosome biogenesis

As stated, there are many types of EVs, so how do we define exosomes and how are they formed? Nomenclature is important to consider and the term exosome should first be defined.[27] Gould *et al.*[28] describes the term exosome used in three different ways. First, the biogenetic definition (see below); second, serving a physiological function within cells; and third, the empirical definition based on vesicles that are isolated only by differential ultracentrifugation at 70 000-100 000 x g. For clarity and within this review, the author defines exosomes by their biogenetic definition, being EVs that originate from multivesicular endosomes (MVEs), which are formed within a cell (Fig. 1a). Microvesicles are defined as those derived from the plasma membrane and it is important to explain the difference between these and exosomes. Microvesicles have a different biogenesis and include shedding vesicles and apoptotic bodies.

Biogenesis of exosomes (Fig. 1) starts within the cytoplasm. Cells are experts at producing and exporting molecular products (for example, the transport of insulin into the bloodstream).[29] These molecules are incorporated into a cell packaging service (exosomes) that are released intracellularly. These internalised exosomes are then incorporated into MVEs in the cytoplasm and the MVEs fuse with the cell membrane releasing the exosomes to the extracellular matrix.[30] The structure of exosomes (Fig. 2) have been found to have a homogenous 'cup-shaped' morphology, as determined by negative staining electron microscopy.[10,31]

Proteomic studies have determined a subset of cellular proteins that are found specifically in exosomes. It has been observed that 80 % of proteins were conserved between mouse and human derived exosomes.[10] Exosomes have been found to be rich with endosomal proteins but lack mitochondrial, nuclear, endoplasmic reticulum or Golgi derived proteins. They have been found to be enriched with membrane transport and fusion proteins as well as cytoskeletal proteins, such as actin and tubulin, which is expected as they are produced within the cytoplasm. Other proteins included heat-shock proteins, integrins (adhesion proteins) and tetraspanins, such as CD63 (a common exosome marker).[10,30] The role of some proteins are still unknown and may be related to biogenesis, or some other currently unknown exosome roles.

The contents of exosomes (Fig. 1) have been shown to change in various diseases including viral infections, neurodegenerative diseases (prion diseases, Alzheimer's and Huntington disease) and cancer. This makes them ideal biomarkers for disease detection. A multitude of reports and reviews have described the functions of exosomes, which are discussed more in the next section. Nucleic acids were first described within exosomes released by mast cells.[33] Since, it has been verified that the mRNA secreted within exosomes is not random, but the export mechanism has not been confirmed experimentally.[32] The fact that the RNA is protected from RNase by the membrane, has led to a surge of research in the area of membrane-bound biomarkers for disease diagnosis, prognosis or identifying the best treatment therapies (using personalised medicine).

Roles of exosomes

Since their discovery 30 years ago, exosomes have been found to play a vital role in many biological mechanisms. These include mediating intercellular communication, immune system functions, development and differentiation, neuronal function, cell signalling, regeneration and viral replication.[26] Exosomes have been isolated from a variety of cell types *in vitro*. In particular, a large number

of exosomes are released from cancer cells (compared to their healthy counterparts), which aid in the transformation of local healthy epithelial cells into cancerous cells, subsequently invading the extracellular matrix and contributing to distal metastasis.[34] Exosomes are involved in the complete cancer life cycle, including the initiation, growth, progression and drug resistance of tumours.[35,36] Zhang *et al.*[36] describes exosomes as "small particles, big players" as they are ideal candidates for generating new and improved cancer therapies.

It is not surprising that exosomes are influential in other diseases. Hill *et al*. have been researching the area of exosomes and their role in prion diseases (neurodegenerative diseases). Their research demonstrated the propagation abilities of disease derived exosomes, which can be translated to healthy cells. This demonstrated the ability of exosomes to establish infections in neighbouring and distant cell types.[37] More recently, they described the involvement of EVs in metal homeostasis and neurodenegeration.[38] Overall, exosomes have the ability to transfer molecular cargo and to be selectively taken up by specific cells, reprogramming the target cell and thus inducing disease. With that said, they can also provide new avenues for treatment and diagnosis.

Applications

Nature Biotechnology released a publication in March 2016 celebrating their 20th anniversary by looking at the "greatest hits".[39] Exosomes were ranked in the top eight twice. First, exosomes were used in liquid biopsies, which used a lab on a chip to detect exosomes derived from diseased cells.[40] A second highlight described using exosomes as nanomedicines to deliver drugs across the blood-brain barrier.[41] However, there are some downsides to creating nanomedicines using exosomes. Although the isolation and purification can be quite simple, the quantity of exosomes is low and expensive to culture and isolate. Exosomes are collected after growing mammalian cells to confluency and proceeding through a process of removing cell debris, proteins and microvesicles. This process can be time consuming from start to finish (weeks) with low yields. This is important in the application of nanomedicines as large quantities are needed for *in vivo* testing. To overcome this issue, higher yields are needed before considering the use of exosomes as drug delivery agents and nanomedicines.

Using exosomes as biomarkers first requires isolation to remove all of the unwanted biological fluid that may interfere with the results. A number of purification methods of exosomes have been developed, including differential centrifugation (the most widely used method), using a step-wise centrifugation process to selectively remove the extracellular debris.[42] Another common method uses solution sedimentation of exosomes and low speed centrifugation, inducing the precipitation of exosomes.[43] Sucrose gradients are commonly employed to take advantage of buoyant density in viscous fluids to aid in the isolation process.[44] Isolation of exosomes has been well documented but there are some discrepancies within the literature. If the reader is interested in the isolation and characterisation of exosomes to ensure sound results, the work conducted by Trau *et al.* is a good reference.[45] This group does extensive research in this area, setting the bench mark for purification and subsequent characterisation of exosomes.

Bacterial derived EVs

It is no surprise that in all domains of life (i.e. eukarya, archae and bacteria), membrane bound vesicles are released as social mechanisms between cells. EVs released by Gram negative bacteria (such as *Pseudomonas aeuringosa* and *Escherichia coli*) and Gram positive bacteria (such as *Listeria monocytogenes*) were first reported in the 1990s and were initially described as 'nanobacteria'.[46,47] Similar to the exosome saga, bacterial derived EVs were originally considered as trash or cell artefacts serving no significant biological purpose. It has only recently been verified that bacterial derived EVs are fundamental in cell survival and cell intercommunication. The mechanism of EV formation is made more complex because the cell wall varies in structure across different bacteria, making the mechanism different to exosomal release. For example, as the name suggests, outer membrane vesicles (OMVs) are formed from the outer membrane, which is only present in gram negative bacteria. Gram positive bacteria have no outer membrane but a thick cell wall of 20-30 nm compared to <10 nm for gram negative.[48] In fact, it was only in 2009 when the proteomics of gram positive bacteria derived EVs were extensively studied.[49] Little is known about the biogenesis of EVs but currently there are three hypotheses. The first concept involves the EVs being forced through the cell wall by turgor pressure (force within the cell, pushing the plasma membrane against the cell wall) after release from the plasma membrane. Regulation of this process and the size of EVs may be driven by pore size or cell wall thickness. The second hypothesis describes enzymes found in EVs that may "loosen" the wall and increase the pore size, facilitating the vesicle release.[50,51] This hypothesis has been rationalised by the cell-wall modifying enzymes that have been found in both fungi and gram-positive bacteria.[49,52] The third hypothesis involves protein channels that may guide EVs into the extracellular matrix. Both tubulin and actin (structural intracellular cables) have been found within EVs derived from fungi, thus providing evidence that the origin of EVs is internal to the cell.[50,51] In summary, vesiculogenesis is a universal phenomenon but this process is different with each type of organism and there are still many unknowns. Our work currently involves the use of OMVs derived from gram negative bacteria but, in the future, we will also look at gram positive bacteria. For this review, OMVs (EVs derived from gram negative bacteria) and their applications in biomedical research will be further scrutinised but can be applied to other bacteria derived vesicles.

Outer-membrane vesicles

Gram negative bacteria have developed mechanisms to deliver information to other cells, including hosts and competing bacteria strains, using OMVs. OMVs are constitutively secreted and they consist of lipids, proteins and lipopolysaccharide (LPS) and are approximately 50-

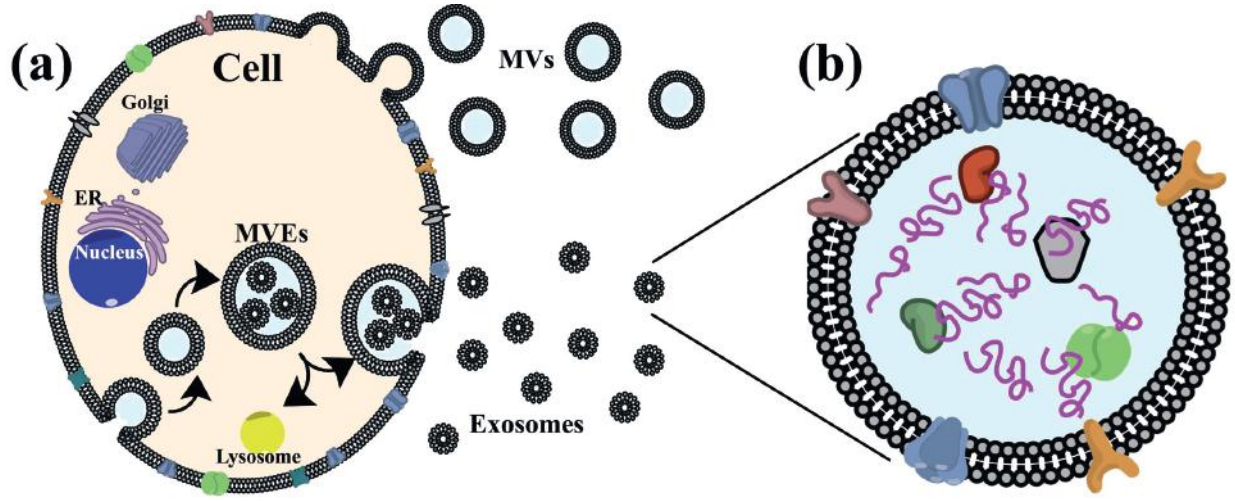

Fig. 1. (a) Schematic representation of a mammalian cell with the simplified biogenesis of exosomes and microvesicles. Firstly, endosomes are formed (MVEs) which encompass exosomes. The MVEs can either fuse with the plasma membrane, releasing the exosomes into the extracellular matrix, or go to the liposomes. Microvesicles are formed via blebbing from the plasma membrane directly. (b) Schematic representation of an exosome containing proteins, DNA and RNA within the exosome, and surface membrane proteins, which are specific to the cell of origin and are not limited to the cell surface proteins.[32] ER=endoplasmic reticulum; Golgi=Golgi apparatus; MV=Microvesicle; MVE=Microvesicular endosomes.

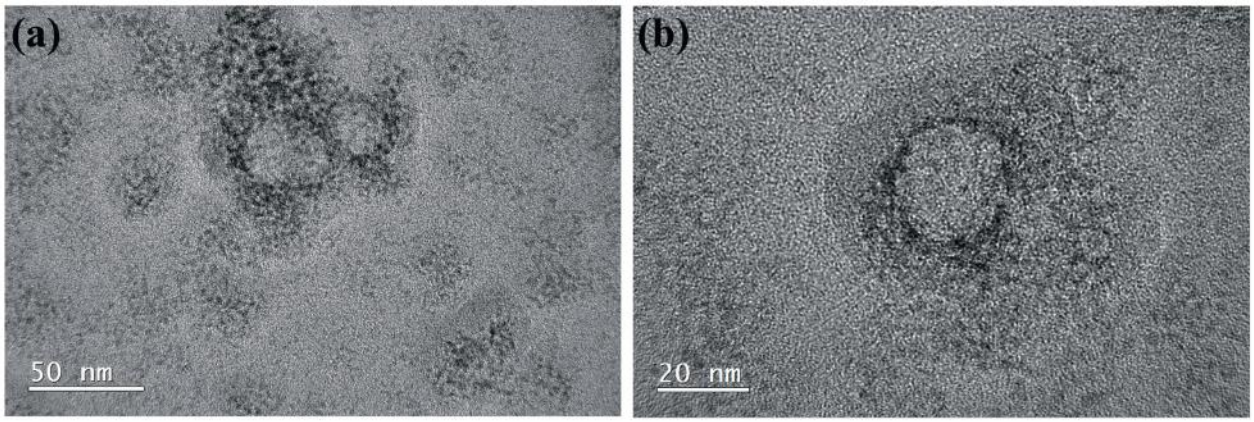

Fig. 2. Transmission electron microscopy of exosomes derived from primary mesenchymal stem cells, negatively stained with uranyl acetate.

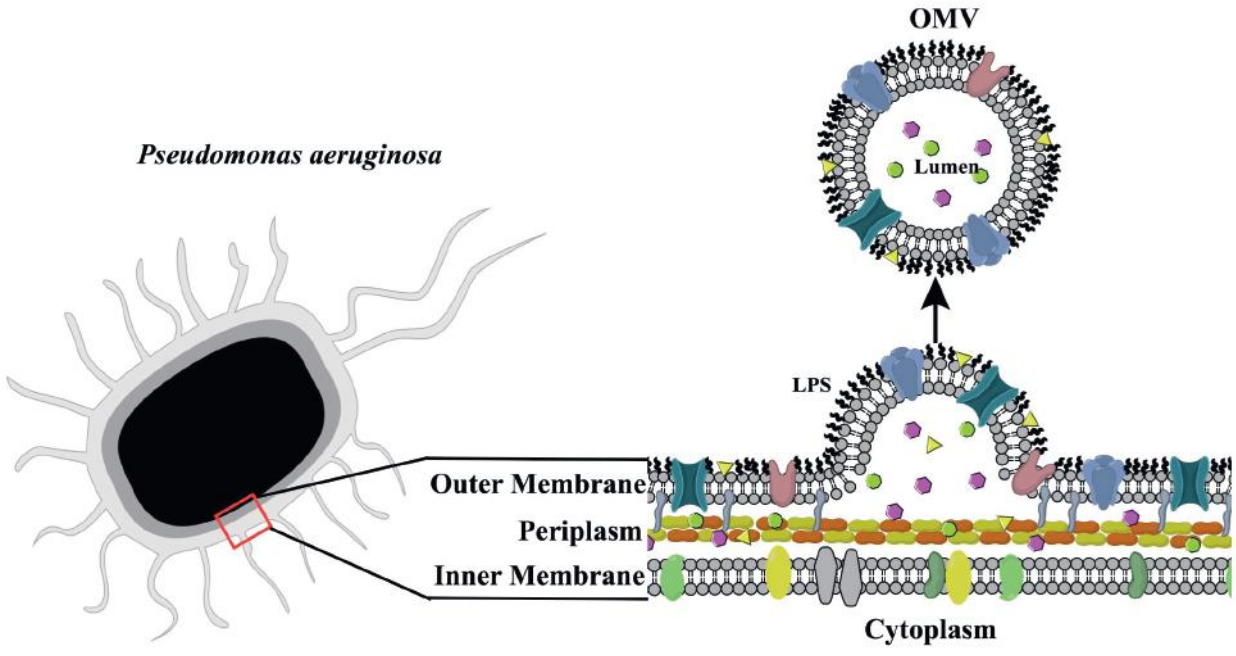

Fig. 3. (a) Cryo-scanning electron microscopy image of Pseudomonas aeruginosa budding EVs after treatment with an antibiotic. (b) Transmission electron microscopy of OMVs isolated from Pseudomonas aeruginosa, negatively stained with uranyl acetate.

300 nm in size (Fig. 3).[53] As shown in the simplified schematic (Fig. 4), the outer membrane of the cell wall forms an OMV through budding, which contains proteins from the periplasm, and surface membrane proteins that are characteristic of the cell of origin.[40] The budding process does not seem to affect the integrity of cell membrane, as shown by McBroom *et al*.[55] using atomic force microscopy and biochemical assays. This is surprising as a lot of energy would be needed for the vesiculation process to occur and the follow-on question to this is why this process is so favourable? This is still being investigated and there are still many unknowns.

As mentioned, OMVs have been found to have many functions and research in this area to elucidate all of these roles is still being investigated. Vital functions are the delivery of virulence factors (toxins and proteases), other pro-inflammatory molecules and antigens (flagella and peptidoglycans),[56–58] attenuation of host-immune system responses[59] to intracellular communication[60] and nutrient sequestering.[61] As OMV biology is a new and rapidly advancing field with more functions being uncovered, it appears that what was previously thought as being a biological artefact is in fact an integral part of cellular biology.

Natural nanoparticles as therapeutics

The question remains, why a predominately nanomaterial-based group at Victoria of Wellington would be researching this field? There are two reasons: detection and delivery.

Extensive research is ongoing to develop the perfect way to deliver drugs to the body and most of this research is in nanotechnology. What if cells have already developed the perfect mechanism? This concept has already been identified for exosomes and, in fact, Alvarez-Erviti *et al.*[41] delivered siRNA across the blood-brain barrier using exosomes derived from self-derived dendritic exosomes to the brains of mice. The self-derived dendritic exosomes reduced any immunogenicity and the cells were engineered to deliver exosomes with a neuron-specific rabies virus glycoprotein (RVG) peptide and loaded the exosomes with the siRNA via electroporation. This was the first time a "nanoparticle" successfully breached the blood-brain barrier and since then exosomes have exploded in popularity as potential drug delivery carriers. With that said, there are many hurdles to overcome such as the extremely low yield of exosomes which hinders their potential use as delivery vehicles or therapeutics. Relatively large amounts of a drug are needed to undertake *in vivo* studies and subsequent human trials. Cell culture is also an expensive process. Although the delivery of siRNA using an exosome was first recorded in 2011, there is yet to be a exosome therapeutic.[62]

Using bacteria-derived EVs, our group aims to create new biocompatible drug delivery vehicles for nanomedicine. EVs derived from bacteria have increased in popularity as they can be easily purified, have high yields, are cheap to process and can be derived from genetically modified bacteria to remove any immune response. There is already a therapeutic drug developed from bacteria derived EVs for meningitis, which was engineered by genetically modifying the bacterial strain that the EVs were derived from.[63] Unlike mammalian derived EVs, bacteria derived EVs deliver cargo over long distances, not only to bacterial cells (inter-species) but to mammalian cells (intra-species). The intra-species delivery of EVs derived from bacteria makes them the ideal bio-camouflage delivery compartment for therapeutics. We aim to develop a method to load EVs derived from bacteria with functional nanoparticles synthesised in our laboratory, thus using "nature's own vehicle" as a nanomedicine drug delivery system.

Another area of interest for our group is sensing. Label-free detection of exosomes was first published in 2014 by Im *et al.*[40] which used surface plasmon resonance to create a high-throughput lab on a chip, called a nanoplasmonic exosome (nPLEX) sensor. An array of evenly spaced nanoholes on a metal film with ligands specific for tumour derived exosomes is undergoing trials for ovarian cancer. Since the first discovery of circulating tumour

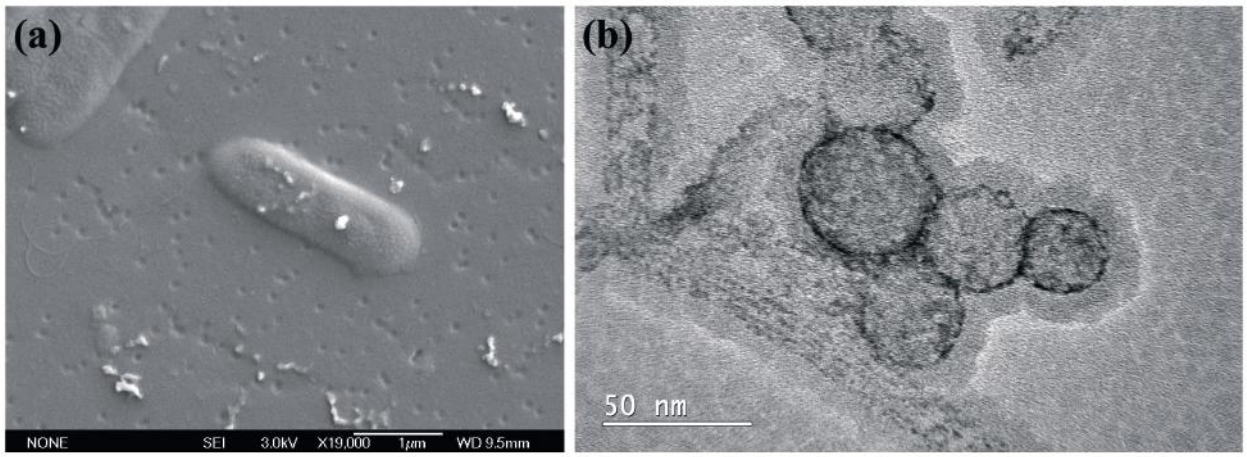

Fig. 4. Schematic representation of OMV biogenesis from gram negative bacteria (Pseudomonas aeruginosa). The membrane consists of two phospholipid layers; the outer membrane contains a layer of LPS (black wavy lines) and outer membrane proteins and periplasmic (luminal) proteins. Surface proteins in the outer membrane are associated with the bilayer membrane of the OMV. The inner membrane is a phospholipid membrane and the cytosolic content (in the cytoplasm) is excluded from the outer membrane. The grey tubes connecting the peptidoglycan (periplasm layer) and the outer membrane are shown and the lack of these may aid OMV blebbing.

cells (CTCs), there has been potential to use exosomes derived from these cells as cancer biomarkers, as they originate from both primary and metastatic lesions and are found in the blood. One main issue with CTCs is they are found at very low numbers relative to white blood cells (1 CTC in 10^7) making them difficult to detect.[64] This number may increase for metastatic cancer patients. The release of EVs is at a higher number compared to the cell of origin, thus providing more targets. In addition, the EVs have surface membrane proteins, RNA and DNA that are specific to the cell of origin and can potentially be used a biomarker. This is not just applicable for cancer but other diseases, such as prions, and other cells, such as bacteria. Also, other information may be assessable, such as the current state of the cell. The area of liquid biopsies using EVs to detect a specific cell is extremely promising for biosensing and subsequent novel therapeutic strategies.[65]

EVs and their applications are still a relatively new concept within the physical chemistry community. Our research treats EVs as nature's own nanoparticles rather than a biological artefact. With our expertise in nanotechnology, we aim to use EVs to detect a target cell and as biocompatible drug delivery vehicles. The phrase "the little exosome that could" rings true and, in the coming years, there will be further breakthroughs in this fascinating area.

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NZIC AGM

The NZIC AGM will be held on Thursday 26th October 2017 in Room 531 at the University of Canterbury Chemistry Department (Rutherford Building).

Drinks at 5.30 pm; Meeting starts 6.00 pm

Agenda:

1. Apologies
2. Appointment of minutes secretary
3. Minutes of 2016 AGM
4. Matters Arising from Minutes of 2016 AGM
5. President's Report
6. Financial report
7. Auditor
8. Move that Greta Vink be appointed auditor

Election of Officers:

Past President Penny Brothers (Auckland) – automatic

President: nominated James Crowley (Otago)

1st Vice President: nominated Sarah Masters (Canterbury)

Treasurer

Honorary General Secretary

General Business

From single molecules to molecular machines

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Keywords: *small rings, valence bond isomers, Platonic molecules, host guest chemistry, self-assembly, molecular machines, nanocars*

This article is based on the lecture *50 Years in 50 minutes* delivered to the Wellington Branch of the NZIC on 10 February 2017.

Introduction

The era of chemistry that encompasses the 50 years that the author has been teaching and researching can best be described as the era of the single molecule. In 1967 when he began lecturing in the University of Florida, organic chemistry research in the USA and NZ was carried out because there were problems to solve with the results added to the stockpile of knowledge that might, if one was lucky, benefit mankind. Grant applications were the norm to gain funding in the USA but were almost unheard of in this country; academics had no managers, and one's duty was to teaching and research in an establishment where the appointees covered the breadth of the subject matter. By far, the most targeted research in organic chemistry was towards a single molecule. In natural products chemistry this was to the isolation, characterisation and identification of the compound and then its laboratory synthesis. For the non-natural products chemist, it was in conceiving a new structure, designing a synthesis, making the compound and then establishing its properties. What follows is a potpourri of the 50 years the author has been fortunate to have spent as a non-natural products academic. It began in Florida as an Assistant Professor and continued in this country as a permanent academic and student of organic chemistry to the present day. It provides a synopsis of the major developments in organic chemistry as the author sees them over this period, and ends with the molecular machines of today and the April 28 nanocar race in France.

Discussion

It is well recognised that total synthesis was regarded as the flagship of organic chemistry throughout the second half of the 20th century. This is best illustrated by Woodward's synthesis of chlorophyll (1960), Corey's longifolene (1961) and the prostaglandins F2a (1969). Then came Kishi's synthesis of tetradotoxin in 1972 and the monumental 600,000 man-hours of effort that provided vitamin B12 from Woodward and Eschenmoser in 1973. Erythromycin, okadaic acid, palitoxin, taxol and vancomycin followed in sequence to 1999.[1] It was in his report of the synthesis of longifolene (Fig. 1) that Corey introduced the concept of retrosynthetic analysis but its widespread acceptance happened only in the early 1980s.

Early 1973 saw Woodward and Eschenmoser announce their synthesis of Vitamin B12 (Fig. 1).[2] It took between 12 and 13 years involving 91 postdoctoral fellows, mostly at Harvard, and 12 PhD students at ETH in Zurich. This gives about 200 man-years of effort (ca. 600,000 man-hours). It was *the* 20th century landmark of organic synthesis and remains as the most outstanding synthetic achievement in organic chemistry. The author was fortunate to hear Woodward at the ACS Organic meeting in 1967 and his brilliance convinced him that non-natural products were better for him!

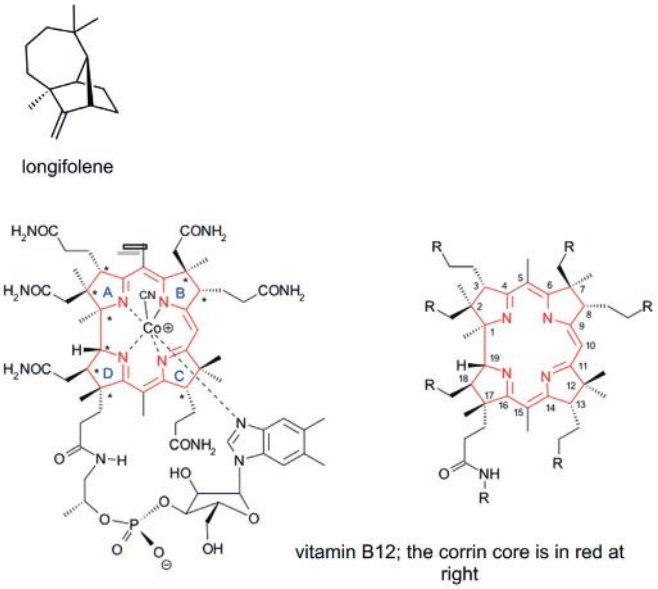


Fig. 1. Longifolene and vitamin B12

Each of the natural products mentioned above provided a challenge to the synthetic chemist. The skill in synthesising them advanced the discipline of organic chemistry, but to this author, the simplicity and aesthetics of small molecules held the attention. It began with hands-on research in the cyclopropanone arena studying methyleneaziridines–molecules isoelectronic with cyclopropanone (Fig. 2). The molecules have analogous valence bond isomers but at the start of the study cyclopropa-

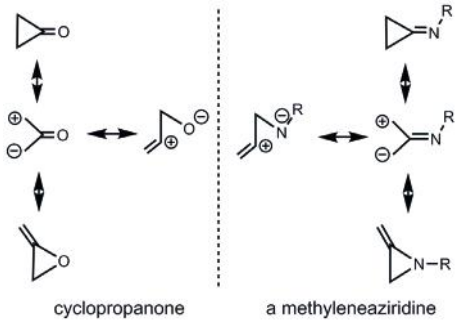
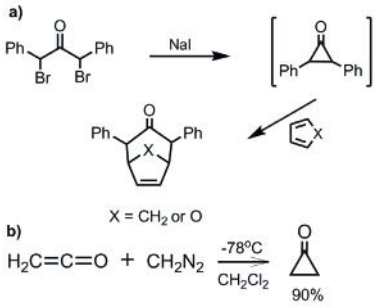
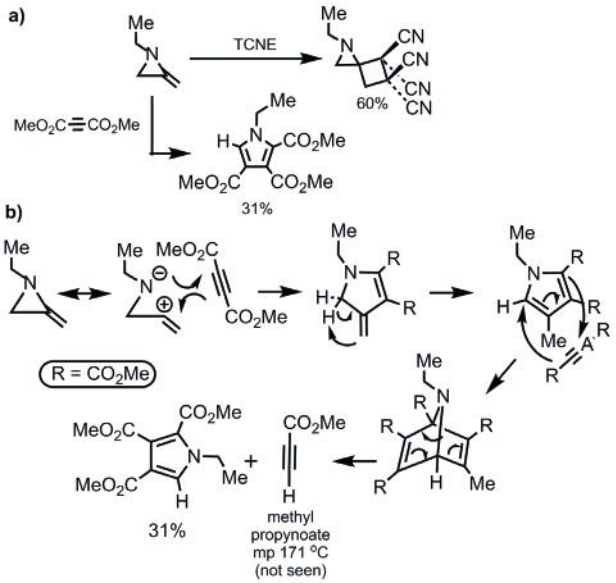


Fig. 2. Isoelectronic three-membered ring structures

none was unknown, even though it had been intercepted as a reactive molecule in [4+2] cycloadditions with dienes (Scheme 1a).[3] The molecule itself was synthesised by Turro at Columbia University from addition of carbene to ketene from a -78°C dichloromethane solution of diazomethane, followed by low temperature purification (Scheme 1b).[4] Involvement was with the isoelectronic methyleneaziridines as summarised in Scheme 2, where the addition of tetracyanoethene provides routine [2+2] addition to the double bond with no involvement of any isoelectronic counterpart. In contrast, dimethylacetylene dicarboxylate delivers a pyrrole product (Scheme 2a) containing three (not two) ester functions and shown to be correct from melting point data with an authentic sample provided by R.A. Nicolaus in Naples. Its possible mode of formation took many hours of thought with the pathway of Scheme 2b appearing only after more than 30 years with significant input from A. Grimsdale, then of the MPIP-Mainz but now at Nanyang Technical University (Singapore). The ring-opened dipolar isomer was proposed to react generating the pyrrole and methyl propynoate as a side product although the latter was never detected or isolated despite it being a solid melting at 171°C, but then this was the first compound ever isolated by the author!



Scheme 1.



Scheme 2.

In 1960 when the author first entered university none of the common valence bond isomers of benzene (Fig. 3) were known, but in 1962 van Tamelen reported the tri-*t*-butyl Dewar derivative and a year later the parent compound (Scheme 3).[5] These were followed by the Tom Katz synthesis of benzvalene in 1971 and in 1973 prismane to complete the series (Scheme 3).[6] The ability of aromaticity to go beyond the benzene ring was also unknown until Emanuel Vogel at Koln synthesised[7] methano[10]annulene. He showed that the aromatic ring current was present from the 10-membered ring being held sufficiently close to planarity for electron delocalisation. The synthesis (Scheme 4) is simple, high yielding and was subsequently carried out in an industry-supplied pilot plant in his department. Vogel was the dominant player in the annulene area.

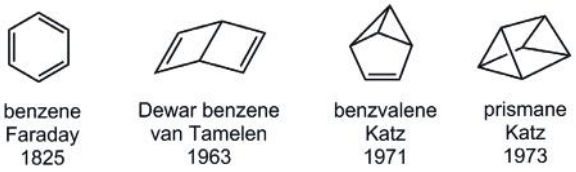
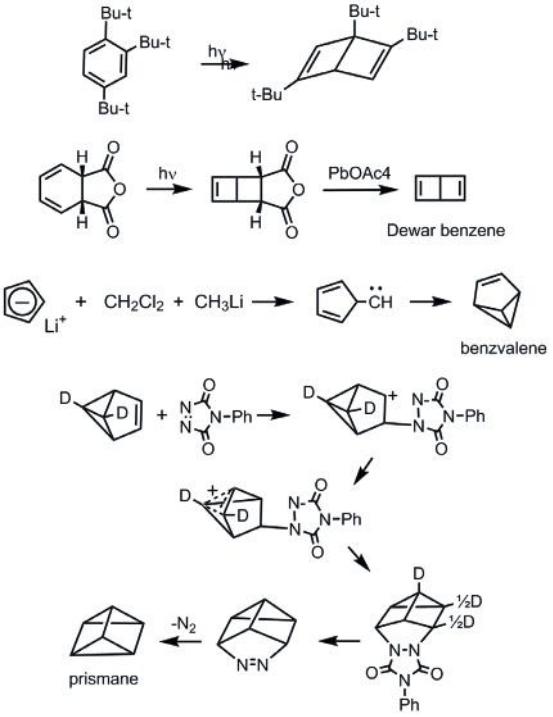
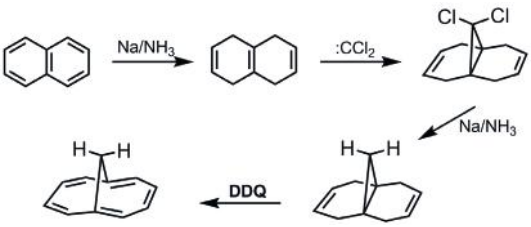


Fig. 3. Benzene and its valence bond isomers.

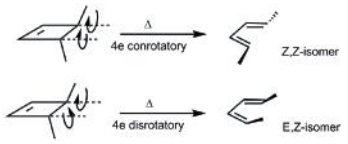


Scheme 3. The Common valence bond isomers of benzene and their syntheses.



Scheme 4.

The era was also one of difficulty for Woodward in his B12 work because of a product with the wrong stereochemistry being obtained. From that came the Woodward-Hoffman rules,[8] illustrated simply by the electrocyclic reactions of 1,2-dimethylcyclobutene (Scheme 5).



Scheme 5. Electrocycic ring opening of 1,2-dimethylcyclobutane.

When the author arrived in this country in 1968, only one of the Platonic solids (Fig. 4) had been transposed into a molecule, namely cubane. It was reported by Eaton and Cole[9] following a 13-step synthesis that started with 2-bromocyclopentadienone (Scheme 6). It was, at that time, clever in the way the four-membered rings were closed. Initial [2+2] photoaddition closes two rings and then a variant on addition-elimination closes the third. Further functional group manipulation and a repeat of the closure leads to the cubane skeleton that subsequently yields the hydrocarbon. The cubane arena provided Eaton with a lifetime of study. It was some 14 years later that the first stable tetrahedrane appeared, and this a sterically protected derivative whose ring skeleton is inaccessible even to simple reagents because of the corseting effect of the four bulky substituents. The key step in this Maier[10] synthesis is the *crossover* [2+2] photoaddition (Scheme 7, shown in blue) that is dictated by the steric distortion of the cyclopentadiene ring forced by the bulky substituents. This was followed by the elegant dodecahedrane molecule prepared by Paquette and his students at Ohio.[11] It took Paquette some 29 steps to obtain the molecule (Scheme 8) and then a few years later Prinzbach (Freiburg University) provided the isomeric structure, the elegant pagoda-like molecule given that name (Fig. 5).[12] Prinzbach's fundamental chemistry led to him becoming the first of only two chemists appointed as *German National Fellows* and brought here under the NZ Universities scheme.

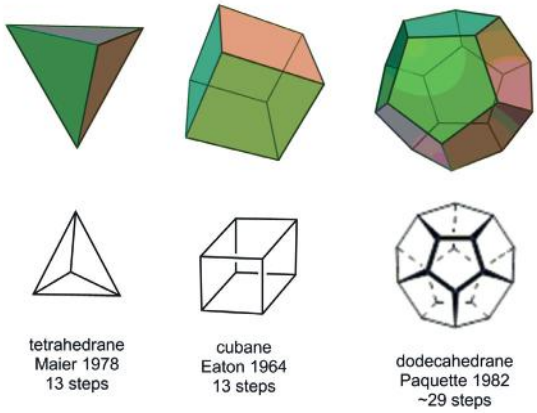
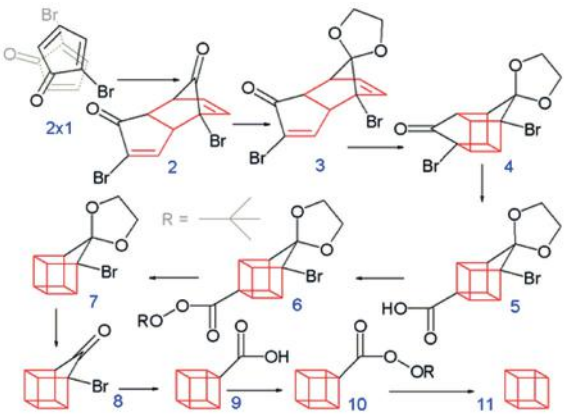
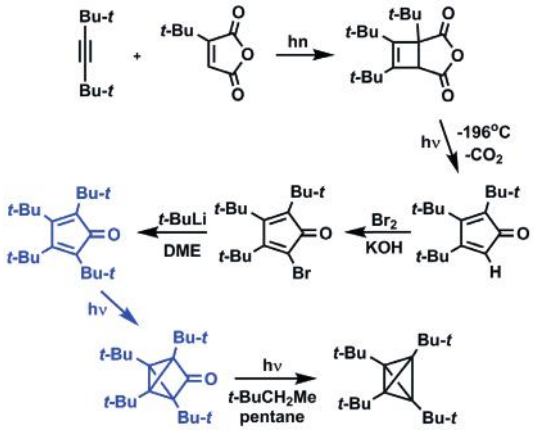


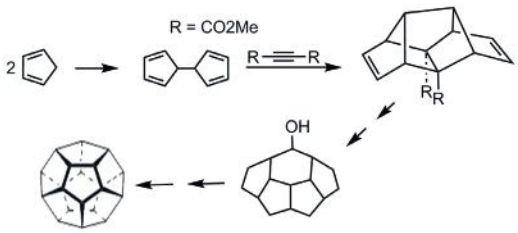
Fig. 4. Three of the five Platonic solids and ther hydrocarbons.



Scheme 6. The synthesis of cubane.



Scheme 7. Synthesis of tetra-*t*-butyltetrahedrane.



Scheme 8. Synthesis of dodecahedrane, $C_{20}H_{20}$ (ca. 29 steps in total).

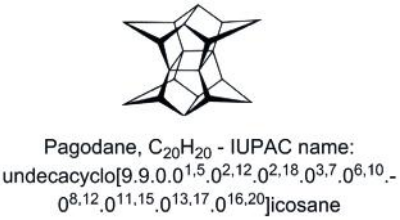
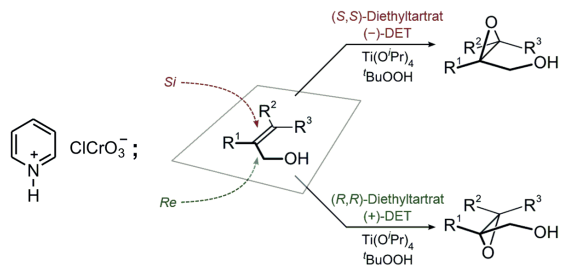


Fig. 5. The pagodane molecule.

The period from the mid-1960s also saw many developments in the tools of synthesis. Examples here include pyridinium chlorochromate (PCC), widely used following the 1975 publication by Corey and Suggs;[13] silanes that became fashionable once TMS was the accepted internal standard for NMR and the chloride readily available, and the Sharpless method of asymmetric epoxidation with tetraisopropyloxysilane [Ti(O-*i*-Pr)$_4$] and enantiomerically pure diethyl tartarate (DET; Scheme 9).[14] Then, from 1968 Pedersen, Lehn and Cram were the first to show us that chemistry beyond the single molecule could more than



Scheme 9. Pyridinium chlorochromate and the Sharpless epoxidation.

fascinate through Pederson's synthesis of polyethers and the cations they occluded, the burial of molecules within molecules – the cryptands of Lehn - and the host guest entities of Cram (Fig. 6). The era of supramolmolecular chemistry was born and this led to the cyclophanes, rotaxanes and the molecular machines of Sauvage, Stoddart and Feringa, last year's Nobel Chemistry Laureates (see below).

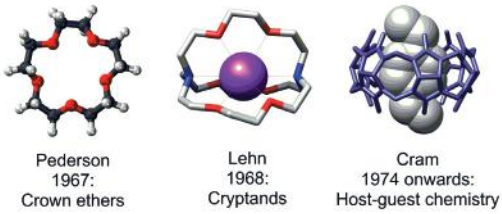
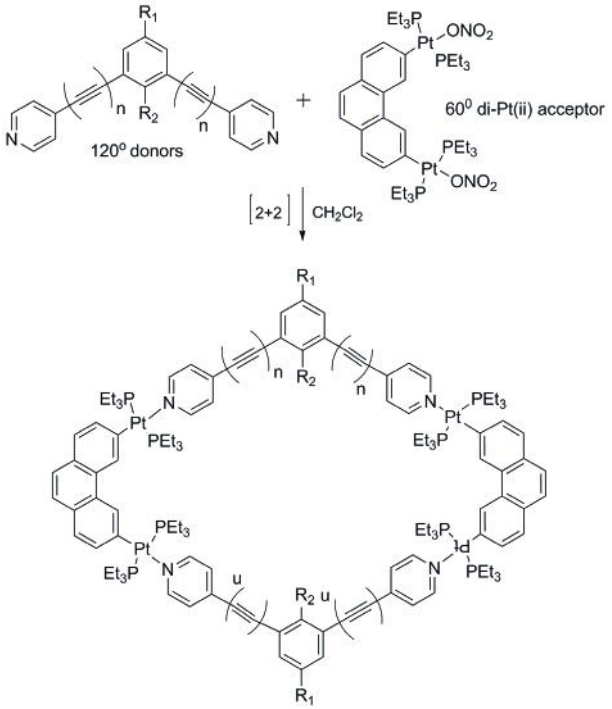


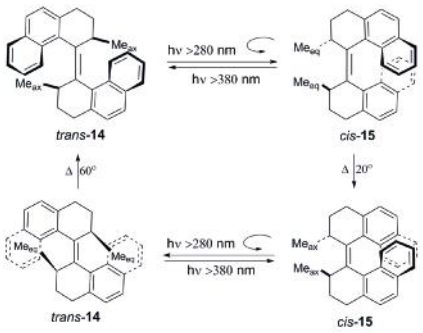
Fig. 6. Crown ethers, cryptands and a host-guest molecule.

Next came self-assembly and all that that has evolved as illustrated by Stang's syntheses of rhomboids from nitrogen donors held at 120° and di-platinum(II) acceptors at 60° (Scheme 10).[15] But it is the work of the 2016 Nobel Laureates and their self-assemblies that provided the path to the first and simplest of molecular machines. Stoddart elucidated the art of rotaxane and catenane chemistry with his elegant syntheses, the establishment of clipping and stoppering, and then in 1994 both Sauvage and he demonstrated that molecular motion was a reality with a ring moving from one binding site to another.[16-18] Clearly molecular machines. The year 2004 saw the Stoddart molecular elevator that was based on his principles exactly[19] but this came after the Feringa molecular motor whose operation depends on two chemical processes: photochemical *trans* to *cis* isomerisation of a double bond and thermal isomerisation from groups passing each other. The elegance in this work was discussed earlier[16] and is not repeated here save for showing the process in Scheme 11, which, at 70°C is able to



Scheme 10. Amine-functionalized D2h-rhomboids (modified from ref. 11, Scheme 2).

proceed continuously – a genuine machine! Feringa took this further by preparing a nanocar whose wheels turned in the same direction and moved across a surface in 2011. It had fluorenylidene wheels that turned in the correct direction from choice of the appropriate optical isomer (Fig. 7).[16,20]



Scheme 11. The Feringa photoisomerisation-thermal cycle for molecular motion.

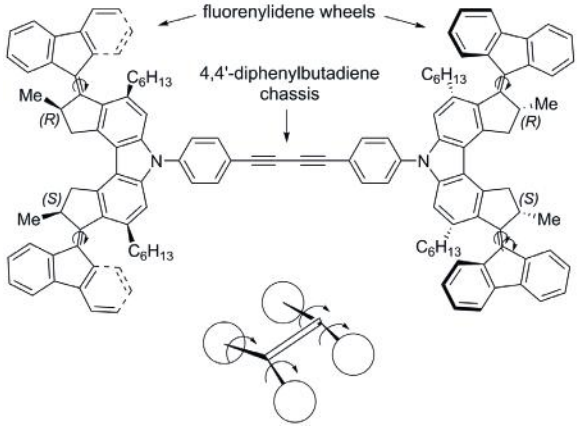


Fig. 7. The first nananocar that comprised fluorenylidene wheels and a diphenyl butadiyne chassis; see ref. 20.

By now there are a good number of synthetic nanocars and the first nanocar race took place in one of the CRNS labs in Toulouse, France, on April 28.[21] However, the six cars involved were not the photochemically or redox driven machines of Feringa or Stoddart but rather cars driven on a gold (or silver – see below) track in an atomic four-tip scanning tunneling microscope. The cars were fueled with electrons and electrical energy and controlled my modulating the tip voltage. Although it took six hours to position the cars on the start line, the race was won by *Dipolar Racer* in 90 min. The team was led by Professor James Tour (Rice University, Houston) in an American-Austrian collaboration.[22] His vehicle was a two-wheeler with tyres made of adamantine and carrying a central strong dipolar moiety (Fig. 8) and it was handicapped by having to travel 50 nm further (150 vs 100 nm) on a slower S-shaped silver track as opposed to the gold track for the four-wheelers. The only four-wheel car to complete the race was the *Swiss Nano Dragster*,[23] a triangular $C_{22}H_{17}N_3$ molecule with no wheels (Fig. 8) that is designed to glide across the gold surface akin to a hovercraft; it got home some five hours later and was declared the co-winner. James Tour's original nanocar was the $C_{430}H_{274}O_{12}$ molecule with bucky ball wheels as shown in Fig. 8.[24]

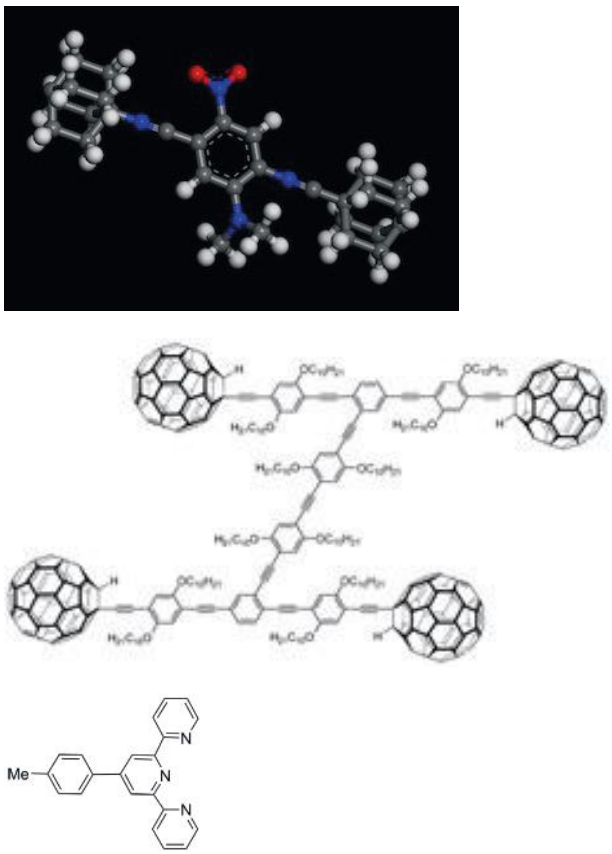


Fig. 8. The Tour nanocars: left: the *Dipolar Racer* (courtesy Prof James Tour, Rice University) and centre: the C_{430} initial Tour nanocar. Right: the C_{22} *Swiss Nano Dragster*.

After all the majestic chemistry from the leaders of the discipline, the author's contribution to the strained aromatics through the cyclopropanes (Fig. 9) pale into insignificance.

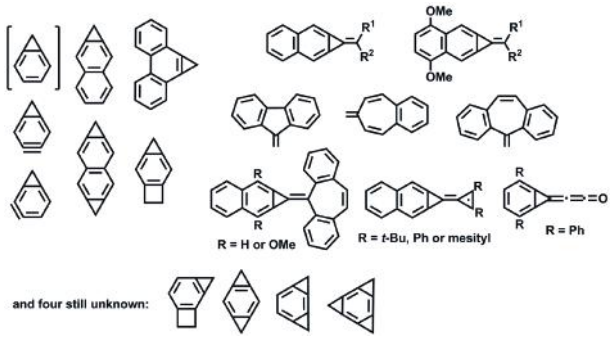


Fig. 9. Some of the cyclopropanes synthesised in Wellington.

Acknowledgments

I thank Dr Rob Keyzers for helpful suggestions and Mike Williams (Senior Media Relations Specialist) of Rice University for facilitating use of the Dipolar Racer image.

References and Notes

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ANISG / NZNIRSS Conference

11 - 18 April 2018, Rotorua

The eighteenth conference of the Australian Near Infrared Spectroscopy Group (ANISG), co-hosted with the New Zealand Near Infrared Spectroscopy Society (NZNIRSS), will be held on 11-18 April 2018 in Rotorua.

NIR technology users, researchers and students with a common interest in NIR research, applications and developments are invited to meet alongside major suppliers of NIR equipment and software to share experiences centred on the versatility and value of NIR.

Short courses on the basics of NIR, hyperspectral imaging, sampling and chemometrics will precede the meeting on Monday 9th April 2018 and Tuesday 10th April 2018.

For more information see: http://www.anisg.com.au/conference-2018

Article

Forensic toxicology – the coolest job in chemistry?

Wendy Popplewell,* Sarah Russell

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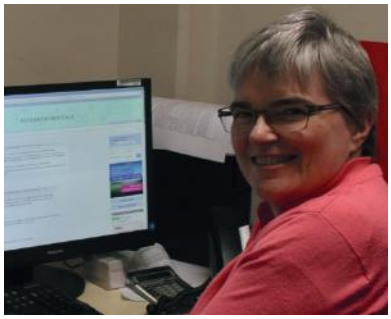
Keywords: *forensics, toxicology, drugs, ESR*



Wendy Popplewell grew up in Wellington, completing a Bachelor of Science with Honours, Bachelor of Commerce and Administration, and PhD in chemistry, all from Victoria University. After so many years in Wellington, Wendy was keen for a change in scene and undertook a postdoctoral fellowship at Rhodes University in South Africa. After a second postdoctoral fellowship, this time at the National Cancer Institute in the US, she was offered her dream position as a forensic toxicologist at ESR and subsequently returned to her home town in 2011. Having grown up enthralled by forensic science, Wendy still gets a thrill telling people her job title.

Sarah Russell is a born and bred Wellingtonian, studying at Victoria University of Wellington for a Bachelor of Science with Honours and a PhD. She then went to the University of Wyoming to apply her knowledge to surfactant chemistry and experience a White Christmas. Luckily a job at ESR as a forensic toxicologist came her way just as her postdoctoral studies were finishing in 1993. This job has kept Sarah interested and motivated since then.

When we asked ourselves why we became forensic toxicologists, our top answers were curiosity, job variety and making a difference to the care and welfare of New Zealanders. All scientists have an ingrained curiosity about the world around them, and that curiosity helps us push boundaries and think outside of the box for complex or unusual cases. Similarly, the diversity of the cases we encounter provides ongoing intellectual challenges. But most of all, we take great pride in applying our expertise in toxicology and analytical chemistry to real life.

What is forensic toxicology at ESR?

"All things are poison and nothing is without poison, only the dose permits something not to be poisonous." Paracelsus, 1493-1541.

This is the maxim of forensic toxicology, which is the study of drugs and poisons for the judicial system. A forensic toxicologist identifies substances and determines their concentration in biological samples. This information, together with an understanding of how drugs are metabolised in the body, can provide an insight into the significance of any findings.[1]

The Institute of Environmental Science and Research Ltd (ESR) is a Crown Research Institute formed in 1992 from parts of the Department of Scientific and Industrial Research (DSIR) and the Department of Health. The predecessor to DSIR, the Colonial Laboratory, performed the first forensic toxicological analyses in New Zealand in 1871.

ESR specialises in science relating to people and communities. We provide knowledge and skills that help safeguard people's health, protect food-based economies, improve the safety of freshwater and groundwater resources, as well as providing expert forensic science to the New Zealand justice system.

The Wellington branch of ESR undertakes the forensic toxicology for the New Zealand coronial and judicial systems. This involves the analysis of a range of biological specimens to determine the potential involvement of drugs and/or poisons in a death or alleged criminal act. We also undertake the analysis of blood samples taken from drivers suspected of driving while impaired by alcohol or other drugs under the Land Transport Act.

Coronial toxicology

The Coroners Act, 2006 states "a death that appears to have been without known cause, or self-inflicted, unnatural, or violent" must be referred to the coroner. The coroner will then evaluate the circumstances surrounding each case to determine the extent of the examination required. The coroner may order an investigation often starting with an autopsy conducted by a pathologist. During these procedures biological specimens are collected for further testing such as genetics, histopathology and toxicology. If deemed pertinent to the case, either by the coroner or the pathologist, biological samples are then sent to ESR for toxicological analysis. The samples collected and submitted for analysis will reflect both availability and case circumstance. We receive blood and urine samples commonly, however, vitreous humour (the transparent jelly-like tissue filling the eyeball), liver, stomach contents, brain, lung and hair samples are often submitted for analysis.

In the case of an unexpected death where no anatomical cause of death was identified at autopsy, a toxicological cause is often investigated, including levels of medication or some other poison. Alternatively, in accidental deaths, toxicological analyses are more likely to focus on drugs that have the potential to impair, and may have been used by the deceased prior to the incident. In cases of suicide, the cause of death may be determined at autopsy (for example a hanging). Here we focus on the potential abuse of illicit or licit drugs, or ascertaining if the deceased had been taking their prescription medication such as antidepressants or antipsychotics.

Criminal toxicology

The toxicology associated with criminal cases may involve the analysis of samples from a deceased person, or samples from a living person such as a complainant or an alleged offender.

In the case of an alleged drug facilitated sexual assault, the complainant will report a crime to the police. During their medical examination samples will be taken for toxicological analysis. In such cases, we are focused on analysing for alcohol and other impairing drugs. Samples from alleged offenders, if available, are analysed for the presence of alcohol and other drugs that may have influenced their behaviour at the time of the alleged incident.

A difficulty associated with samples taken from the living is that drugs are continually metabolised and eliminated from the body. A delay of several hours, or sometimes days, between the time of an incident and the time the samples are taken, can mean that any evidence of drug use is lost. The potential for drug consumption after the time of the incident, but prior to sampling, adds to the complexity of our interpretation of any analytical results.

Ultimately, the types of analyses carried out depend on the purpose of the investigation. As forensic toxicologists, we carry out analysis for evidence of the presence of a vast array of compounds, from prescribed or over-the-counter medication, to illicit drugs and poisons.

Our daily grind

Assessing new cases

When a case is received our first task is to evaluate the information that arrives with the samples. This documentation should have a case history, ideally including a list of drugs or poisons available to the deceased or found at the scene, and relevant information from any scene examination and autopsy. The context of the case is crucial for planning which analyses are required.

Sample selection

When available, blood is usually the primary sample of interest in post-mortem cases as it represents the drugs acting on the body at the time of death. Ante-mortem, drugs in the body will be deposited in different organs at different concentrations based on the characteristics of the drug and its affinity for various tissues in the body. For instance high concentrations of drugs are often found in the liver and the lungs. Post-mortem, the high concentration of drugs in these organs can diffuse out into the blood and other surrounding tissues. This diffusion is referred to as post-mortem redistribution. Therefore it cannot be assumed that post-mortem drug concentrations represent those at the time of death, especially for blood sampled from the central vessels and the heart which are close to such organs. For this reason, post-mortem blood is preferentially sampled from sites further from these organs, such as the large veins in the legs.

For criminal cases where there is a delay of hours to days between the incident and the time the samples were taken, often urine is the preferred primary sample. Many drugs can be detected in the urine for a longer time than in the blood. As urine is a body's waste product, compounds detected in the urine represent the drugs that have been acting on the body and are now being excreted. Urine composition is constantly changing due to factors such as a person's hydration level. This dilution variability coupled with the fact the some drugs are only excreted as metabolites in the urine make it impossible to say from a urine sample exactly when or how much of a drug was consumed. However, detecting the presence of a drug or its metabolites in the urine indicates that the drug was acting on the body some time prior to the sample being taken.

When there is a long delay (weeks or more) between an incident and sampling of biological samples for toxicology, analysis of the hair can be extremely useful. Various drugs become incorporated from the blood into the growing hair root. Subsequently, such drugs remain fixed in that part of the hair as it grows out from the scalp providing a drug-use history.

Analytical strategy

The amount of each biological sample we receive is finite. Therefore, it is crucial to triage the desired analyses in order to achieve the best results from the available samples.

Typically, the sample will first be 'screened' for a wide variety of drugs. Based on the results of this screen, we then determine what, if any, more targeted analyses may be required to confirm the presence of certain drugs, or to determine their concentrations.

Most biological samples are complex matrices with low levels of the drugs or poisons of interest. Toxicologically significant levels of drugs can be extremely low, some less than a microgram per millilitre of blood. Various methods are used to reduce the chemical complexity of the sample and to concentrate any drugs present to optimise detection. The most common preparation methods we current employ are protein precipitation and liquid-liquid or solid-phase extraction. Protein precipitation involves removing the unwanted protein content from the biological matrix (such as blood) through precipitation and filtration. This can be followed by one of the extraction methods. In liquid-liquid extraction the target drugs are transferred from the sample into a solvent layer based on the chemical properties of the drugs of interest. Solid-phase extraction is a simple form of column chromatog-

raphy where the sample is passed through a solid material and washed with various solutions to separate the target drugs from the matrix.

Certain drugs remain difficult to detect even after a sample has been purified and concentrated. Such drugs may benefit from a derivatisation step such as esterification of a carboxyl group to help stabilise certain chemical functionality and improve the analytical detection of the target drug.

Once the sample is in a suitable state for detection we analyse the extract, usually via liquid or gas chromatography with mass spectrometric detection.

Currently our ESR toxicology laboratory uses liquid chromatography with time of flight mass spectrometric detection to screen for hundreds of drugs from a single blood extract. This is a powerful screening tool, with the added benefit of stored data that can be mined and reprocessed at a later date when new information or drug standards become available. The major disadvantage of our method is the volume of blood required (1 mL).

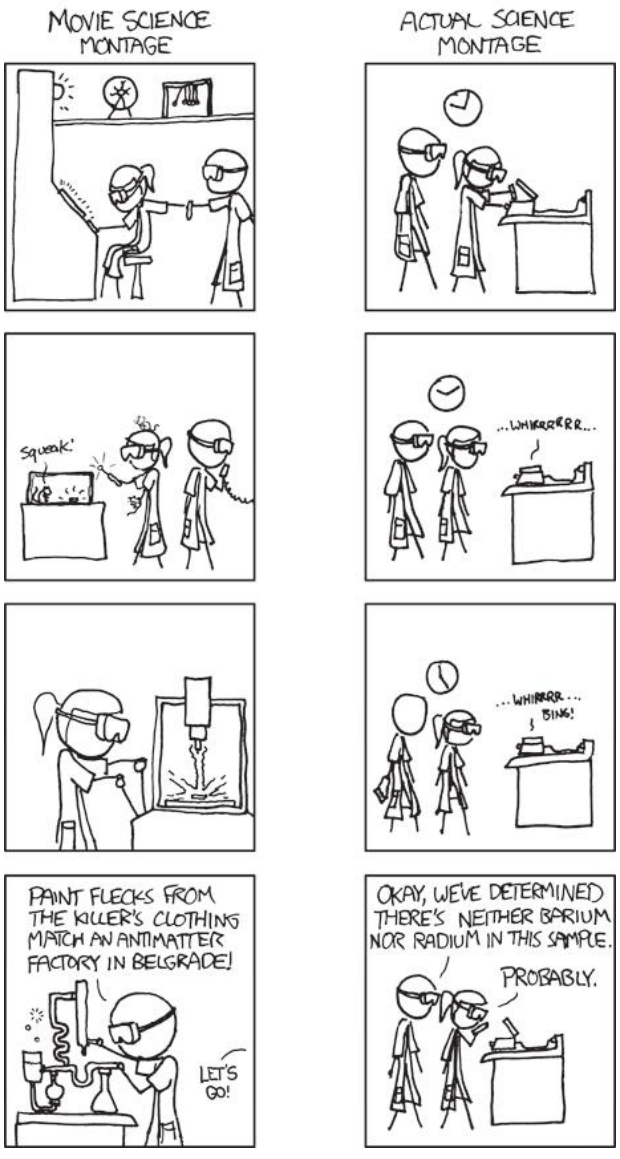


Fig. 1. Movie science vs. actual science! Cartoon licensed under a Creative Commons Attribution – NonCommercial 2.5 License, https://imgs.xkcd.com/comics/science_montage.png

This can impact sample volume available for subsequent analyses, or the ability to use this technique in the first instance.

Despite advances in modern technology, there is no single method for detecting everything of interest to our investigation. Scenarios depicted by fictional TV series (like CSI) where the presence of organic and inorganic compounds is determined by direct injection of a blood sample into an instrument, are not accurate. A magic black box delivering the complete list of complex toxicological results, within one hour, simply does not exist (Fig. 1).

Reporting

Once we are satisfied that all analyses are complete and the appropriate drugs have been investigated, the results are collated and reported. Interpretation of the significance of analytical findings is achieved by comparison with previously encountered levels, both from collated in-house data and data published in the scientific literature. The report will include a comparison of the detected drug level to levels reported for normal use of the drug or levels that have been associated with causing death. However, it is not our job as toxicologists to draw definitive conclusions as to the cause of death; that is the responsibility of the coroner.

There are factors other than drug levels that must be considered when we report a case. These include the presence of other drugs which may interact; the deceased's age, medical history and any concurrent disease; the stability of the drug both in the body and in the stored biological samples; post-mortem processes such as post-mortem redistribution; and the individual's tolerance to a drug based on use or abuse history.

In the case of coronial deaths, our report is prepared for the pathologist, coroner and police inquest officer. The report can also be accessed by family members. Care is required to ensure that a report can be understood by all parties. It is the coroners' prerogative in New Zealand to decide the cause of death based on advice received from the pathologist and other experts. The pathologist evaluates our toxicological results along with their pathological findings and other information.

The results of our analyses for criminal cases are generally reported directly to the police in the form of an expert witness statement that can be read in a court without the need for our presence. These statements describe our qualifications and expertise, the results of all analyses and our interpretation of the results. The statements may include opinion evidence and any assumptions that we made in order to reach our opinions.

All of the reports and statements provided to the police, pathologists or coroners are subject to review and scrutiny by other toxicologists at ESR, before they are released. This process of auditing involves ensuring all relevant analyses have been undertaken (the reviewers may suggest further analyses), the proper technical procedures have been followed, and the results are correctly reported with any relevant interpretation and opinions.

The chain of custody for each item is maintained by the chronological documentation showing the custody, control, transfer, analysis, and destruction, retention or return of samples from the date they are received by ESR. This is a critical component of an ESR toxicology file as it proves that the results reported arose from analysis of the documented samples.

Court

If requested, we are required to give evidence in person at coronial or judicial hearings. Our toxicology laboratory carries out analyses for the whole of New Zealand so court attendance may be anywhere from Kaitaia to Invercargill. ESR expert witnesses, such as forensic toxicologists, are not concerned with the legal outcome of a court hearing; our job is to assist the court with unbiased results and interpretations, not to support either side of the criminal proceeding. Giving evidence is a situation controlled by the court. It is essential to ensure that our reports and statements, or verbal answers, are succinct and given in comprehensible layman's terms, so that the evidence is useful to the court system.

Having the responsibility to communicate our results to a wider audience is a highlight for many of us.

Accreditation

ESR's forensic laboratories are independently accredited. Accreditation is the formal recognition of the competency of the laboratory to carry out, and report on, a specific range of tests. This process of endorsement looks at the proficiency of the staff, the validity of equipment, materials, methods and results, and compliance with the relevant standards. Each of the forensic disciplines of ESR undergo a yearly in-house review, with a four yearly inspection from authorised overseas inspectors. In this job, as the saying goes; Quality is not an act, it is a habit!

The icing on the cake - research opportunities

The ESR toxicology group is primarily focused on service delivery, with the reporting of analytical results to our clients. This leaves minimal time for publishable research. We are also constrained by a range of rules detailing what can be studied and published, as documented in various New Zealand legislation such as the Coroners Act, 2006. All research must also comply with any relevant ethics obligations. However, our case work has sometimes led to a deeper study of a particular topic, such as sports supplements or poisonous plants, which have been presented at in-house or overseas conferences. This is part of what makes forensic toxicology especially fascinating to us as there aren't always simple answers to our questions. Even if we detect something in this research, what does it mean? Our group is in the unique position to have access to a large amount of data on a small and biased portion of the New Zealand population. This has enabled the publication of some interesting research including those outlined below.

Drug impaired driving

The prevalence of drug use by New Zealand drivers has been collated for many years.[2] One part of the study showed that the use of cannabis by drivers killed on our roads is almost as common as the use of alcohol. The combined use of alcohol and cannabis is known to result in an increased crash risk when compared with the use of either alcohol or cannabis alone. More of the deceased drivers had used the combination of alcohol and cannabis than had used alcohol by itself.

A recent study targeted a group of impaired drivers stopped by police due to unsafe driving. Samples of blood taken from these impaired drivers were tested for the presence of GHB (gamma-hydroxybutyrate, Fantasy). GHB is an illicit drug abused for its euphoric effects that are similar to alcohol. Anecdotal information from overseas was that illicit drug users were regularly consuming GHB in conjunction with methamphetamine (P). The study found 14.5% of the drivers that tested positive for methamphetamine were also positive for GHB.[3]

Methamphetamine in children's hair

There are various mechanisms for the incorporation of drugs into hair. As mentioned previously, the hair root has a rich blood supply, so any drug circulating in the blood can be incorporated into the growing hair. Drugs can also be deposited onto the outer surface of the hair via sweat, or external contamination such as spilling a drug on the hair or through exposure to smoke or vapours. When we analyse hair samples, they are washed with a solvent to remove drugs present on the surface of the hair prior to extraction. The amount of drug extracted from within the hair compared with that in the wash can be used to indicate ingestion or external contamination.

In New Zealand many children have been removed from clandestine laboratories following police intervention. For several years it was standard procedure that hair samples were taken from these children and the samples were submitted to ESR for analysis. The hair samples were analysed for methamphetamine and amphetamine. From the 52 cases analysed, 38 (73%) were positive for methamphetamine, while the metabolite amphetamine was detected in 34 of these cases. In no case was amphetamine detected without methamphetamine. The analysis of the hair washes showed only three were indicative of a low level of external contamination.[4] This low level of evidence of external contamination suggests that the children are ingesting methamphetamine and are incorporating it into the hair through the blood stream.[4] Such ingestion may be through passive inhalation of vapours, or contamination of food and other household surfaces that then gets ingested by hand transfer into the mouth.

Hydrogen sulfide poisoning - Rotorua

In late 2007 and early 2008 two men were found dead in, or near to, enclosed hot pools fed with Rotorua's geothermal waters. Following post-mortem examinations, blood and urine samples were frozen and sent to the ESR for toxicological analysis. These were then stored frozen until analysis. Hydrogen sulfide (H_2S) is a potentially deadly gas at elevated levels, but it is rapidly eliminated from the body and is unstable post-mortem. Thiosulfate

is a marker for the exposure to H_2S, and as it is stable post-mortem, the samples were analysed to determine the thiosulfate levels present. The urine thiosulfate levels detected were above those seen in the urine samples measured from the only previous study of people exposed to the Rotorua thermal area.[5] The thiosulfate blood levels found in the two men were similar to literature values from fatalities resulting from exposure in workplaces such as sewage treatment plants where H_2S is produced.

At the end of the day, the forensic toxicologist never knows what tomorrow will bring. It is an interesting job where we get to apply science and continuously add to our skill sets. Constant scrutiny, both by our in-house peers as well as in the court, helps keep our knowledge current and relevant. Is it the coolest job? No. Is it as glamorous as the likes of CSI like to imply? Certainly not. But the daily challenges and diversity make for very few dull days.

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A new registered IP right in town – what is a geographical indication and how does it compare to other intellectual property rights?

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On 27 July 2017 the Intellectual Property Office of New Zealand starting taking applications to register geographical indications (GI) for wines and spirits. What is a geographical indication and how does it compare to other intellectual property rights that are registered at the Intellectual Property Office?

Geographical indications

A geographical indication identifies a product as originating in a region of a country where a given quality or reputation of the product is attributable the geographical origin. The current situation in New Zealand is that a geographical indication can only be registered in relation to wines and spirits. In other countries, and maybe in the future in New Zealand, geographical indications can be registered for other agricultural products and foodstuffs.

One of the most famous examples of a geographical indication for wines is Champagne, i.e. in order to be called Champagne it must come from a designated area of France.

Unlike most registered intellectual property rights, you do not need permission from the owner to use a geographical indication. You just need to meet the requirements of the geographical indication. For a New Zealand registered geographical indication for wine from a designated region, that means at least 85% of the wine must be made from grapes harvested from the designated region. The remainder of the wine can be made from grapes harvested in other regions in New Zealand (but not other countries). For a spirit, it must have originated from the designated region. In some cases there will also be other requirements set by the registration which must also be met.

Since the owner does not have the right to stop others from using the geographical indication, it is usually associations of producers or traders that apply to register a geographical registration, but by law any "interested person" can apply.

To register a geographical indication the applicant must supply geographical data demonstrating the boundary of the proposed geographical indication and evidence to demonstrate the quality, reputation or other characteristic that is essentially attributable to the area within the geographical boundary.

Breaching the restrictions of a registered geographical indication is deemed as misleading and deceptive conduct under the Fair Trading Act. Geographical indications are therefore closely linked to consumer protection measures set out in the Fair Trading Act.

How do geographical indications compare to trade marks?

Trade marks are also used to identify the origin of good or services, but they don't usually indicate geographical origin, rather they indicate the identity of the marker or

distributer. For example, when buying a computer you want to know whether it is from Microsoft® or Apple®. The symbol ® means it is a registered trade mark, whereas the symbol ™ means it is being used as a trade mark, i.e. being used to denote origin, but it has not been registered at the Intellectual Property Office.

In some cases trade marks and geographical indications can overlap. For example, some vineyards are named after their geographical location. If there is an identical or similar existing registered trade mark related to wine and spirits the Intellectual Property Office may refuse to register the geographical indication.

Registered trade mark owners can take action against others using their trade mark under the Trade Marks Act. If the trade mark is not registered, action can be taken under the Fair Trading Act or Passing Off. Registered trade mark owners will often take action using a combination of all of these.

So what does a patent protect?

This column usually talks about patents, so how do they fit in? A patent protects a new invention. Because the invention must be new, i.e. there must be no public disclosure or sale of the invention before the patent application is filed, it will often be the first type of intellectual property that is applied for to protect a new product. A patent will not refer to the trade mark name that the product later becomes known as.

For example, a patent for a new pharmaceutical drug will just call it by the chemical (usually IUPAC) name. Later, when the drug is on the market, it will be given a trade mark name by the company selling it. Once the patent has expired and others are allowed to sell the drug, they will not be allowed to use the trade mark name, they will need to come up with their own trade mark to show the drug is not from the same origin.

Copyright and registered designs

Copyright and registered designs protect the way something looks – rather than the way it works which could be covered by a patent (if it is new and inventive).

Registered designs are applied for at the Intellectual Patent Office whereas copyright does not need to be registered in New Zealand.

If the design of a product becomes well known and indicative of the source of the product, it can also be registered as a 3D trade mark. An example is the classic shape of the Coca-Cola bottle.

There are lots of types of intellectual property, including others not discussed here. They interrelate and overlap to cover the different aspects of a product. A product can make use of many types of intellectual property to protect it from competitors. Usually value and trust can be built up in a product by understanding and utilising the different types of intellectual property.

If you have any queries regarding intellectual property related matters (including patents, trademarks, copyright or licensing), please contact:

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Article

Dr Wohlmann's radon cure: the story of the Rotorua Bathhouse radium activator

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Keywords: *radium, radon water, Rotorua Bathhouse, Arthur Wohlmann*

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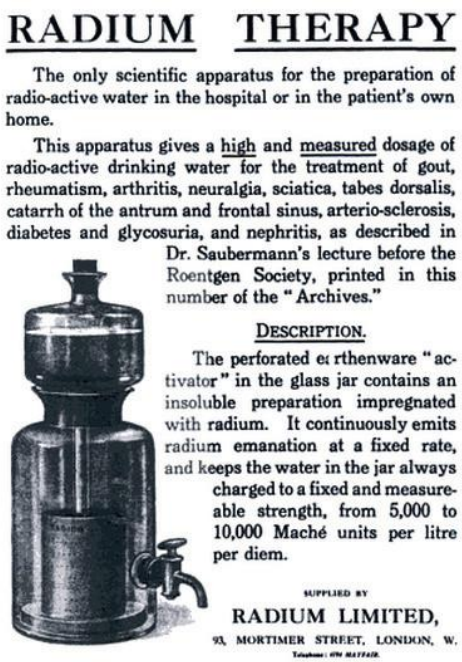
In New Zealand today, radium is imported and used under strict controls set out under the Radiation Safety Act 2016 and the Radiation Safety Regulations 2016. But in the early 20th century there were no regulations to control the use of ionising radiation and both medics and entrepreneurs promoted radium therapy for a range of perceived or actual ailments, including "irregular or excessive menstruation … acne, ringworm and birthmarks". New Zealand consumers were spared some of the more bizarre applications of radium to household products – for banishing unwanted facial hair, or as an additive in toothpastes, contraceptives and face creams – but they did participate in the international fad for the use of radon water as a therapeutic tonic (Fig. 1).[1]



RADIUM THERAPY

The only scientific apparatus for the preparation of radio-active water in the hospital or in the patient's own home.

This apparatus gives a high and measured dosage of radio-active drinking water for the treatment of gout, rheumatism, arthritis, neuralgia, sciatica, tabes dorsalis, catarrh of the antrum and frontal sinus, arterio-sclerosis, diabetes and glycosuria, and nephritis, as described in Dr. Saubermann's lecture before the Roentgen Society, printed in this number of the "Archives."

DESCRIPTION.

The perforated earthenware "activator" in the glass jar contains an insoluble preparation impregnated with radium. It continuously emits radium emanation at a fixed rate, and keeps the water in the jar always charged to a fixed and measureable strength, from 5,000 to 10,000 Maché units per litre per diem.

SUPPLIED BY

RADIUM LIMITED,

93, MORTIMER STREET, LONDON, W.

Fig. 1. In the northern hemisphere radium activators, which infused water with radioactive radon gas, were promoted for home as well as hospital use. This 1913 advertisement shows a device made by the same London firm that made the Rotorua Bathhouse's radium activator. Source: https://en.wikipedia.org/wiki/File:Radium_therapy_-_1913.jpg

The Rotorua Bathhouse radium activator

The imported device that arrived at the Rotorua Bathhouse in 1914 looked much like a regular ceramic water filter – there was a lid for pouring in water at the top and a spigot for draining off water at the side – but it was special. Inside the jug was a second ceramic container holding a small amount of a radioactive compound; it was probably radium sulfate. Any water stored in the jug would be irradiated with radon gas, a radioactive decay product of radium. Dr Arthur Wohlmann (Fig. 2) ordered the 'radium activator' after a 1913 trip to Europe, during which he visited several spas offering radioactive water therapy and met Dr Sigmund Saubermann, a Berlin-based doctor who had designed a radium activator that was widely used on the Continent. Like similar devices used in health spas and private homes throughout Europe and North America, the Rotorua Bathhouse radium activator was used to produce irradiated drinking water that doctors, patients and domestic consumers believed was a therapeutic tonic.

Dr. Arthur Stanley Wohlman, M.D., Lon., L.R.C.P., B.Sc., M.R.C.S., Eng.

Fig. 2. The enterprising idea of adding radioactive water to the Rotorua Bathhouse's list of treatments came from government balneologist Arthur Wohlmann, who said the New Zealand public was 'mad on radium' and the radium activator was well worth the £250 investment. Ref: 1/2-037890-F, Alexander Turnbull Library, Wellington, New Zealand.

Arthur Wohlmann, government balneologist

Wohlmann, an Englishman who had trained as a medical doctor in London, was appointed as New Zealand's first government balneologist – an expert in the therapeutic use of mineral waters – in 1902. As an Englishman in a colonial position, Dr Wohlmann naturally looked back to Europe for the latest therapeutic treatments and therapies. As well as keeping up to date with medical literature, he made several journeys to visit European spas, including the 1913 tour during which he made a 'prolonged and close investigation of the principal English spas', conferred with many leading British and continental balneologists and met Saubermann.[2] On his return, Wohlmann

convinced the government to invest in a radium activator, which was designed to irradiate water with radon gas. In making his case to the general manager of the Department of Tourist and Health Resorts, Wohlmann described radon therapy as a treatment that had 'come to stay' and offered assurances that the apparatus would soon pay for itself, as the New Zealand public was already 'mad on radium', which was then widely used as a cancer treatment.[3] The manager was convinced, as was the Cabinet: in June 1914 they approved expenditure of £250 – equivalent to $40,000 in today's money – on a radium activator. One was immediately ordered from Radium Ltd in London, who made it to Saubermann's design and shipped it to New Zealand on the SS *Pakeha*. The carefully packaged device, which stood 65 centimetres tall and weighed 27 kilograms, arrived in Auckland in September 1914 and was in use at the Rotorua Bathhouse by late October.

In his 1914 book, *The Mineral Waters and Spas of New Zealand*, Wohlmann described the portals by which radium emanation, or radon, could enter the body. The most important, he said, were the lungs, the skin and the mouth, though radon could also be administered by injection, by vaginal or rectal douches, or by insertion into tooth cavities. But Wohlmann, perhaps to the relief of his patients, had decided that the preferred way was orally, in a glass of drinking water: 'Not only is the dosage easy to determine and the method of administration simple, but the period of retention in the body is markedly longer than in the case of inhalation.'[4]

When the radon water went on sale at the Rotorua Bathhouse in October 1914 (Fig. 3), Wohlmann advised each patient to take four to six glasses of radon water a day, at threepence (now equal to about two dollars) per glass. Because radon-222 has a half-life of only four days, patients were advised to drink the water while it was still 'fresh' and before the radon gas had decayed away. Wohlmann recommended that they linger over each glass, sipping rather than gulping the tonic. 'Taking sips at frequent intervals,' he said, helped to 'maintain the charge in the blood.'[5]

Fig. 3. In 1914, a new therapy arrived at the Rotorua Bathhouse: patients with such chronic conditions as gout, diabetes or constipation were offered glasses of radioactive drinking water produced by a radium activator. This image shows the Bath House, Rotorua, c. 1909, photographed by C.P. Parkerson. Ref: OP-2489, Rotorua Museum Te Whare Taonga o Te Arawa.

Wohlmann recommended the new treatment for a range of chronic conditions, particularly gout and diabetes. Radium water 'looks and tastes exactly like pure water,' said the *Rotorua Times*, 'but it has very different properties. The emanations which it contains have been proved valuable in the treatment of diseases affecting the joints, especially gout, and of diabetes. They are also useful as a nerve soother, and they also have the singular property of tightening loose teeth.'[6]

The curative power of radon

Today it seems like the worst kind of quackery to prescribe radioactive water as a 'treatment' for chronic illness, but Wohlmann was no charlatan. A colonial doctor and a government employee who got no personal financial gain from prescribing radon water, he was striving to keep up to date, or ahead of, England and continental Europe when it came to the application of his science. In giving radioactive water to his patients, he was acting according to scientific beliefs based on work by Marie Curie and others that suggested moderate doses of radioactivity could invigorate healthy cells and kill cancerous cells.

Radium, though discovered by Curie only in 1898, was by 1914 used widely as a treatment for cancer. A small quantity of radium, or an amount of radon gas sealed in a small capsule, could be placed in close proximity to an external tumour or inserted into an internal tumour. It was known that exposure to radium could cause burns, but the properties of this new element were still being investigated and radon, its daughter gas, was considered relatively benign and therefore suitable for spa treatment of the chronically rather than the acutely ill. What's more, mineral water from hot springs had been used for many centuries and was generally believed to have a curative effect. When radon was discovered in a German hot spring long believed to have curative powers, the theory emerged that radon was responsible for the tonic effects of bathing in or drinking those waters. Some of the principles of homeopathy were involved here: even if radium was potentially harmful, it was believed that the much diluted version, the radon gas in water, would have an invigorating effect.

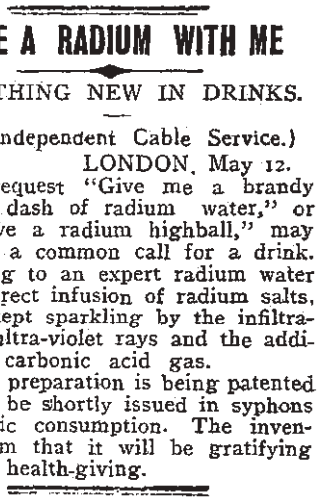
In his justification of radon therapy, Wohlmann referenced the published research of German physicians Saubermann and Paul Lazarus who claimed that:

… radium emanation in moderate doses promotes the multiplication and growth of healthy cells and the decay of morbid ones.

1. Emanation increases the output of urine.
2. Emanation increases the activity of the digestive tract, and especially the excretory activity of the bowels.
3. It increases the excretion of uric acid …
4. It dilates the blood vessels.
5. It diminishes the viscosity of the blood …
6. It lowers the blood pressure.
7. It increases metabolism …

8. It has a profound nerve-soothing effect.
9. It increases sexual activity.
10. It modifies the constitution of the blood, causing first hyper-leucocytosis, then leucopenia and increase in the number of red corpuscles.[7]

Whatever its actual efficacy, the therapy was popular (Fig. 4). As word spread, patients flocked to the Rotorua Bathhouse for a course of treatment. Sales of radon water peaked in 1916, when 8500 glasses were sold. To 'save cripples the constant journey to the baths', Wohlmann also arranged for the water to be dispensed in glass-stoppered bottles that each held six glasses of radioactive water.[8]



HAVE A RADIUM WITH ME

SOMETHING NEW IN DRINKS.

(Per Independent Cable Service.)

LONDON, May 12.

The request "Give me a brandy with a dash of radium water," or "I'll have a radium highball," may soon be a common call for a drink. According to an expert radium water has a direct infusion of radium salts, and is kept sparkling by the infiltration of ultra-violet rays and the addition of carbonic acid gas.

A new preparation is being patented and will be shortly issued in syphons for public consumption. The inventors claim that it will be gratifying and also health-giving.

Fig. 4. Radium highball anyone? Radioactive water was seen as fashionable and sophisticated and not just for therapeutic use. When added to a soda siphon, radium could deliver a cocktail with a blast of radon infused carbonated water. Source: Grey River Argus, 1 May 1914, p.8, Courtesy of the National Library of New Zealand.

The end of the radon water fad

Sales of radon water declined after 1916. Wohlmann, who had changed his Germanic surname to Herbert during the First World War, returned to Britain in 1919 and was replaced by Dr Campbell Duncan. In 1923 only 300 glasses of radon water were sold. This was partly because radon water was a fad – there was no credible evidence that it did any of the things that were originally claimed. Despite this lack of therapeutic evidence, an American-made radium activator called the Revigator was now available to domestic consumers. This product, distributed by a Wellington business calling itself the Radium Ore Revigator Agency, irradiated water via a jar lining of radium ore, and produced water of a much lower radioactivity than the Rotorua Bathhouse device. As one American doctor put it, such devices included 'a few cents worth of crude ore, having a low grade of radioactivity, and possessing no more therapeutic value than do the luminous figures on the dial of a two dollar watch'.[9] Radon water remained popular with domestic consumers until the widely publicised 1932 death of American golfer and industrialist Eben Byers from cancer linked to drinking radioactive water. Radithor, the water Byers drank, contained minute amounts of radium, so was much more potent than the Rotorua radon water or that from domestic devices like the Revigator.

Wohlmann's successors, however, displayed a startling ignorance of the nature and potency of the Rotorua Bathhouse radium activator. In a 1922 memo, Duncan said that the public rarely asked for radon water, and he now rarely prescribed it. 'I would not be prepared to say that the water now possesses any radium properties,' he added.[10] In 1925 the tourist agent at Rotorua described the activator, which was now chipped and broken and sitting in a storeroom, as having 'what appears to be a kind of earth' inside the porcelain cylinder. 'Whatever efficacy this may have had has long ago been expended,' he added, stating that the device was now 'quite valueless'.[11] This showed a total ignorance of the properties of radium and how the radium activator worked. With a half-life of 1620 years, radium would go on releasing radon gas almost indefinitely – as Wohlmann had promised when making the case for the expensive purchase: 'the initial cost is high owing to the price of radium, but the upkeep is nil and the material is to all intents and purposes everlasting'.[12]

The ultimate fate of the Rotorua Bathhouse radium activator is unknown. Rotorua's acidic mineral waters damaged the furnishings and fittings of the bathhouse, necessitating costly repairs and contributing to the building's poor financial performance. By the 1940s the bathhouse was extremely run down and the baths were eventually closed in 1966. The radium activator, with the radium sulfate in its inner chamber continuing to irradiate the air or water surrounding it, probably ended up in a dump somewhere.

From therapeutic device to quack curiosity

The Rotorua Bathhouse radium activator arrived in New Zealand as a piece of scientific equipment, a medical device that issued a substance, radon water, believed to be capable of curing or relieving people of symptoms of chronic ailments like depression, arthritis and constipation. By 1925 it was surplus to requirements, perhaps a bit of an embarrassment to the medical staff, an example of a past fad, an oddity that no one quite knew what to do with. Today we would see an intact radium activator as something sinister and dangerous, a frivolous use of a potentially dangerous carcinogen. With all traces of the radium removed, we could see this as a curiosity, a relic of a time when we were ignorant of the potentially harmful effects of radioactivity. Such items have now become collectibles. A hundred years ago the radium activator purchased by the Rotorua Bathhouse was regarded as a sophisticated medical device; now we are most likely to find such devices in a museum of quack curiosities.

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Eric William Ainscough BSc(Hons), PhD (Qld), FNZIC

Eric Ainscough passed away on 25 March 2017 aged 75 years. He completed his BSc(Hons) (1964) and PhD degrees (1968) at the University of Queensland studying with Professor Ron Plowman and undertook postdoctoral research first at Simon Fraser University in Canada under the supervision of Louis K. Peterson, followed by a year with Stephen Robinson at Kings College London. He was appointed as a lecturer in chemistry at Massey University in 1971 and promoted to Associate Professor in 1984. In 1977 he was a Visiting Professor at the University of British Columbia and in 1999 was elected to the Fellowship of the New Zealand Institute of Chemistry.

Eric was a very likeable chap who was passionate about chemistry. Many fond memories were shared at his funeral, highlighting his passion for the subject and the unique ways he communicated this to the students. His impressions of a gecko and gas molecules are things of legend, as was his ability to use his entire body as a human pointer. While perhaps not coming easily to him, Eric did have a flair for a performance. Eric's enthusiasm and love of chemistry carried over to some fantastic magic shows. With his sly smile and sparkle in his eye, he was the quintessential image of the mad scientist, crouched behind the front bench, hammering in nails with a banana, letting off bangs and flashes, fireballs rising to the ceiling, lots of smoke. There was always something of the little boy in Eric. Of course it all took a lot of work, but he quite selflessly volunteered. And he loved it.

A truly inquisitive mind was one of the things that drove the direction of Eric's research. He published about 160 papers which have received more than 3000 citations. He along with Andrew Brodie and Graham Freeman formed a partnership that endured for decades. Eric was a vital half of a very successful collaboration with Professor Andrew Brodie. Together they published many papers with a recent focus on metallo-phosphazene chemistry. Earlier research included the iron binding human milk protein lactoferrin and complexes with low coordination numbers. They were jointly awarded a Marsden Fund grant in 2002 and the New Zealand Institute of Chemistry Prize in 2007. Eric loved to get into the lab with students. Andrew recalls walking along the corridor one day when a mighty bang came out of the lab on his right. He went in to see Eric lying flat on the floor and a very startled honours student looking at him. Eric, in typical fashion had been helping the student and told her to be careful with the perchlorate compound she had made as it could be explosive. It was! She never forgot that lesson.

Eric had tremendous energy and was always busy, always in a hurry. He would throw himself at everything as well. In a recent staff-student cricket match just a few years ago, Eric was fielding at square leg, diving left and right to take catches. He took this energy into his lectures and in conversation. He was tremendously passionate and enthusiastic about chemistry, extremely well read and generous with his time.

In keeping with Eric's wishes and his spirit, his funeral was marked with many past and current pupils and staff wearing bright colours. A fitting farewell for such a well loved and admired man.

Paul Plieger

Article

Infrared and Raman spectroscopy of graphene nanoribbons

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Keywords: *graphene*, *nanoribbons*, *Raman*, *infrared*, *spectroscopy*

Introduction

Two-dimensional nanomaterials, such as graphene, have attracted a lot of attention in recent times[1,2] due mainly to new physical phenomena that arise from the unique symmetry of two-dimensional lattices (in the case of graphene[3]) or more generally, from increased correlation effects due to confinement of charge-carriers such as electrons and holes, and other quasi-particles, such as phonons and plasmons in the two-dimensional plane.[2] The majority of physical measurements have been made on samples with large lateral dimensions (where "large" is in relation to the length scale of the measurement technique) so that phenomena due to the atoms at the edge of the sheet have only a negligible effect on the total response of the system.

Reducing the lateral dimensions of two-dimensional nanomaterials to create nanoribbons[4–6] means the boundaries (edges) of the system now have an influence on the physical properties. The most obvious is the confinement effect that is analogous to the quantisation of electron energy levels that are observed in the familiar particle-in-the-box model. For graphene, we must also consider that the atomic structure of the edge has two distinct forms, the arm-chair and zigzag structures shown in Fig. 1. Even the most elementary level of theory predicts armchair and zigzag edges to possess different physical and chemical characteristics.[7,8]

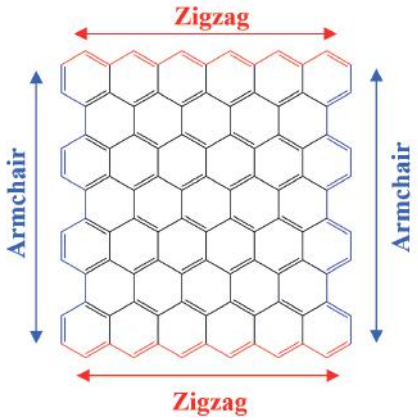


Fig. 1. Zigzag and armchair edges of graphene lattice

With all the attention on the physical properties of graphene it is very easy to overlook the fact that graphene is made from carbon and is therefore amenable to the methods of carbon-based synthetic chemistry.[9] The chemistry of graphene is dominated by reactions on the basal plane,[10,11] largely due to the prevalence of basal plane atoms. However, the proportion of edge atoms increases significantly (in relative terms) for graphene nanoribbons and this provides opportunities for investigating the chemistry of graphene nanoribbon edges. Edge atoms also allow the functionalisation of graphene, without altering the structure of the basal plane, which allows independent control over the chemical and electronic properties of the graphene nanoribbons. The reactivity and electron transfer rates of edge atoms are also much greater than basal plane atoms.[12]

There are several methods for producing graphene nanoribbons including total synthesis from polyaromatic hydrocarbon precursors,[13,14] oxidative "unzipping" of carbon nanotubes,[4] lithographic etching of single-layer graphene[15] and mechanical fracturing of bulk graphite (in the form of highly oriented pyrolytic graphite, HOPG).[16] Each method has advantages and disadvantages; there appears to be a perverse "uncertainty principle" operating whereby a method can produce high quality nanoribbons but in very low quantity, or low quality nanoribbons in much higher quantity. Lithographic techniques fall in the first category, while oxidative unzipping is in the latter. Total synthesis has the potential to produce high quality material in reasonable quantity but the drawback with total synthesis is the time and effort required to produce the material. The process of mechanical fracturing is depicted in Fig. 2, where a diamond knife mounted on a standard laboratory microtome is used to cleave ribbons of graphite from an HOPG block. The graphite ribbons can then be subjected to exfoliation procedures, to produce, ideally, graphene nanoribbons.[17–19] A unique advantage of the mechanical fracturing technique is purity; because the fracturing technique involves only a mechanical process no other reagents are introduced and the nanoribbons retain the purity of the HOPG (99.9999% C). As depicted by the cartoon, the fracturing process causes the fission of covalent carbon-carbon bonds, thereby producing reactive carbon atoms that, presumably, restore their tetravalency by reaction with molecules in the surrounding environment (most likely dioxygen and water but also possibly dinitrogen).

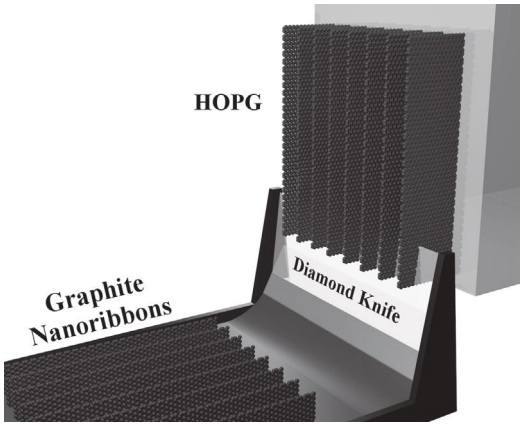


Fig. 2. Mechanical fracturing of graphite (HOPG) using a diamond knife mounted on a microtome

The chemistry of graphene nanoribbon edges presents two significant challenges: (1) armchair and zigzag edges exhibit different reactivity and (2) the characterisation of chemical reactions at the nanoribbon edge is made difficult by the low (absolute) number of edge atoms. For nanoribbons produced via mechanical fracturing, the fractured edge structure and chemical functionalisation at the edge is largely unknown and this presents another challenge – attempting chemical reactions with unknown starting materials. Here we describe recent work with vibrational spectroscopy that shows how Raman spectroscopy is a very useful tool for determining the type of nanoribbon edge,[20] while IR spectroscopy provides useful information on the functional groups at the edges.

Nanoribbons by mechanical fracturing

Fig. 3 shows selected TEM images of nanoribbons produced by mechanical fracturing. Following the fracturing of the graphite block, individual nanoribbons may be obtained by supplying sufficient energy via sonication to overcome the cohesive forces between the ribbons. The selection of solvent is critical in this process as the graphene-solvent interfacial energy must be greater than the adhesion energy between graphene layers to produce nanoribbons that are stable to aggregation.

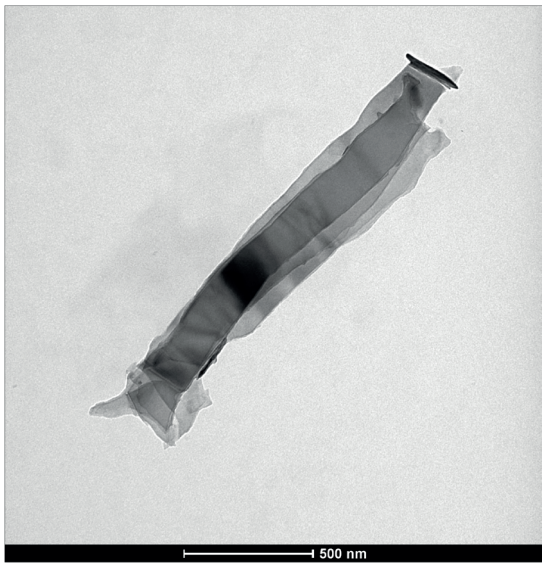
The width of the nanoribbon is controlled by the step-size of the microtome which is limited to 50 nm. The mechanical properties of the nanoribbons result in the folding and twisting behaviour shown in Figure 3a. Although the intrinsic tensile strength of graphene is very high (130 GPa with a breaking strength of 42 N m^{-1}),[21] it is easily deformed by forces transverse to the basal plane. Adhesion and cohesion forces generate the morphology observed in Figure 3a where strong cohesion between areas on a single ribbon results in folded morphologies and cohesion between different ribbons results in stacking of ribbons.

For comparison, the edge structure of few-layer graphene obtained from HOPG grown by chemical vapour deposition (CVD) methods is shown in Fig. 3b. The random growth of the graphene layers via CVD results in the fractal-like structures, which can be compared to the more ordered edge structures obtain via mechanical fracturing. The chemical structure of these edges, as revealed by IR spectroscopy, is also very different as discussed below.

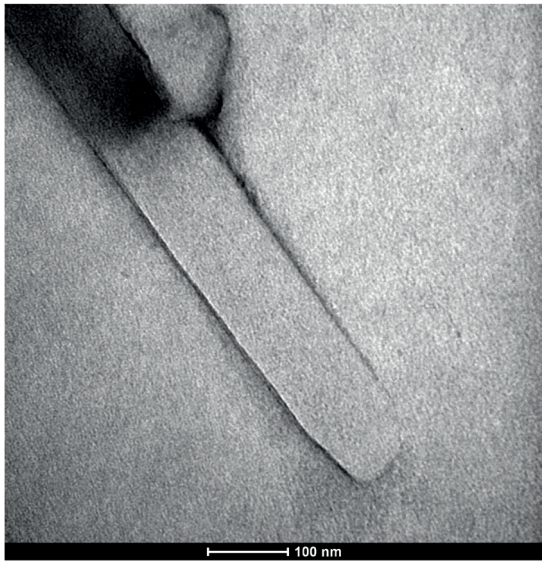
Surface enhanced Infrared absorption spectroscopy (SEIRAS) for graphene

The challenge of developing a sensitive but simple and accessible method for analysing the chemical structure of graphene nanoribbon edges is highlighted by a simple calculation of the number of carbon atoms available for reaction, $n_{C,reactive}$ in a 5 mg sample of graphene nanoribbons. Assuming a 50:50 mixture of zig zag and armchair edge structures, $n_{C,reactive} \cong 10^{-14}$ mol (a typical 5 mg sample might be suspended in a volume of 1 mL). The IR spectra of graphene nanoribbons shown in Fig. 4 are acquired using an IR microscope with a focused beam diameter of 20 μm. If a carbonyl group (with an absorption

(a)



(b)



(c)

Fig. 3. TEM images of graphene nanoribbons: (a) well exfoliated, flexible GNRs twist and fold to minimise surface area, (b) partially exfoliated GNR stack showing fraying GNRs and coiling of ends to minimise surface area, (c) thicker stacks of GNRs are rigid and lie flat on the TEM substrate, revealing straight edges. Imaged at an angle of 50 degrees to perpendicular.

coefficient of ≅ 10 m^2 mol^{-1})[22] is attached to each reactive carbon, and if the entire 5 mg sample is contained within the focused IR beam, then Beer's Law predicts an absorbance of ≅ 3 x10^{-4}, a value that is not far above the noise level of most FTIR spectrometers. This is a best-case scenario as concentrating 5 mg of sample into a 20 µm spot is difficult and we have assumed 100% functionalisation of the reactive carbon atoms.

With only two identical atoms in its unit cell, single-layer graphene has no IR active modes[23] and this confers an advantage to IR spectroscopy over Raman when analysing edge functional groups with vibrational spectroscopy – there is no strong basal plane mode that swamps the signal from the (much sparser) edge functional groups. The E_{2g} (around 1590 cm^{-1}) and A'_1 (around 1300 cm^{-1}) modes become weakly allowed when the symmetry of the graphene lattice is broken through interactions with a second graphene layer, or defects in the basal plane or edge effects are present.

Some method for enhancing the IR signal from the functionalised edge atoms is required and enhancement through resonance with the plasmon modes of adsorbed silver nanoparticles (for historical reasons this technique is known as Surface-Enhanced Infrared Absorption Spectroscopy, SEIRAS,[24] where "surface" indicates proximity of the sample to a nanostructured silver, or gold, surface) provides sufficient enhancement to enable clear detection of functional groups on graphene nanoribbon edges as illustrated in Fig.4. Plasmon enhancement is well-known in Raman spectroscopy where coupling to both the incident and scattered fields can produce enhancements sufficient to allow observation of Raman scattering from single molecules.[25–27] As IR is a "one-photon" process, only the incident field provides enhancement, but this is still sufficient to enhance the signal to a level where strong IR signals can be observed.

The enhancement generated in the SEIRAS technique can be seen in Fig. 4. The sample in this case is graphene exfoliated from HOPG by electrochemical methods. The bottom spectrum, from a 10 µm thick exfoliated graphene film on copper-coated silicon wafer, is dominated by CO_2 and H_2O bands at approx. 2340 cm^{-1} and 1600 cm^{-1} respectively, with the graphene signal barely discernible in the H_2O bands. Depositing silver nanoparticles with the graphene gives the spectrum shown in the upper panel, and the extent of enhancement is immediately obvious by comparison to the intensity of the CO_2 bands. The enhanced spectrum is remarkable for the appearance of a series of four medium intensity bands between 1700 cm^{-1} and 1900 cm^{-1}. These bands are known in condensed phase spectra of substituted monobenzenes, and are known as "benzene fingers".[28,29] As well as suggesting the edges of graphene sheets exfoliated from CVD-grown HOPG sheets are terminated by structures similar to mono- and disubstituted-benzenes, these spectra illustrate the ability of SEIRAS to provide high quality spectral information about the functional groups at the edges of graphene sheets.

This technique, then, solves the problem of characterisa-

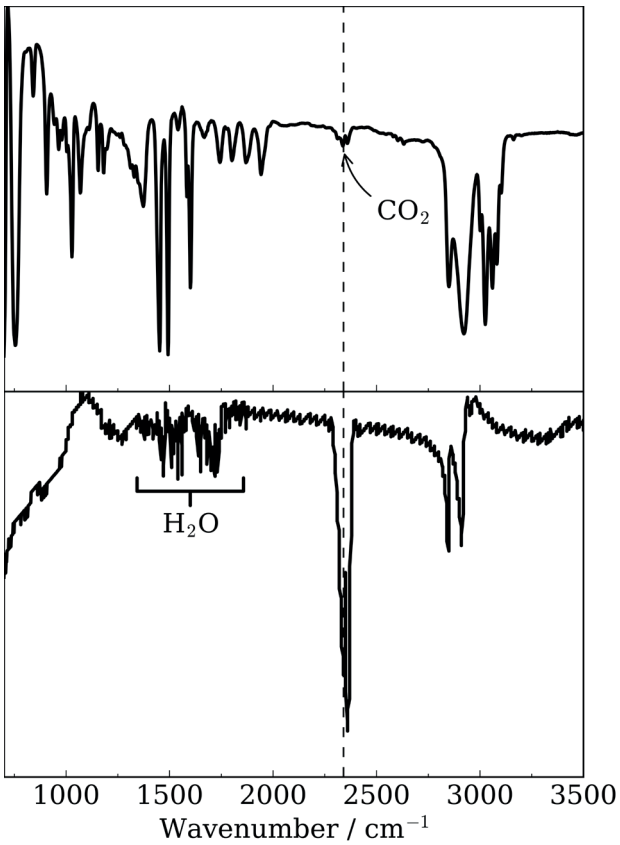


Fig. 4. FTIR spectra of graphene nanoribbons. Top: thin film of graphene nanoribbons, with intensity enhanced by addition of silver nanoparticles. Bottom: thick film of nanoribbons only.

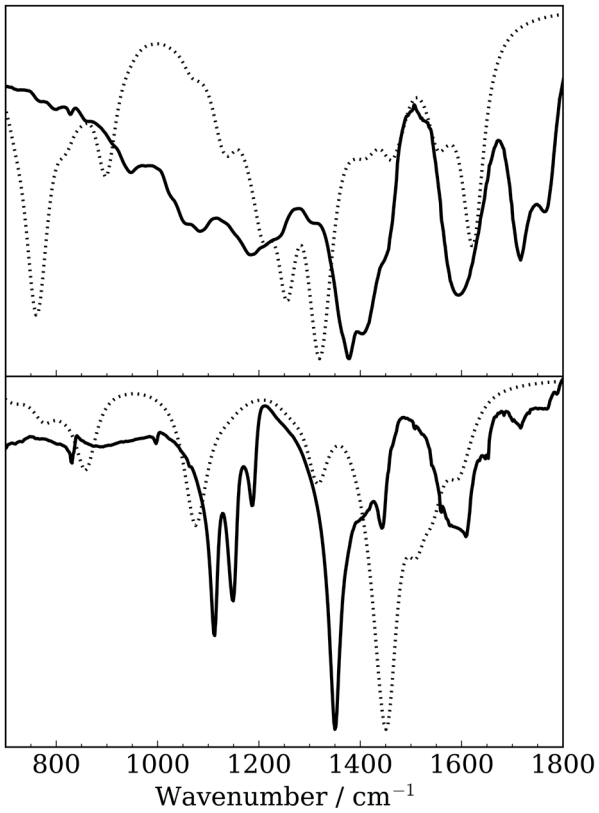


Fig. 5. FTIR spectra of graphene nanoribbons collected from *t* = 0 to *t* = 15 mins (top) and from *t* = 15 mins to *t* = 30 mins (bottom). Solid traces show experimental data, dotted lines show calculated spectra of graphene fragments.

tion of functional groups at the edges of nanoribbons despite the low (absolute) number of edge atoms. SEIRAS can be used to characterise the nanoribbons following the fracturing, but prior to functionalisation, and then to confirm attachment of a functional group following a reaction. Fig. 5 (solid lines) shows SEIRA spectra for nanoribbons collected for two sequential 15 minute periods of fracturing (the spectrum in the top panel was for nanoribbons collected first). Apart from collection time, the fracturing conditions are identical. Despite this, the SEIRA spectra appear very different. A possible explanation might be due to the mosaicity of the graphene planes (about the c-axis). Mosaicity results in the diamond knife of the microtome fracturing the graphene planes at different angles as cutting proceeds through the HOPG block; at one extreme the knife cuts along the zigzag direction while at the other extreme the knife cuts along the armchair direction. Most likely the ratio of zigzag and armchair nanoribbon edges changes as the knife cuts through the HOPG block and the changing proportion of edge type is reflected in the features observed in the SEIRA spectra. An alternative interpretation is that the top spectrum is merely a broadened version of the bottom spectrum. This might suggest that the sample heterogeneity changes as the knife cuts further into the HOPG block, and the sharper features in the lower panel arise from a more homogeneous sample. Although high level *ab initio* studies of graphene nanoribbons are prohibitively expensive, useful results can be obtained using small polyaromatic hydrocarbons that are often used as models for graphene fragments. The computed IR spectra of fragments with zigzag and armchair edges are shown in Fig. 5 (dotted lines) and the computed spectra also show clear differences between edge type. We are currently investigating methods for computing the IR spectra of graphene nanoribbons with more realistic numbers of atoms and various distributions of edge types.

Edge structure from polarised Raman spectroscopy

Although SEIRAS provides very useful information on functional groups, there is no obvious relationship between the number and intensity of bands in the IR spectra and the structure at the edge, by which, we mean zigzag or armchair. Raman spectroscopy has long been recognised as a useful technique for characterising the structure and nature of defects in carbon nanomaterials, such as determining the diameter of carbon nanotubes from the frequency of the radial breathing mode.[30–34] Defect-free, single-layer graphene exhibits a single Raman active mode, the E_{2g} mode, more commonly known as the G-mode. Defects in the basal plane, or scattering from the graphene sheet edges activates the A'_1 or D-mode (D for disorder).[35,36]

Raman scattering, as an example of inelastic light scattering, is usually presented in the language of solid-state physics in the graphene literature.[37] A basic assumption is the graphene lattice has an infinite extent and edge effects can be ignored, and this is certainly a good approximation for single-layer graphene sheets that can have dimensions on the order of centimetres. For nanoribbons edge effects must be included and the theoretical convenience of an infinite periodic lattice is lost when edge effects are considered.

Both energy conservation and momentum ($\vec{p} = \hbar\vec{k}$) conservation must be considered for scattering from lattices. For elastic scattering the equations that describe these conditions are:

$$\omega = \omega_0$$

$$\vec{k} - \vec{k}_0 = \vec{G}$$

where ω_0 and k_0 are the frequency and wavevector of the incident radiation, ω and $\vec{k}$ are the frequency and wavevector of the scattered radiation and $\vec{G}$ is the reciprocal lattice vector (these equations apply to any elastic radiation scattering process, such as elastic scattering of X-rays from lattices). Inelastic scattering occurs when a time-dependent process, such as oscillation of a lattice phonon, occurs during scattering of the photon. The analogous equations are then:

$$\omega = \omega_0 \pm \omega_{\text{phonon}}(\vec{q})$$

$$\vec{k} - \vec{k}_0 \mp \vec{q} = \vec{G}$$

where $\omega_{\text{phonon}}(\vec{q})$ is the frequency of the lattice vibration that is generating the Raman scattering, and $\vec{q}$ is the reciprocal space vector of the phonon. It is possible to associate a quasi-momentum with $\vec{q}$given by $\hbar\vec{q}$. The first equation is found in any introductory text on Raman spectroscopy, and it describes the frequency dependence of Stokes and Anti-Stokes Raman scattering. It is useful to note that, due to graphene's zero band gap, Raman scattering from graphene always satisfies the *electronic* resonance condition that enhances scattering intensities in resonant Raman spectroscopy. The second equation is perhaps less familiar to chemists; its meaning can be illustrated by inserting some relevant numerical values. For visible light (λ = 500 nm), the incident photon wavevector is $\vec{k}_0 \cong 10^5$ cm^{-1}. The maximum value of $\vec{k}$ occurs for back-scattering and then $\vec{k} = -\vec{k}_0$. By convention the initial value of the reciprocal lattice vector is set to $\vec{G}$ = 0 and so momentum conservation requires:

$$\vec{q} = \pm 2\vec{k}_0 \cong 2 \times 10^5 \text{ cm}^{-1}$$

To put this value into perspective, consider the maximum value for the phonon wavevector, given by $\omega_{\text{phonon}} = \pi/a \cong 10^8$ cm^{-1} (where a = 1.42 Åis the graphene unit cell length). On this scale $2\vec{k}_0$ is insignificant and to a good approximation inelastic scattering with visible light occurs at $\vec{q} \approx 0$. The simple interpretation is that Raman scattering with visible light occurs at $\vec{q} \approx 0$ where atomic displacements in all unit cells have the same phase.

The reciprocal space description of inelastic scattering can be used to explain the activation of the D-mode in graphene, via a process known as double-resonance scattering.[35,36,38,39] As mentioned above, Raman scattering in graphene is always resonantly enhanced by virtue of the zero band gap in graphene. Fig. 6 shows the Dirac cones for the valence and conduction bands; note that any photon will have sufficient energy to connect states in the

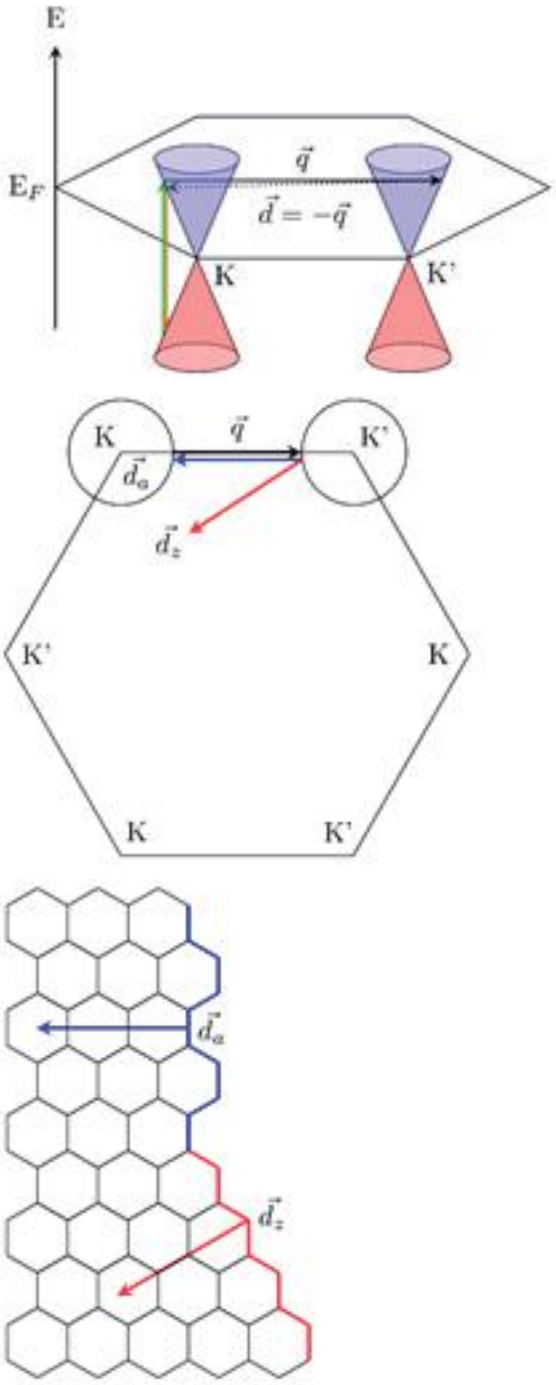


Fig. 6. Top: Dirac cones showing valence (red) and conduction (blue) bands in reciprocal space. Middle: a projection of the top figure showing more clearly the orientation of reciprocal space vectors associated with the armchair ($\vec{d}_a$) and zigzag ($\vec{d}_z$) edges. Bottom: the armchair ($\vec{d}_a$) and zigzag ($\vec{d}_z$) edges represented on the real space graphene lattice.

valence and conduction bands. Fig. 6 also illustrates the 6 equivalent points in reciprocal space that arise from the symmetry of the graphene lattice. Double-resonance occurs when photon absorption creates an electron-hole pair within one Dirac cone (at K), and inelastic scattering transfers the system to an equivalent Dirac cone (at K'), with momentum transfer due to $\vec{q}$. *Elastic* scattering from a defect (*i.e.* the graphene edge) transfers the system back to the Dirac cone at K, where electron-hole recombination occurs and the scattered photon is created. A key point is that the lattice momenta of zigzag and armchair edges have different directions and only armchair edges return the electron and hole to the Dirac cone at K *via* back-scattering to allow recombination of the electron and hole and subsequent photo emission. As a result, only armchair edges should exhibit Raman intensity for the D-mode.

Thus, it should be possible by Raman scattering to determine the edge type of a graphene sheet. In practice there are several other factors, such as the unknown relative orientation of the laser polarisation to the edge, that prevent a simple assignment of edge type from D-mode intensity. The polarisation dependence of scattering from the graphene edge can be used to identify edge type. The definition of a pure edge requires a length scale, determined by the time-scale of the Raman scattering (given by $1/\omega_D$ = 1/1350 $cm^{-1} \cong 3$ fs) and the velocity of the electron-hole pair $\upsilon \cong 1.1 \times 10^6$ ms^{-1}, then υ/ω_D = 4 nm. This places a fundamental limit in terms of spatial resolution on the ability of Raman scattering to determine the edge type. Keep in mind that the incident wavelength is typically λ = 500 nm; then the far-field optical diffraction limit of $\approx \lambda/2$ places a more practical restriction of the spatial resolution obtainable with Raman scattering. The double-resonance mechanism above predicts that zigzag edges should have zero D-band intensity; in practice this means zigzag edge segments of lengths of several hundred nanometers are required to completely extinguish the D-band intensity. Studies of the polarisation dependence reveal the D-band intensity does not reach the limit for a pure zigzag edge,[20] which suggests that "pure" edges are difficult to achieve in mechanically cleaved graphene (via the scotch tape method) over the length scale of a few hundred nanometers. This is not particularly surprising, since HR-TEM studies often show both zigzag and armchair edges even on a length scale of a few nanometers.[7] But as far as the information that the Raman spectrum does provide is concerned, it is possibly a case of "getting what is needed rather than what is wanted" (with apologies to M Jagger and K Richards). The D-mode intensity reports the "average" edge type over the diameter of the laser spot. As our nanoribbons have lengths which are comparable to the laser spot diameter, the D-mode intensity effectively corresponds to the fraction of zigzag and armchair edges for a given nanoribbon sample. This information helps with the first challenge mentioned above because reactions can be designed to take into account the fraction of available armchair or zigzag sites (noting that zigzag sites have a preference for radical chemistry, whereas armchair edges have a preference for addition reactions).

The reciprocal space description starts with a relatively simple description of scattering from a "perfect" lattice and adds increasing sophistication to describe scattering from lattices with defects. There is another approach that starts with a description of Raman scattering in small "molecular" fragments[40–43] (where small is defined relative to the length scale described above) and then considers the graphene lattice to be a patchwork of these fragments. This approach is ideal for describing the Raman scattering from graphene edges and can be described as a "molecu-

lar" approach to Raman scattering from graphene. One advantage of this approach is the Raman spectrum of any edge structure can be calculated. This also presents some computational challenges as even the smallest ribbons contain thousands of carbon atoms, but a very effective "molecular" method has been developed that takes advantage of the fact that only carbon atoms constitute the lattice. By using a simple Hückel approximation (aka the tight-binding approximation when applied to extended lattices), the Raman response of the graphene lattice is expressed using a Raman bond polarisability[40] which can be directly linked to properties such as a bond order matrix that describes the electronic structure. The Raman bond polarisability describes the contribution of a single C-C bond to the Raman scattering intensity. The structure of the lattice and the bond displacements for a vibrational mode (phonon) of interest then determine the Raman intensity for the vibrational mode, directly linked to the electronic structure. It should be possible to describe the IR response of a graphene fragment of arbitrary size and shape using this approach and we are currently investigating how to adapt the results for the Raman response to give the corresponding IR expressions.

Summary

Vibrational spectroscopy is a useful and convenient tool for investigating the structure and chemistry of graphene nanoribbons. IR and Raman spectroscopy provide complementary information, with IR spectroscopy reporting on the nature of the functional groups at the edges whereas Raman spectroscopy can be used to determine the geometry of the edge. Concepts from condensed matter physics and molecular spectroscopy can be used to provide a description of Raman scattering in graphene nanoribbons, with the condensed matter approach most useful for perfect graphene lattices, and the molecular approach most useful at highly disordered graphene edges.

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Feature Series

Some Unremembered Chemists

A series of articles 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.

Carl Friedrich Accum (1769-1838)

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Friedrich Accum is one of those chemists of whom it has been said '[he] is representative of a chemist who is largely forgotten these days but nevertheless contributed to important changes in our society […]'.[1] He was an apothecary who then established a chemicals and equipment business in early 19th century London where he provided popular practical and theoretical instruction in chemistry. He became interested in gas lighting and was intimately involved with the design of London's first gasworks. Most importantly, Accum was the first to publicise the need for protecting the quality of foodstuffs with his popular book *The Adulterations of Foods and Culinary Poisons*,[2] which sold 1000 copies within a month of its 1820 publication. It was reprinted and ran to a second edition in the same year, with a third the following year. It was published in Philadelphia (1820), and it had a German translation published in Leipzig in 1822.

Friedrich Christian Accum was born on March 29, 1769 in Bückeburg, a former capital of the tiny principality of Schaumburg-Lippe in Lower Saxony some 30 km southwest of Hanover in Germany. His father, Markus Herz, was of Jewish descent born in nearby Vlotho on the Weser River and had served as a carbineer in Count Wilhelm von Shaumburg-Lippe's infantry. In 1755 Markus converted from Judaism to Protestant Christianity changing his name to Christian Accum (*Accum* or *Akum*: non-Jewish). Within a few months of his conversion Christian married Judith Susanne Marthe Bert La Motte, the daughter of a hat maker whose Huguenot family had also suffered persecution, and with whose hand came with an ancestral home at 141 School Street in Bückeburg.[3,4] Accum senior used the home as his business premises as a merchant and soap boiler and became moderately prosperous. The couple had seven children born in that home with Friedrich the sixth. Sadly, only he, his elder brother and a sister (Wilhelmina) survived to adulthood. Christian Accum died in 1772, soon after his last child was born and when Friedrich was merely three-years old. It was his older brother Philip who took over the family business and perhaps instilled an interest in chemistry in his sibling.

Fredrich Accum in 1791 – a painting by brother-in-law Wilhelm Strack, husband of his sole surviving sister, Wilhelmina.

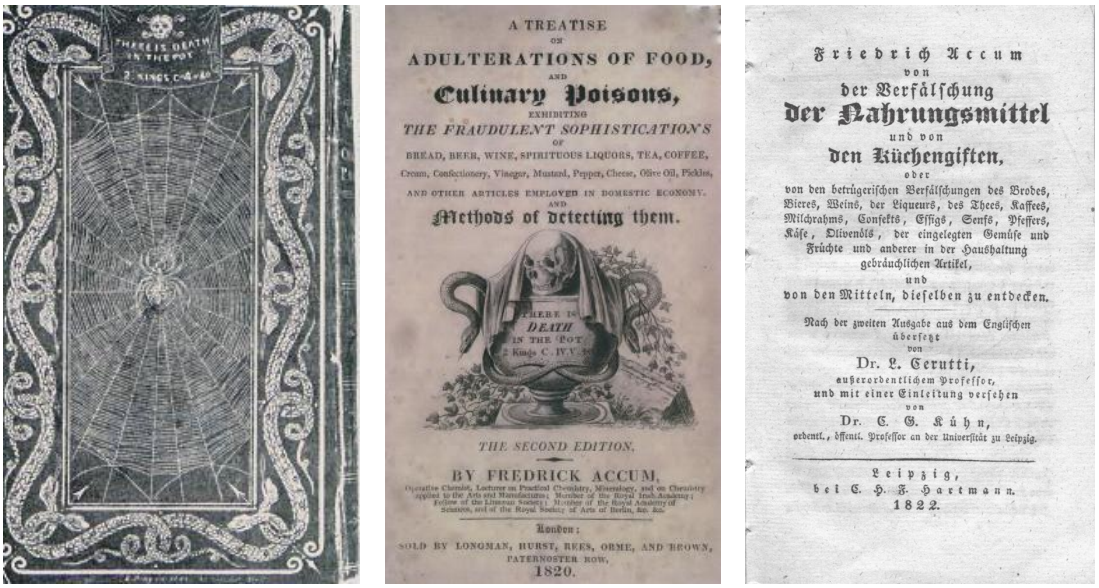


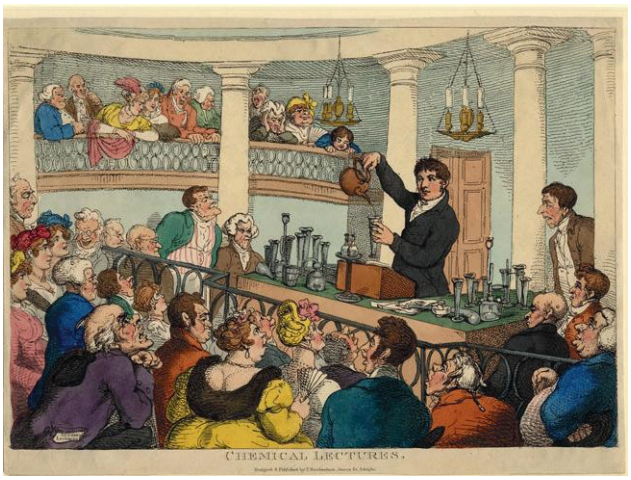
Figure 1. Left: The cover of the 1st edition of Accum's popular book *The Adulterations of Foods and Culinary Poisons* (1820) (see ref. 2) illustrated by a spider's web, centre: *Death in the Pot* frontispiece from the 2nd edition, 1820, that emphasises the content; right frontispiece from the 1822 German translation.

Friedrich attended the Bückeburg Gymnasium. It had a good reputation as several of its headmasters subsequently moved to academic professorships. The curriculum was of the classical type and young Friedrich received essentially no scientific education until after he had graduated. Shortly afterwards he became associated with the Brande family, who were apothecaries to George III, King of Hanover and Great Britain, and family friends. He trained as an apothecary prior to moving to London in 1793 where he was an assistant at the Brande pharmacy in Arlington Street (off Piccadilly and close to Green Park). He was classified as a chemist in the register of the Alien Office. The pharmacy proprietor was the father of noted chemist William Thomas Brande, but it was run by his elder brother Everard. Accum remained at the pharmacy until about the turn of the century gaining knowledge and friends, one of whom was the gifted chemist William Nicholson. He assisted Nicholson with his writings becoming very useful. Accum also became one of the most frequent early contributors to the *Journal of Natural Philosophy*, subsequently better known as *Nicholson's Journal*, which first appeared in 1797. From 1798 to 1803 Fredrick had seven contributions on a variety of topics as appropriately described by Cole.[5] However, his second paper[6] *An attempt to discover the genuineness and purity of drugs and medicinal preparations* marked his first foray into erroneous analysis and misrepresentation, and the beginning of his food technology and analytical expertise.[7] The September and October issues of Nicholson's 1799 Journal carried a translation of Achard's report on his sugar production from local German sugar beet. Accum took it upon himself to obtain a sample for Nicholson whose analyses led him to the conclusion that there was little difference between the beet sugar and loaf sugar. This sugar beet sample was the first to be admitted to England and marked the beginning of importation that reached 70,000 tons in 1900.[3]

During the 1790s Accum anglicised his given name from Friedrich to Fredrick. Fredrick Accum married Mary Ann Simpson of London on May 10, 1798. They had eight children but only two survived birth or infancy, namely their eldest child Flora Eliza (b. May 17, 1799) and Friedrich Ernst (b. April 3, 1801).[4] In 1800 they moved house from 17 Haymarket to what became their home of 20 years at 11 Old Compton Street, off Tottenham Court Road and parallel to Shaftesbury Avenue. It was there that Fredrick set up his laboratory and business for the analysis and examination of commercial products, and supply of chemicals and apparatus. Once on a firm footing he expanded by providing instruction in the theory and practice of chemistry. His activities at Old Compton Street were described on his business card as:[5]

Mr Accum acquaints the Patrons and Amateurs of Chemistry that he continues to give private Courses of Lectures on operative and Philosophical Chemistry, Practical Pharmacy and the Arts of Analysis, as well as to take resident Pupils in his House and that he keeps constantly on sale in as pure a state as possible all the Re-Agents and Articles of research made use of in Experimental Chemistry, together with a Complete Collection of Chemical Apparatus and Instruments calculated to Suit the convenience of Different Purchasers. Philosophical Gentlemen residing in the Country or Abroad desirous of becoming purchasers of large or small Collections of Chemical Preparations, etc., may have explanatory Lists previously made out to the Expense they are willing to incur, and Chemical catalogues may be had at the laboratory, Old Compton Street, Soho, London.

For many years, Accum's establishment was the only one to offer lectures on the theory of chemistry, with practical training in a laboratory. Amateurs were welcome to perform simple experiments on site. His teachings attracted various prominent students. These included Lord Palmerston who later became England's Prime Minister, and then the first American scientists of whom Benjamin Silliman became Professor of Chemistry at Yale College, giving the first chemistry lectures there in 1804 and furnishing his laboratory with equipment from Accum. Another was William Dandridge Peck, a botanist and subsequent Professor at Harvard.

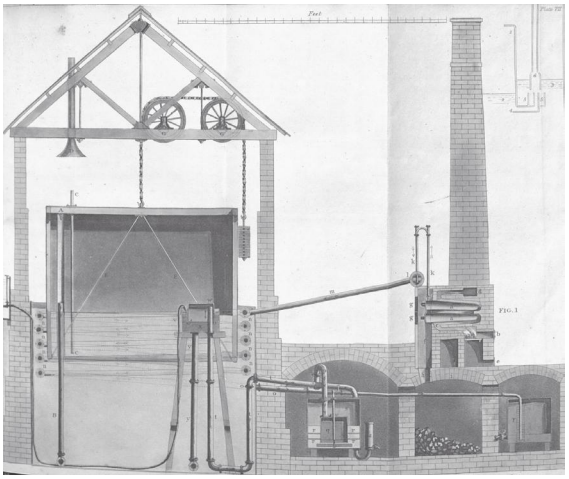


Left: Lecture Hall of the Surrey Institution, illustrated by Thomas Rowlandson and Augustus Charles Pugin 1808 (Wikimedia). Right: *Chemical Lectures*, contemporary caricature by Thomas Rowlandson, 1810. The inscription *Surrey Institution* is on the door frame and the title *Accum's Lectures* appear on the dust jacket of the book in the pocket of the older man sitting lower left. The cartoon has Accum lecturing and (on his right) R. Ackermann (publisher and Accum's and Rowlandson's friend standing), and Sir J. Hippisley (Manager-Royal Institution) and (an on his left) Count Rumford (sitting with his back to the audience), and (possibly) Sir Humphry Davy standing between the columns (see ref. 9).

In 1801 Accum was appointed as *Assistant Chemical Operator* at the Royal Institution (RI) when Humphrey Davy was Director of the Laboratory. His skill and ability in constructing apparatus had become known before this appointment and it gained further recognition from those who attended the Institution lectures. The appointment at the RI lasted for two years as Accum resigned shortly after his supporter, Count Rumford, left England for Paris to marry Lavoisier's widow.[5] In that same year of 1803 and before he left the RI, Accum published his two volume *System of Theoretical and Practical Chemistry*.[8] Its importance lies in the fact that this was the first textbook of general chemistry to be written in English based on Lavoisier's principles. It was much expanded and improved for the 1807 second edition. In the City of London, it was increasingly felt that there was room for an establishment, separate from the RI, which would ally more closely its commercial and manufacturing concerns. By 1808 the Surrey Institution had been established for this purpose. It was located in the former home (1789-1806) of the Leverian Museum at 3 Blackfriars Road, on the south side of Blackfriars Bridge, and remained there until its closure in 1823. Its lecture theatre was known as the Rotunda. Here, Fredrick Accum initiated the chemistry programme with the Institution's second course, his January 1809 lectures on Chemistry and Mineralogy. This was followed by Chemistry of the Arts (1811) and Chemical Phenomena of Nature and Art (1812). He returned to provide the chemistry course in 1819 (Chemistry Applied to the Arts and Manufacture) and 1820 (Chemical Phenomena in Nature and Art). The Rotunda was caricatured in 1808 by Thomas Rowlandson and Charles Pugin, and with Accum lecturing there in 1810 by Rowlandson.[9] There was debate on the identity of this lecturer with some[3,5] suggesting that it could be Davy. However, the history of the Surrey Institution by Kurzer[9] makes it clear that Davy never lectured there and that the cartoon is of Accum with dignitaries from the RI in attendance and that it is from 1810.

The Surrey Institution became a significant centre in the intellectual life of London, with its lecture theatre one of the most elegant institution rooms in the city. It contained two galleries within its diameter of about 12 metres, with the ground floor holding nine rows of seats that gradually rose above each other. Seating was for up to 500 persons in total. The courses on chemistry were one of the mainstays of the Institution programme. In those days chemistry was regarded as the foremost of all the sciences and an essential adjunct to all the others by providing rational explanations of familiar and obscure phenomena. It was of the utmost importance to manufacture and commerce, and its relevance to medicine and pharmacy was equally obvious. Thus, a course on chemistry was an invariable component of the season's activity at the Surrey Institution. It was the most systematic course and generally the longest, with greatest content of all the programmes offered. That Accum gave the first courses stemmed from his expertise in the analysis of ores and minerals, the detection of adulteration of drugs and medicinals and his experience in conducting courses in chemistry in his own laboratory.

Accum's lectures on experimental chemistry and analytical mineralogy actually commenced at the Chemical Laboratory, Compton Street, Soho, on October 18, 1808. They comprised the practical operations of the scientific laboratory, general rules to be observed in the performance of experiments, and experimental elucidations in the science of Chemical Philosophy and its application to the useful arts. Accum's remit was to provide instruction *for the purpose of initiating into the principles of chemical philosophy those who possess no previous knowledge of it*. While these principles remained the core of his teaching, he changed the emphasis from year to year, widening the coverage of the subject and sustaining the interest of a regular audience. His successive courses highlighted the relationship of chemistry with mineralogy, metallurgy, natural phenomena, and application to the manufacture and the arts.[10] To assist his audience, Accum issued a booklet listing the *Heads of Topics* of his 17 lectures. His first course dealt with minerals, ores, metals, and their analysis. In 1810 he published a more elaborate Companion to his subsequent lecture courses, providing a permanent record of his chemical teaching.



Left: A Peep at the Gas-lights in Pall Mall, a humorous caricature of reactions to the installation of the new invention of gas-burning street lighting on Pall Mall, London. Engraved by Thomas Rowlandson (1809) after a drawing by Woodward. Right: The first London gasworks, 1814. Plate from Accum's *A Practical Treatise on Gas Light* (1815). The retorts are set transversely, directly under the chimney; the gasometer is on the left (Wikimedia).

It was during the 1800-1810 period that Accum became fascinated with coal gas production.[5,11] He appears to have attended the first demonstrations of gas lighting in London by the German technologist, H.A. Winsor. Winsor illuminated the Lyceum Theatre during the 1803-1804 winter and then gained a patent for illuminating gas production in 1804. He gleaned promotors for a company to generate and use coal gas. Winsor went on to demonstrate that gas lighting was practical after he had purchased a home on Pall Mall. He piped gas from his home to street lights that he had erected in the Mall to provide the first public street lighting[12] on January 28, 1807. By then, Accum had shown interest in gas production and had been approached by the promoters of Winsor's proposed company. He conducted a long series of experiments to provide supporting scientific evidence. These and the data from them formed the basis of his chemical expert testimony before the Commons and then the Lords Committees in 1809.[11] Accum paid particular attention to the by-products of gas manufacture and provided samples of them. Interestingly, theses samples were held at the Old Ashmolean Museum in Oxford in 1938 and, as Browne states,[4] it would be very interesting to have that labelled *Highly Rectified Essential Oil* analysed to see how closely it compares to Faraday's first sample of benzene discovered in 1825, 16 years later.

The Commons and Lords committees finally gave Winsor the needed approval for a Chartered Gas-Light and Coke Company in 1810, but it stipulated that £100,000 had to be raised before the company could be given its charter. This happened in 1812 and the Gas Light and Coke Company became incorporated with Accum as its chemist and Board member. The charter states that the company was formed to provide *inflammable air for the lighting of the streets, oil, tar, pitch, asphaltum, ammoniacal liqor, and essential oil from coal and for other purposes relating thereto.* It was Accum who planned and oversaw the construction of the gas plant on Curtain Road, the first such plant in the history of gaslight. On December 31, 1813 Westminster Bridge was lit by gas and in the City of London gas lighting began on Christmas Day in 1814.[13] Accum resigned from the company in November 1813,[5] though he went on to install a number of other plants. He was the recognised expert and had some 15-year association with coal-gas technology. His publications on the subject provided all the detail needed to build a plant, even to the extent (noted in his book) of giving the cost of having Accum install the plant (1st edn.: £1940-11-0).[14,15] The rapid growth of gas works in London led to sewer and river pollution from discharge of the sulfur and tar by-products. Accum demanded legal measures to prevent the discharge of these materials but his criticisms met with little support; the various gas explosions that happened from mismanagement had more impact.[1]

Fredrick Accum suffered financially following the end of the Napoleonic wars in 1814. Nevertheless, he was much in demand as an expert witness as illustrated in his role for the Severn, King & Co., sugar refiners.[11] There was a fire that almost destroyed the refinery in 1819, some three months after oil heating was installed to boil the sugar. This heating led to less caramelisation when the oil was heated to 180-200°C. The Imperial Insurance Co., refused to meet the company claim because, in its view, the traditional open fire was safer. Accum provided chemical evidence and testified that had there been an explosion in the oil gas in the fill house, as claimed by the defendants, the noise of the explosion would have been heard throughout London. Michael Faraday appeared for the insurers but the experiments he had conducted and described as evidence were shown not to comply with the actual conditions. The jury found in favour of the company and Faraday refused to serve as an expert witness ever again.

In addition to operating his supply house, teaching, industrial gas working, and being a prolific author, Accum also provided various preparation for industrial purposes. Of these his compound for welding iron is notable.[11] Here he found combining flowers of sulfur (1 ounce) with sal ammoniac (NH_4Cl, 2 ounces) and iron dust (16 ounces) gave the best mix. For welding, 1 part of this mixture was to be ground in a mortar with 20 parts of fine iron filings and water added to give a paste of good consistency. The paste was then smeared on the broken joint. Chemically, iron sulfide is produced and generates sufficient heat to weld the broken joint; it was extensively used in its time. Not only this, but he also offered public service. The small town of Thetford north-east of Cambridge engaged him to analyse their mineral spring and comment on the merits of its waters, a topic which he had studied from 1808 and published extensively on. This he did, providing a most satisfactory report on the chemical and medicinal properties of the water that led to him being commissioned to provide plans for a bathing establishment. It opened in 1820, a year after his book *Guide to the Chalybeate Spring of Thetford*[16] was published; it was 'for the convenience of the public'.

Despite his significant reputation, Fredrick Accum went from saint to sinner within just a few months of the publication of his most famous work *The Adulterations of Foods and Culinary Poisons* (see Fig.1).[2] As mentioned earlier, in 1798 he published an article in *Nicholson's Journal* on drug and medicinal purity[6] that formally marked the first chemical attempt to raise matters of drug (and food) safety by drawing attention to the prevalence of adulteration and the dexterity with which it was practised. It was the continuation of this as occurred in foods that led to his downfall in England and his subsequent return to Germany. In January 1820 his book on food adulteration appeared and gained immediate popular acclaim.[2] It is a classic, in that it was the first such book to deal with the subject and the difficult problems of its subject matter. It was from his experiences, beginning in 1797, as an analyst and food technologist that gave him a knowledge of the subject far exceeding that of any other chemist of the time. He exposed practices that led to enormous comment and aroused feelings among those who were involved in adulteration. It has been claimed[11] that the text is probably the most extensively reviewed book on chemistry ever written. In his essay, Browne provides two and a half pages of small print reproductions

of reviews, and these are only from the first edition of the book, which also drew attention in the US. Accum's downfall stems from his listing at the end of each chapter the names of those who had been guilty of adulteration. He made the comment that *the man who robs a fellow subject of a few shillings on the highway is sentenced to death; while he who distributes a slow poison to a whole community escapes unpunished*. However, he did state in his *Preface* that he found naming people and companies an *invidious office* and a *painful duty*. Moreover, he only published the names of those who had been authenticated in Parliamentary documents and other records.[17] His book is written in a straight forward manner with description of simple analytical tests provided for is readers. It was a time when the move to more central industrial manufacture and the availability of additives (chemicals) were increasingly employed. The proliferation of newly discovered chemicals and the absence of laws controlling their usage meant that unscrupulous merchants could adulterate foods and boost their profits at the expense of public health.

The book's content alternates between harmless forgeries such as the mixing of dried pea grounds in coffee and the use of markedly more dangerous additives.[1] As an example, the high lead content of Spanish olive oil came from lead containers used to clear the oil, so Accum recommended the use of oil from countries where this was not the practice. Vinegar was often contaminated by addition of sulfuric acid to increase the acidity. Many green sweets sold by merchants on the streets of London were adulterated with sap green (from buckthorn berries) that have a high copper content. James Millar in a letter dated September 22, 1819 to the *Philosophical Magazine* drew attention to a charwoman whose green tea was adulterated with copper as proved by Accum's analyses;[18] this is described in detail by Cole.[5] Particular attention was paid to beers. English beer was sometimes contaminated with molasses, honey, vitriol, pepper and occasionally opium. One of the worst contaminations was the addition of fish berries (from the Menispermaceae family) to port as they contain picrotoxin. His analyses were supported with evidence from the quantity and time of imports and the consequential variation in the cost of the berries. Accum's book cover and its frontispiece, illustrated as shown in Fig.1, was clearly provoking. He designed most of his book covers himself, none more imaginative than his book on food adulteration. The cover depicts a spider web with the spider hovering over its victim, the whole encased by 12 serpents with forked tongues and intertwined tails, while the frontispiece carries a pot holding a death's head with the inscription: *There is death in the pot*, a name by which the book became known.

Noel Coley in his article[19] *The Fight against Food Adulteration* comments on Accum's work stating that by the early 19th century "… tea and coffee drinking had become popular in England but, being imported, both were expensive and as the fashion spread, cheaper varieties were needed for sale to the masses". Many of these were not genuine tea and coffee but were made to look like the real thing by chemical treatment. Spent tea leaves and coffee grounds could be bought for a few pence per pound from London hotels and coffee shops. The used tea leaves were boiled with copperas (ferrous sulfate) and sheep's dung, then coloured with Prussian blue (ferric ferrocyanide), verdigris (basic copper acetate), logwood, tannin or carbon black, before being resold. Some varieties of cheap teas contained, or were made entirely from, the dried leaves of other plants. Exhausted coffee grounds were treated in a similar way, adulterated with other roasted beans, sand and/or gravel, and mixed with chicory, the dried root of wild endive, a plant of the dandelion family. Chicory itself was sometimes adulterated with roasted carrots or turnips and the dark brown coffee colour was achieved by using 'black jack' (burnt sugar).

It is not surprising, therefore, that Accum's 1820 publication drew much praise from the public as evidenced by the appearance of a reprint and the second edition in that same year. But it also drew its critics, especially from those practicing adulteration. Subsequent events led to Accum being discredited. A few months after publication of the *Adulteration of Food* book one of the library staff at the RI, assistant librarian Mr Sturt, took to the managers a complaint against Accum claiming that he had torn pages out of the books he had been reading. Although there have been many commentaries of this and subsequent incidents,[1,4,5,7,11] that of Cole[5] reproduces various minutes of the Managers' Meetings of the RI. From these it is evident that Sturt saw Accum in the library and that pages of books and journals were removed. This was and still is done by library users today, but in the early 19th century it was more common than now as scrap paper was not as readily available then. Sturt was asked to drill a hole in a partition so as to watch Accum more closely. This he did and on the evening of December 20, 1820, he watched him closely for some two hours. He saw Accum remove pages from *Nicholson's Journal* and an account was passed to the RI secretary the next morning. This led to Mr Birnie, the sitting magistrate at Bow Street, issuing a warrant to search Accum's house. Leaves from RI books were found and Accum was prosecuted and brought to trial. After hearing all the evidence, the magistrate who tried the case delivered the opinion that *however valuable the books might be from which the leaves found at Mr Accum's house had been taken, the leaves separated from them were only waste paper.* If they had weighed one pound he would have committed Mr Accum for the value of a pound of waste paper, but as they did not he discharged him.

This was not the end of the matter as the managers of the RI chose to have a Bill of Indictment drawn up against Accum for the offence at the next Westminster Sessions. A supporter of Accum (likely Anthony Carlisle[5]) wrote to Earl Spencer, the President of the RI seeking the proceedings to be stopped. This did not happen and trial was set for April Sessions. Accum and his two sureties appeared in court and were set recognisances of £200 and £100, respectively. When the April Sessions came and the Accum trial was called, Accum could not be found; he had returned to Germany, his reputation in England in shreds. The bail was forfeited when it became obvious he was

not to return to England. Whether the enemies that Fredrick Accum made from his food adulteration book were behind the forceful RI indictment or not remains unclear, but seems likely. The remainder of Accum's career was worked out teaching in Germany.

Left: Fredrick Accum from the *European Magazine* (1820) (engraving by James Thomson; Wikimedia). Right: Fredrick Accum, ca. 1820 by Samuel Drummond (Wikimedia).

At time of his return to Germany in 1821, Accum was 52 years old and a widower who had spent close on 30 years in England. On his return he went to the town of Athaldensleben, near Magdeburg, where his friend, Johann Nathusius, had established a factory for tobacco production in 1787 and a factory for sugar production from sugar beet between 1813 and 1816. Nathusius had an extensive library which Accum used, but he also enjoyed his enforced freedom and the hospitality it offered. After some time a joint post as Professor of Technical Chemistry and Mineralogy at the Royal Industrial Institute (the Gewerbeinstitut) and Professor of Physics, Chemistry, and Mineralogy at the Royal Academy of Construction (the Bauakademie) was made, and in 1822 Fredrick accepted it. The latter academy saw the publication *Physiche und chemische Beschaffenheit der Baumäterialen, deren Wahl, Verhalten und zweckmassige Anwendung* that appeared in two volumes published in Berlin in 1826. It was the only publication written in German by Accum and the last of his offerings.

A few years after settling in Berlin, Accum had a house built at 16 Marienstrasse (later No. 21) where he lived until his death. He suffered from gout during the last years of his life and, after taking a turn for the worse in June 1838, he died aged 69 years on the 28th of that month. His wife Mary Ann had died in London on March 1, 1816.

Accum's publications were extensive and include numerous papers and some 16 books.[1] Of the books not discussed above, his *Chemical Amusements, a Series of Curious and Instructive Experiments in Chemistry Which Are easily Performed and Unattended by Danger*, *A Treatise On The Art Of Making Wine From Native Fruits*, *A Treatise On The Art Of Brewing*, *Culinary Chemistry*, and *Elements of Crystallography: After the Method of Hauy*, illustrate the breadth and depth of his writings.

Some 12 years after Accum's death, Sir Charles Wood, the British Chancellor of the Exchequer attested that there was no chemical test to prove that coffee could be adulterated with chicory. However, Arthur Hill Hassall, a medical practitioner, microscopist and chemist, knew the statement to be untrue. He bought samples of coffees in London and examined them microscopically showing that the chicory in the coffee was easily distinguishable. He took it upon himself to prove that such adulteration was common. Between 1851 and 1854, as analyst for the new Analytical Sanitary Commission, he assessed some 2500 food and drink samples (microscopically and by chemical analysis) and showed the presence of alum in bread, iron, lead or mercury in cayenne pepper, copper salts in bottled fruits and pickles, iron oxide in sauces, and that there was 1 part of tumeric powder in 547 parts of mustard. These studies appeared in *The Lancet* as anonymous reports from the commission, only to be subsequently published by Hassall under his own name.[20] This accelerated the moves for reform with *The Times* of July 24, 1855 stating in its *Editorial*:

> *Some 30 years ago the British Public was frightened by the cry of 'Death in the Pot;' but we might now, it seems, re-echo the alarm with greater force than ever. Death is not only in the pot, it is everywhere; not only in our food and drink, but in the very medicines that should cure our diseases. The matter is now under investigation before a Parliamentary Committee, and it has been shown by evidence of the most convincing kind that of the articles of daily use and first necessity a very great portion is subjected to foul and systematic adulteration. But how, the reader may ask, has the discovery at this particular period been made or certified? Partly through material improvements effected in the means of detection, but mainly by the skill and perseverance of Dr Hassall, who, by devoting to this subject the energies of a scientific mind, and pursuing it with that steady zeal that its importance justified, has thus become a public benefactor of no common order.*

The first Food Adulteration Act was passed in London in 1860. Subsequent concerns led to the privileged position that food safety holds today.

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"It's great fun to follow": A review of *Chemistry in the Marketplace*, by Ben Selinger and Russell Barrow

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In university corporate-speak the words 'interdisciplinary' and 'multidisciplinary' are once again being included in strategies for research development.[1] Thinking about this welcome change, and recalling the television programme of years ago – *Connections,* where the presenter made fascinating links between history and the technology of the time,[2] I had high expectations for *Chemistry in the Marketplace*,[3] for which the publisher had written, albeit stolidly, "This new edition has been completely revised and updated to align with today's chemistry in the home, marketplace and environment." I was not disappointed.

The publisher observed that the book has been written "in an engaging style, mixing facts with amusing anecdotes". Engaging it certainly is: I read it from cover to cover over a couple of winter evenings. However, the facts and anecdotes are not 'mixed'; rather they are carefully and cleverly intertwined, each adding effect to the other. Under the cloak of humour, on occasion the authors are frank – almost brutal – in their criticism of those who market some products (e.g., cosmetics) and those who legislate about them (e.g., sunscreens, in Chapter 8; and sunglasses in Chapter 15). As expected, the book touches on some of the 'big' issues of the present day, including climate change and low carbon economies, but it takes a dispassionate approach to the discussion, pointing out, for example, the chemical basis for the limitations of batteries, the energy yield of fossil fuels compared to wind and water power. Also, the authors encourage the reader to think holistically about things such as the real costs of energy production and of bringing food from farm to plate (Chapter 10, Chemistry in the energy sector).

The chapter 'Chemistry in the swimming pool' reminded me of that National Science Foundation project – 'Chem Study' – of the 1960s, wherein a large section of the early part of the course comprised an integrative approach to the chemistry and physics of a burning candle.[4] From the reactions that define the relative proportions of chlorine (Cl_2), hypochlorous acid (HOCl) and hypochlorite ion (^-OCl), the reader encounters in this chapter:

- the varying chlorine content of products and thus their effectiveness in chlorinating pools;
- the controls on pH, including the reaction of HOCl with ammonia and ammonia-like compounds formed from organic waste (including that from swimmers) to form chloramines (the cause of the 'chlorine smell' complained of in chlorinated public water supplies),[5] leading to the measurement of pH in pools, which leads to a discussion of the effects of dissolved CO_2 on the pH of chlorinated water, buffers and a tilt at titrations;
- the recognition of HOCl as an oxidising agent, which effortlessly leads to an E-pH diagram;
- the loss of chlorine from the pool by photolysis at higher pH, leading to a discussion of 'stabilisers' such as cyanuric acid, and how its concentration might be measured, in turn leading to introducing turbidity as a measure of the concentration of anionic surfactants in waterways;

- 'dealing with algae', introducing the 'old' use of aluminium and iron (III) to bind to the phosphate associated with algae, then leading to a 'newer' approach using lanthanum sulfate and touching on "a lanthanum-modified bentonite for professional use in dealing with phosphate eutrophication of lakes and rivers…."; and
- 'dealing with muddiness'.

En route, sidebars and insertions provide links to other parts of the book. Examples include: in the section on stabilisers, we are invited to "see experiment 'Oxidation of glucose by air on p. 424"; in the section on algae, we are referred to a later chapter on the rare earths; in the 'muddiness' section dealing with the clarification of muddy pool water, a parenthetic remark captures interest: "As well as coagulating clay suspensions, aluminium ion is used in sticks to coagulate blood from shaving cuts and in antiperspirants to coagulate sweat from pores under the skin. See Chapters 3 [Chemistry of surfaces] and 8 [Chemistry of cosmetics]." In summary, the chapter follows an ordered sequence through a range of chemical processes and ideas related to its central theme, while providing connections to other parts of the book in such a way that the reader feels motivated to follow them up. I've used 'Chemistry in the swimming pool' as an example of the way the book works: many of the chapters are organised similarly.

Even (Chapter 12) 'Chemistry in the Garden' which opens somewhat tediously with a soil profile and a triangular diagram showing the distribution of sand, silt and clay in various types of soils, sparks up once the question is asked "What really is a cabbage?", and proceeds to talk about fertilisers (including a story about how cadmium contamination of a farm from fertiliser imported from China was narrowly averted), trace elements, the 'organic' food debate, grey water, and on to insecticides (with an aside on nerve gas), fungicides, herbicides (including glyphosphate and its role in gene protection of crops), pesticides and biological methods of pest control.

Although still informative and interesting, the chapters in the middle of the book lack the vibrancy of the previous and subsequent chapters: they tend to be descriptive, with more emphasis on classification. Perhaps the complexity of the organic chemistry that is the basis of cosmetics (Chapter 8), medicines (Chapter 9) and polymers (Chapter 10) inhibits the application of the approach used so well elsewhere in the book.

Overall though, a retrospective piece written about James Burke's *Connections* documentary series seems to fit *Chemistry in the Marketplace* remarkably well; Chris Higgins wrote in 2008 that the series "sought to explain human history through an alternative view of change" in which multiple aspects of history, including technology, religion, and finance combine to bring about social change. This mode of analysis moves beyond conventional linear narrative, and as a result embraces complexity. Each episode [of the *Connections* series (or each chapter of this book)] is an essay connecting several seemingly disparate events or technologies through an extended web of logic… It's great fun to follow." [6]

I have a copy of the fourth edition of this book, published in 1989.[7] The intention of that edition seems to have been the same as the 2017 edition, although the style of writing of the older work is a bit more restrained. Nearly 30 years have elapsed between the two editions, and if the *Connections* analogy has merit, some differences might be expected between the two books because of changes in societal norms and priorities, at least as perceived by the authors; and also because, as noted in the Preface (p. vii), "both industry and government have become more open and user friendly".

Both editions open with an introductory chapter and the length of this has been used to scale the lengths of the other chapters (i.e., relative number of pages in Chapter *N* = actual number of pages in Chapter *N* / number of pages in Chapter 1), as shown in Fig. 1. The chapters in the earlier edition that are notably relatively longer than those in the 2017 edition are those related to 'chemistry in the dining room' (Chapter 6), chemistry in the garden (Chapter 12), the energy sector (Chapter 17) and ionising

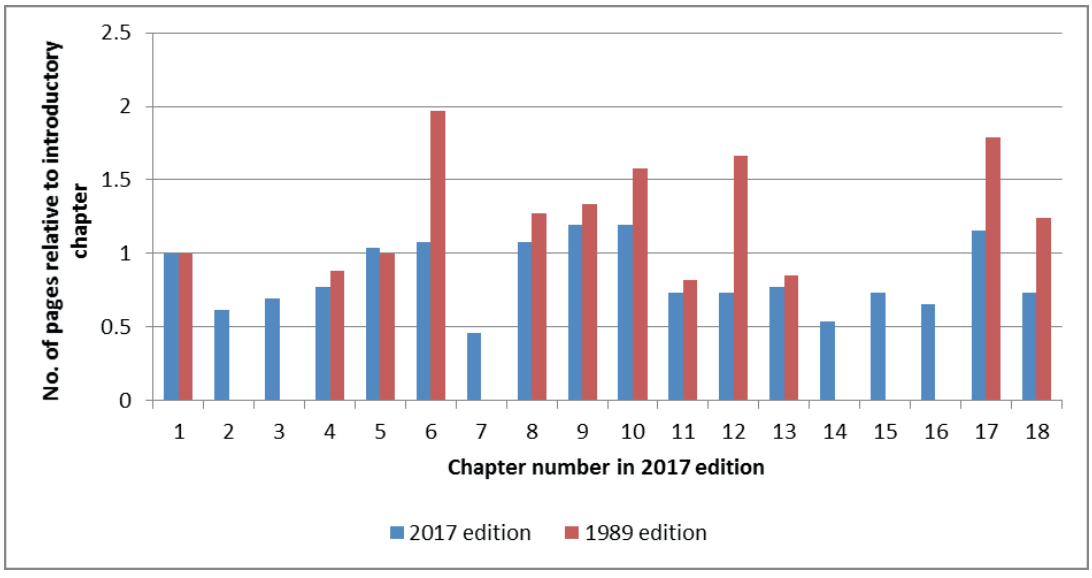


Fig. 1. Comparison of chapter lengths in the 2017 and 1989 editions of *Chemistry in the Marketplace*. The titles of the numbered chapters are listed in Table 1.

radiation (Chapter 18). The potential actual shortage of oil and its political availability[8] and concerns over nuclear power and weapons[9] were prominent social issues of the 1980s, and perhaps people were more inclined to gardening as recreation than is presently the case.

Among the new chapters in the 2017 are 'chemistry and health risk' (Chapter 2), consistent with the current global concerns over risk management; 'biochemistry of metabolism and sport' (Chapter 7), reflecting both a greater concern over health and fitness and increased public exposure to sport through the media; and 'chemistry in the swimming pool' (Chapter 14) and 'chemistry at the beach' (Chapter 15), perhaps indicative of an increased interest in the leisure activities component of the 'work-life balance'. The two new chapters on the chemistry of surfaces (Chapter 2) and on 'biological effects of metals and metalloids' may reflect the developing interests of the authors as much as their societal implications. Finally, in this inter-edition comparison, the cover images suggest a shift in the emphasis in the 'marketplace' for this book from the household consumer to wider concerns (Fig. 2).

Chemistry in the Marketplace includes 25 experiments (Table 1), each of which is signalled in the relevant chapter, although the experiment is rarely cross-referenced

Table 1. Experiments in *Chemistry in the Marketplace* 2017

Experiment	About	Chapter*	Safety†
Copper acetone catalysis	The catalysis of the oxidation of acetone vapour	1, 2	**L**
Steel wool in vinegar	Oxidation of iron when particle size is small and surface-to-volume ratio is large	3, 5	**H**
Powders to burn	The effect of surface area on burning (needs Bunsen burner)	4	**L**
Insurance reaction	Change in bulk properties with particle size ($KMnO_4$ + ethylene glycol)	4	**L**
Beating heart	The effect of surface charge on surface energy	4	L
Conductivity of emulsions	Determine which is the outer continuous phase in an emulsion	3	H
Foaming colours	Change in colour of a foam (mostly for fun!)	3	L
Falkland foam	Explosive foams (as used by the British Army to detonate land mines on the Falkland Islands after the war with Argentina in 1982)	3	L
Chemistry in a jam	Effect of metal ions on the viscosity of jam	5	H
Effect of salt on a copper pot	Effect of chloride ion on copper oxide $CuO + 2Cl^- + H_2O \rightarrow CuCl_2 + 2\ HO^-$	5	H
Restoring tarnished silver	Removal of tarnish with aluminium $3Ag_2S + 2Al \rightarrow 6Ag + Al_2S_3$	5	H
Induction, my dear watts-on	The induction of eddy electric currents in a non-magnetic material by moving a strong (neodymium) magnet close by	5	L
Fridge and freezer performance	The temperature control quality of a refrigerator	5	H
Heavy load of sugar	Change in density between normal and sugar-free soft drinks	6	H
Detecting borax	Detection of borax used as an food adulterant, replacing MSG	6	H
Oxidation of glucose by air	Oxidation of glucose in solution by the oxygen from air via a reversible intermediate, using methylene blue to simulate the ATP – ADP biochemical system	7	H
Testing the oiliness of antiperspirants	Identifies propellant (usually LPG), silicone oil, and white 'active ingredient' aluminium chlorohydrate	8	H
Disappearing tricks	Use of refractive index to distinguish original Pyrex (borosilicate glass) from tempered soda lime glass that was later used	10	H
Making a polymer ball	Making a silicon-based polymer from sodium silicate solution	10	H
Testing polymers	Identification of different polymers	10	L
Determining soil type	Grain size distribution and tactile investigations	12	H
Life support for flowers	Observation of wilting for different additives to water containing cut flowers	12	H
Making ink	A simple ink from teabags, steel wool, vinegar, and H_2O_2	13	H
Preparing cook's gold	Reaction between sulfides released from cauliflower and leek soup with iron in aluminum foil to form iron (II) sulfide, creating a golden colour on the foil	5	H

**Chapters (referred to in text or inferred from index)*: 1, Molecular musings; 2, Chemistry of health and risk; 3, Chemistry of surfaces; 4, Chemistry in the laundry; 5, Chemistry in the kitchen; 6, Chemistry in the dining room; 7, Biochemistry of metabolism and sport; 8, Chemistry of cosmetics; 9, Chemistry in the medicine cabinet; 10, Chemistry of plastics and glass; 11, Chemistry of fibres, fabrics and other yarns; 12, Chemistry in the garden; 13, Chemistry of hardware and stationery; 14, Chemistry in the swimming pool; 15, Chemistry at the beach; 16, Biological effects of metals and metalloids; 17, Chemistry in the energy sector; 18, Chemistry of ionising radiation.

† *Safety:* ■, Can only be done in a Laboratory (**L**) under professional supervision; ■, Should only be done in a laboratory (**L**) under professional supervision; ■ Can be undertaken in a laboratory (**L**) or, where the equipment or chemicals are relatively easy to obtain, at home (**H**).

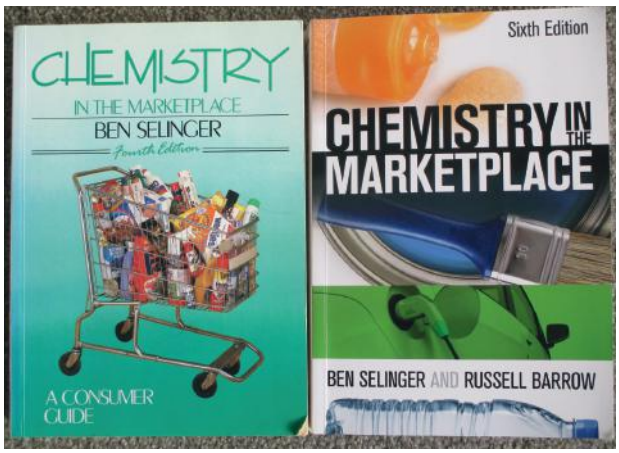


Fig. 2. Comparison of cover images. Left: Household consumer goods dominate the cover of the 1989 edition; the tag-line 'A consumer guide' confirms the emphasis. Right: Taking a wider view of the marketplace, the cover of the 2017 edition features cosmetics, paint, fuel for transport, and the plastic in water bottles.

to the chapter (which might be a good idea in a future edition). It is not specified who might undertake these experiments, although some could form the basis of science-fair[10] or CREST[11] investigations by keen school students, or be incorporated into laboratory work or demonstrations for undergraduate university chemistry courses. Although the authors "do not warrant that any instruction, recipe or formula in this book is free of possible danger to the user", they signal those experiments which "can only…" or "should only…" be done under supervision. These suggested restrictions are shown in Table 1, as well as those which – by virtue of the chemicals or equipment required – could be undertaken at home.

To further expand the usefulness of this book, it contains appendices which give additional details for some concepts introduced in the text.[12] Again these are not referenced back to the chapter; clearly they are not really intended to be read on their own. There is also a comprehensive glossary, which is useful for the few occasions when the authors introduce scientific terms for which there is no definition or explanation in the text.

In summary, this is an attractively presented book, full of interesting chemistry which makes it highly recommended for chemistry students and their teachers, but which is tempered by mini case-studies providing a fascinating social context, which increases its potential audience to include those interested in marketing and, more generally, in environmental and social issues.

Notes

1 . Victoria University's most recent strategic plan advocates enhancing its research quality, quantity and impact, proposing to "undertake more collaborative, translational, multidisciplinary research to complement its strengths in investigator-led, fundamental, discipline-based research". *Victoria University of Wellington Strategic Plan – Capital thinking. Globally minded*. Victoria University of Wellington: Wellington, 2014, p.15.

2 . The television programmes led to the publication of a book: Burke, J. *Connections*. Little, Brown: Boston, *c*.1978, 304 pp.; after which there were sequels of both the programmes and the book.

3 . Selinger, B.; Barrow, R. *Chemistry in the Marketplace*, 6th edition. CSIRO Publishing: Clayton South (Victoria Australia), 2017, 535 pp.

4 . Chemical Education Material Study; Piementel, G. (ed.). *Chemistry an Experimental Science*. Freeman: San Francisco, 1963. The textbook, teacher's guide and a book of experiments are all available on line at: https://archive.org/details/chemistryexperim00chem (accessed 06/06/2017).

5 . This is a topical issue in New Zealand after the health problems and deaths caused by sheep fecal contamination of an aquifer in Hawkes Bay in 2016 resulted in the chlorination of the Havelock North water supply. Similarly, possible contamination by *E coli*, inferred to have been result of the magnitude 7.8 November 2016 Kaikoura earthquake, led to the chlorination of natural spring water in Petone (near Wellington), which had been long appreciated by locals as an source of untreated drinking water.

6 . Higgins, C. Connections TV series now on line: http://mentalfloss.com/article/26632/connections-tv-series-now-online (accessed 08/06/2017).

7 . Selinger, B. *Chemistry in the Marketplace*, 4th edition. Harcourt Brace Jovanovich: Marrickville (NSW, Australia), 1989, 674pp.

8 . Sha, S. *Crude – the Story of Oil*. Allen and Unwin: Crows Nest (NSW Australia), 2004, 315 pp.

9 . Priestley, R. *Mad on Radium: New Zealand in the Atomic Age*. Auckland University Press: Auckland, 2012, 296 pp.

10 . Science and Technology fairs: https://www.niwa.co.nz/education-and-training/science-and-technology-fairs (accessed 09/06/2017).

11 . About CREST awards: https://royalsociety.org.nz/what-we-do/funds-and-opportunities/crest-awards/about/ (accessed 09/06/2017).

12 . In Appendix 3, the authors propose a logarithmic scale for perception of risk that mirrors sound loudness (dB), noting that "All our physical senses respond roughly logarithmically. One major intellectual response (economic utility) behaves likewise. Why not another, such as risk perception? Our perception of risk appears to be proportional to the background level of that risk to which we are already exposed". They suggest "a table of risk (or safety) that mirrors a table in sound loudness (dB), calling it, say sels dB", concluding, "Instead of quoting odds of risky events, quoting the logarithmic sels would compress the risk scale in a manner more attuned to our perceptions and make acceptable a spread of resources on risk reduction more in keeping with our perceptions." This is a good example of Higgins' concept (see footnote 6), where "analysis moves beyond conventional linear narrative, and as result embraces complexity".

Dates of Note

October

22 ***Frank Harold Spedding***, the American chemist, who during the 1940s and 50s developed processes for reducing individual rare-earth elements to the metallic state, was born in 1902.

23 In 1947, ***Carl*** and ***Gerty Cori*** (née Radnitz) of Washington University Medical School, were awarded the Physiology or Medicine Prize for the discovery of how glycogen is converted to glucose in the body, and for the effects of hypophysis (pituitary gland) hormones on sugar metabolism. They were the first US married couple so honoured. Gerti died on October 26, 1957.

24 ***Hippolyte Mège Mouriés***, the French inventor of margarine with a process based on the cold saponi-

fiation of milk in fat emulsions (Fr. Pat No. 86489) and who began his science career at age 16 as a chemist's assistant, was born 200 years ago today.

25 ***Evangelista Torricelli***, the Italian physicist and mathematician who invented the barometer, died in 1647.

26 ***Arthur Kornberg***, the American biochemist and physician who shared the 1959 Nobel Prize for Physiology or Medicine (with Ochoa) for the discovery of the mechanisms in the biological synthesis of DNA, died 10 years ago.

27 ***Marcellin Berthelot*** was the French chemist, science historian, and government official whose creative thought and work had major impact on the development of chemistry in the late 19th century. He helped found thermochemistry, introduced a standard method for determining the latent heat of steam, measured vast numbers of heats of reactions and coined the words exothermic and endothermic. Berthelot systematically synthesised many organic compounds, including some not found in nature, thus helping remove the classical division between organic and inorganic compounds. He was born in 1827.

28 ***Alexander Crum Brown***, the Scottish Professor of Chemistry at Edinburgh University and first Doctor of Science at the University of London whose pioneering work concerned the development of representing chemical compounds in diagrammatic form, died in 1922.

30 ***Hermann Franz Moritz Kopp***, the German chemist and historian of chemistry whose studies of the relation of physical properties to chemical structure and who pioneered physical organic chemistry, was born 200 years ago today.

31 In 1992, the Vatican admitted that for over 360 years it had erred in formally condemning ***Galileo Galilei*** for his scientific truths e.g. the Earth revolves around the sun.

November

1 In 1772, ***Antoine Lavoisier*** reported in a note to the French Academy of Sciences that during the previous week he had discovered that sulfur and phosphorus increased in weight when burned because they absorbed *air*, while the metallic lead, formed when litharge (PbO) was heated with charcoal, weighed less than the original litharge because it had lost *air*.

2 In 1957, the first titanium mill was opened in Toronto, Ohio by the Titanium Metals Corp. of America (TIMET).

4 ***James Douglas***, the Canadian-American metallurgist, mining engineer and philanthropist who developed the copper mining industry in the US Southwest and co-invented the Hunt-Douglas copper extraction process, was born in 1837.

5 ***Edmund Davy***, the English chemist who discovered acetylene, was born in 1857.

25 years ago in 1992, ***Michel, McGovern, and Badler*** reported evidence in the journal *Nature* of ancient beer in a 5,000-year-old jug at Godin Tepe in the central Zagros Mountains of Iran. It is the earliest trace of beer ever discovered.

In 1662, ***Robert Hooke*** was appointed Curator of Experiments to the Royal Society, London.

7 ***Marie Sklodowska Curie***, was born 150 years ago in 1867.

8 The Bodleian Library was established in Oxford in 1602.

9 ***Ronald G.W. Norrish,*** the British chemist who shared the 1967 Nobel Prize for Chemistry (with Porter and Eigen) for their very fast chemical reaction studies, was born in 1897.

Chaim Weizmann, the Russian-British-Israeli chemist who used bacteria for the synthesis of organic chemicals, died in 1952.

It was this day in 1877 that the American Chemical Society was chartered.

12 Nobel physics laureate ***Sir John Rayleigh***, the English scientist who made fundamental discoveries in the fields of acoustics and optics, was born in 1842.

In 1847, Sir ***James Young Simpson***, employed chloroform for the first time as an anaesthetic in an operation.

In 1901, decisions for the first Nobel Prizes for Physics and for Chemistry were made with the Prize in Physics awarded to ***Wilhelm Röntgen*** for his discovery of X-rays and the Prize in Chemistry to ***Jacobus H. van't Hoff*** for his work on rates of reaction, equilibrium and osmotic pressure.

In 1912, the body of Sir ***Robert Falcon Scott*** was discovered in the Antarctic.

13 ***Étienne-François Geoffroy***, the French chemist who was the first to recognize the relative fixed affinities of reagents for one another and provided tables that stood through most of the 18th century, was born in 1672.

This is the day in 1912 that ***Robert Millikan*** began collecting data from his famous oil drop experiment.

14 ***Herbert A. Hauptman***, the American mathematician and crystallographer who shared the 1985 Nobel Prize for Chemistry (with Karle) for outstanding achievements in the development of direct methods for the determination of crystal structures, was born 100 years ago today.

15 ***Elmer McCollum***, the American biochemist who originated the letter system of naming vitamins, died in 1967.

Franciscus Sylvius, the Dutch physician, chemist, physiologist and founder of the seventeenth century's *iatrochemical school of medicine*, died in 1672

It was the day in 1492 that ***Christopher Columbus*** noted the use of tobacco among Indians in his journal.

16 ***Wallace Carothers*** received the patent for nylon this day in 1937.

17 This marks the 95th birthday of ***Stanley Cohen***, the US biochemist who shared (with Levi-Montalcini) the 1986 Nobel Prize for Physiology or Medicine for their discoveries of growth factors.

18 ***Niels Bohr***, the Danish physicist who was the first to apply quantum theory, died in 1962, 50 years ago.

19 ***James B. Sumner***, the American biochemist who shared (with Northrop and Stanley) the 1946 Nobel Prize for Chemistry as the first to crystallise an enzyme and show it to be a protein, was born in 1887.

20 ***James Bertram Collip***, the Canadian biochemist who co-discovered insulin, was born in 1892, 125 years ago.

Casimir Funk, the Polish-American biochemist who coined the term *vitamine*, died this day 50 years ago.

21 ***Vladimir Nikolayevich Ipatieff***, the Russian-American chemist who developed a process for manufacturing high-octane gasoline and was one of the first to investigate hydrocarbon high-pressure catalytic reactions, was born 150 years ago today. He died on November 29, 1952.

23 ***Johannes Diederik van der Waals***, of equation fame, was born in 1837.

26 ***Charles-Adolphe Wurtz***, the French chemist and educator noted for his research on organic nitrogen compounds, hydrocarbons, glycols, and especially the reaction named after him, was born 200 years ago today.

28 ***Hans Wynberg***, professor of organic chemistry at the University of Groningen who was mainly concerned with the stereochemistry and organic synthesis, was born in 1922.

29 ***Robert A. Swanson***, the American chemist who co-founded Genentech, Inc., the research-based company that pioneered the biotechnology industry, was born in 1947.

December

2 ***Luis Federico Leloir***, the Argentinian biochemist who won the Nobel Prize for Chemistry in 1970 for his discovery of sugar nucleotides and their role in the biosynthesis of carbohydrates, died in 1987.

Enrico Fermi and his team achieved the world's first artificial nuclear chain reaction, in a makeshift lab underneath the University of Chicago's football stands at Stagg Field 75 years ago today.

It is the day in 1877 that oxygen was liquefied for the first time - by ***Louis-Paul Cailletet***.

3 ***Peter C. Schultz***, the American ceramicist who with Corning Glass researchers Maurer and Keck, made optical fibre (capable of carrying 65,000 times more information than conventional copper wire) a practical reality, was born 75 years ago.

Ellen Swallow Richards, the founder of home economics in the United States and the first woman admitted to the MIT (see: *This journal,* **2016**, *80*, 195-201), was born 175 years ago.

Johannes Wislicenus, the German chemist whose pioneering work with lactic acid led to the recognition of the importance of the spatial arrangement of atoms within a molecule, died in 1902.

6 ***Nicolas Leblanc***, the French surgeon and chemist who developed the process for making sodium carbonate from sodium chloride in the process which carries his name, was born 275 years ago in 1742.

8 ***Thomas Robert Cech***, the American biochemist and molecular biologist who (with Altman) was awarded the 1989 Nobel Prize for Chemistry for discoveries concerning RNA, has his 70th birthday today.

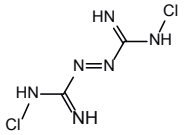
9 ***Carl Wilhelm Scheele***, the Swedish chemist who discovered oxygen in 1772, was born this day in 1742, 275 years ago.

Karl August Folkers, the American chemist whose research on vitamins resulted in the isolation of vitamin B12, died in 1997.

10 ***Carl Wagner***, the German physical chemist, metallurgist and father of solid-state chemistry by pioneering chemical metallurgy to become an exact science, died in 1977.

11 Sir ***William Cecil Dampier***, the British scientist who developed a method of extracting lactose from surplus whey, died in 1952; he was born on December 27, 1867, 150 years ago.

Franz Carl Schmelkes, the Czech-born chemist who discovered azochloramid (chlorazodin) [1-(amino-chloroiminomethyl)imino-2-chloroguanidine] used to sterilise wounds and burns, died in 1942.



chlorazodin

In 1922, the discovery of hafnium by ***Coster*** and ***von Hevesy*** was announced by Neils Bohr as he concluded his Nobel Prize lecture.

14 It is 50 years today since the first synthesis of biologically active DNA in a test tube. It was announced at a press conference by ***Arthur Kornberg*** who had worked with Goulian at Stanford and Sinsheimer of MIT.

15 ***Henri Becquerel***, the French physicist who discovered radioactivity in fluorescent salts of uranium, was born in 1852.

17 ***Johannes Nicolaus Brønsted***, the Danish physical chemist known for his acid-base concepts, died in 1937.

Baron ***William Thomson Kelvin***, the Irish physicist,

mathematician and engineer who made a name for himself beyond the temperature scale, died in 1907.

22 ***Lewis Hastings Sarett***, the American chemist who prepared a synthetic version of cortisone in 1944 over 36 steps, was born 100 years ago today.

Axel Fredrik Cronstedt, the Swedish chemist and metallurgist who isolated nickel in 1751, was born in 1722.

23 This day in 1947 saw the transistor first demonstrated by ***Brattain*** and ***Bardeen*** at Bell Laboratories.

25 ***Vladimir Vasilyevich Markovnikov***, the Russian organic chemist known for his addition rule, was born on Christmas Day in 1837.

Sir ***Isaac Newton*** was born on Dec 25 in 1642, 375 years ago.

27 ***Louis Pasteur*** was born in 1822.

Gerardus Johannes Mulder, the Dutch chemist who coined the name *protein*, was born in 1802.

31 ***Vaughan Frederick Randal Jones***, the New Zealand mathematician who was awarded the Fields Medal in 1990 has his 65th birthday today.

January

1 In 1888, ***Robert Kane***, then a 24-year-old Irish chemist, published the first proposal of the ethyl radical ($-C_2H_5\bullet$) in the *Dublin Journal of Medical and Chemical Sciences*.

In 1913 ***William M. Burton*** patented a process for the cracking of petroleum to produce gasoline that was used by Standard Oil.

George Washington Carver was the American agricultural chemist who helped revolutionize the agricultural economy of the US South by demonstrating how soil fertility could be restored to land by diversification (especially the planting of peanuts and sweet potatoes). He also showed that peanuts contained several different kinds of oil, which led to manufacture of peanut butter. He died 75 years ago today.

Louis-Paul Cailletet, the French physicist and iron master and first to produce droplets of liquid oxygen, hydrogen, nitrogen, carbon monoxide, nitrogen dioxide and acetylene, died in 1913.

6 ***Fausto D'Elhuyar,*** the Spanish chemist and mineralogist who assisted his older brother Juan José in experiments to separate tungsten metal from *wolframite* ore in 1783, died in 1833.

7 Sir ***Henry Enfield Roscoe*** was the English chemist who founded the Manchester School of Chemistry from Owens College and greatly improved science education following his study at Heidelberg under Bunsen. His 30 years at Owens led to the college to one where original research by students and demonstrators had produced 120 published papers. He was born in 1833.

This day marks 80 years since the superfluidity of liquid helium at a temperature near absolute zero was reported in *Nature*.

8 ***Søren Peder Lauritz Sørensen***, the Danish chemist who introduced the concept of pH and was head of the prestigious Carlsberg Laboratory, Copenhagen (1901-1938), was born 150 years ago today.

Fukui Kenichi, the Japanese chemist who shared the 1981 Nobel Prize for Chemistry (with Roald Hoffmann) for the concepts of conservation of orbital symmetry, died this day in 1998.

Willis R. Whitney, the American chemist and research director who founded the General Electric Company's research laboratory, died in 1958.

9 ***Isidor Isaac Rabi***, the Austrian-American physicist who was awarded the Nobel Prize for Physics in 1944 for his invention of the atomic and molecular beam magnetic resonance method of measuring magnetic properties of atoms, molecules, and atomic nuclei, died in 1988.

13 ***Paul Niggli***, the Swiss mineralogist who originated the idea of a systematic deduction of the patterns in the internal structure of crystals by means of X-ray data and provided a complete outline of methods that have since been used to determine these patterns, died in 1953.

Today marks 60 years since ***Linus Pauling*** presented the petition of 9,000 scientists to the UN, asking to halt the testing of nuclear bombs. In October, after more tests by both sides, talks began in Geneva to discuss details of a possible test ban.

16 It was this day in 1953 that a sample amounting to about 200 atoms of fermium (Fm; At. no. 100) was discovered by ion-exchange chromatography and identified at the University of California, Berkeley. Like einsteinium, fermium was first isolated from the debris of the November 1952 test of the hydrogen bomb conducted at Eniwetok Atoll in the Pacific Ocean.

18 ***Joseph Farwell Glidden***, the US inventor of barbed wire who formed the Barb Fence Company of De Kalb, Illinois, was born in 1813.

19 Sir ***Henry Bessemer***, the British industrialist, metallurgist, inventor and engineer who developed his process for manufacturing steel inexpensively, was born in 1813.

Sir ***Chester Beatty***, American-British mining engineer who perfected a method of extracting copper from low grade ore, and was active in developing the copper deposits of central Africa, died 50 years ago.

Henri-Victor Regnault, the French chemist and physicist noted for his studies of gas properties done as a skilful, thorough, patient experimenter to determine the specific heat of solids, liquids, gases, and the vapour-tensions of water and other volatile liquids, as well as their latent heat at different temperatures, died in 1878.

21 ***Felix Hoffmann***, the German chemist who discovered aspirin, was born 150 years ago today.

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