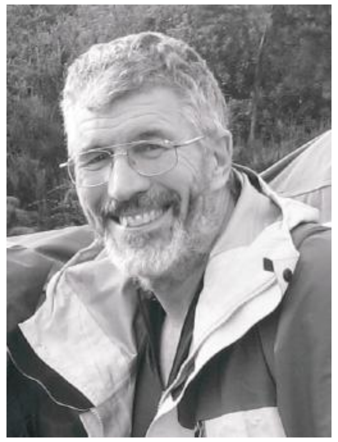
Chemistry in New Zealand

Volume 79, No.3, July 2015

Articles and Features

Other Columns

Comment from the President.



This issue I'd like to draw your attention to the need to sustain and grow our technical and science technician workforce in the face of changing tertiary education structures, the changing needs of employers and a future where demand for these skills is certain to grow. Having worked within the government science system since 1979, I've seen big changes in the way that we as a nation have managed the training and qualifications for science technicians. I recall that every year throughout the 1980s at DSIR Chemistry we took on a cluster of bright new high school students enrolled for NZCS or NZCE qualifications. The students worked within assigned research teams, learning the essentials of laboratory skills development while undertaking course work most days at the local polytech. It wasn't a perfect system, but it placed young people into laboratories and enabled them to work alongside scientists and engineers. For many it was a direct path to a career outside DSIR in industry - an important conduit to get sharp young people trained and into our manufacturing sector. For some, the career path stayed within DSIR and its successors. For a few, there was a desire to take on more rigorous study within a university course structure. Many of us know current and former colleagues who took one of these paths, and the value that this created for them, for their employers and for our economy.

The much respected NZCS/NZCE education pathway didn't last. The NZ Qualifications Authority, established in 1989, initiated changes in the structure, function and funding of polytechs and heralded a new technical education path, with the introduction of a National Diploma in Science in 1997. The mechanism for training students *in situ* within the government agencies and other bodies dried up. No longer was there a stream of bright young technicians growing and learning in our labs and project teams and feeding through to our oil, paint, milk, food and other manufacturing industries. More recently, this qualification has been reviewed and is to be again replaced by the New Zealand Diploma in Applied Science beyond December 2016.

Is the current process delivering skilled science technicians to meet our needs as scientists and science employers, and in the wider industrial community? Does it meet the students' needs in terms of gaining suitable experience and skills to springboard to a career? Does this meet New Zealand's anticipated demand for technicians in terms of the relevance of training and in the quality and quantity of students being trained? So many questions.

The Royal Society of New Zealand is considering forming an expert advice panel to look at the future science technician workforce. Wearing both my NZIC and RSNZ hats, I would welcome your feedback and comments with respect to what extent there are perceived to be problems and what those problems are. This would certainly assist the Royal Society to decide how high a priority to give to this issue and help in framing the future work programme. We in the chemistry profession can only benefit through improved structures and processes that lead to enhanced quality and quantity of trained science technicians. We as a nation need to get it right.

Finally, as we went to press, we learnt that Distinguished Professor Margaret Brimble of the University of Auckland has received a global award for being an outstanding achiever in her field. She was named as one of this year's Distinguished Women in Chemistry or Chemical Engineering by the International Union of Pure and Applied Chemistry. Margaret has been a Fellow of our Institute since 1999 and is the first New Zealander to be named for this biennial award. Our very best congratulations.

Ian Brown
Callaghan Innovation
NZIC President 2015

From the Editor

Following on from the reader survey results reported in the October 2014 issue, you may have noticed some changes that have been made to our journal this year in response to suggestions for improvements. Our publisher, Rebecca Hurrell, has updated the fonts to give the articles a fresher look and some regular features now have a new format. A change of printer has also improved the overall appearance of the journal. One consequence of the latter change is that photographs and images must be of sufficiently high resolution to ensure they are good quality once printed. Please bear this in mind when contributing your articles or news – it is preferable to send the original images separately rather than resized within a document.

I have also been contacting people directly to solicit contributions which I hope will be reflected in more articles from chemists in industry and those in schools/education as well as other disciplines. There have been a number of high profile scientists who have visited various institutions throughout the country over the past few months but unfortunately it has not been possible to extract articles from them. Once again I would encourage you to get in touch if you have any ideas for a special feature to appear in our journal from a distinguished visitor you are hosting. The reader survey highlighted the fact that members would appreciate some more variety in content so let's try to make that happen.

Cath Nicholson

New Zealand Institute of Chemistry

supporting chemical sciences

July News

NZIC NEWS

David Bibby, former Dean of Science at Victoria University of Wellington, was appointed a Companion of the Order of New Zealand (CNZM) in the Queen's Birthday Honours.

MEMBERSHIP

New Members 2014-2015 (MNZIC)

Auckland Branch: Dr *Robyn* ***Somerville*** (ESR); Dr *Ivanhoe* ***Leung***, A/Prof *Christian* ***Hartinger*** (University of Auckland).

Waikato Branch: Dr *Anatoly* ***Chemyshev*** (Ruakura Research Centre); Dr *Andrew P* ***Vogt*** (Scion).

Manawatu Branch: Dr *Catherine* ***Whitby***, Dr *Andrew* ***Sutherland-Smith***, Dr *Patrick* ***Edwards***, Mr *Nigel* ***Kerr*** (Massey University); Dr *Maurice* ***Judd*** (IPC Tertiary Institute); Mr *Allan* ***Dodge*** (Moed Consulting).

Canterbury Branch: Mrs *Lesley* ***Parker*** (Westmount School); Mr *Scott* ***Franklin*** (Christ's College); Ms *Miriam* ***Bugler*** (Linwood High School).

Otago Branch: Dr *Anna* ***Garden*** (University of Otago).

Overseas: Dr *Erin* ***Leitao*** (Bristol, UK).

Student members

Auckland Branch: *Winnie* ***Cao***, *Yu* ***Li*** (University of Auckland).

Manawatu Branch: *Ewan* ***Fisher***, *Josh* ***Blazek*** (Massey University).

Wellington Branch: *Benjamin* ***McVey***, *Emma* ***Wrigglesworth***, *Taitusi* ***Taufa,*** *Victoria* ***Woolner,*** *Sophie* ***Geyrhofer*** (Victoria University).

Canterbury Branch: *Vivek* ***Poonthiyl***, *Jean-Batiste* ***Lena***, *Nic* ***Bason***, *Benjamin* ***Wilson***, *Lance* ***Buckett***, *Shane* ***Verma***, *Alexandra* ***McNeill*** (University of Canterbury).

Otago Branch: *Hannah* ***Davidson*** (University of Otago).

Resigned

Auckland Branch: Mr *Malcolm* ***Smith***, Mr *Thilliar* ***Varnakulasingham***, Mr *Amir* ***Ali***, Mr *Lindsay* ***Main***.

Manawatu Branch: Mr *Christopher* ***Rowse.***

Wellington Branch: Dr *Barry* ***Dent***, Dr *David* ***Bull***, Dr *Hilary* ***Hamnett***, Dr *David* ***Herman.***

Canterbury Branch: Dr *William (Bill)* ***Swallow***, Miss *Anne* ***Wignall.***

Overseas: Dr *Campbell* ***Page.***

Deceased

Auckland Branch: Mr *Birger* ***Nordmark***.

Wellington Branch: Dr *Anthony* ***Woolhouse.***

Otago Branch: Mr *Rex* ***Malthus.***

AUCKLAND

The University of Auckland

The School of Chemical Sciences centenary was celebrated with two days of events to showcase the wealth of talent that resides within the School and a look back at a rich history of transformation, from humble beginnings in an old courthouse in the 1800s, to a diverse School thriving across campuses at six different locations.

Owing to the special anniversary, the annual Research Showcase was held at the Auckland Museum where the school's PhD students presented their research. *Matthew* ***Calvert*** was awarded first place for his 15-minute oral presentation, *A biomimetic synthesis and structural revision of Yuremamine*, winning the $500 Thermo-Fisher prize. The day was also marked by three-minute talks and poster presentations from PhD students.

After the keynote address from Professor *Robert H* ***Grubbs*** followed by Professor *Russell* ***Egdell***, the School posed for the centenary celebration photo. The day ended with cocktails and canapés and a self-guided tour of the Museums' WWI exhibition.

On the Saturday, a day of lectures aimed at a more general audience was presented to a near full lecture theatre, including a lively talk by Professor *Gordon* ***Miskelly*** about the history of the school and the "academic lineage" of alumni.

The *whizz bang chemistry* display was a highlight of the day that saw the children in the audience mesmerised by exploding balloons and frothy, fizzy and bubbly lab experiments. Tours of the glassblowing laboratories proved very popular, as did the tours of the newly renovated chemistry laboratories.

Two days of celebrations concluded with the exclusive gala dinner held in the University marquee on the Old Government House lawn.

Congratulations to Distinguished Professor *Margaret* ***Brimble*** being named as one of this year's Distinguished Women in Chemistry or Chemical Engineering. The biennial awards, which honour prominent women chemists from around the world, were handed out by the International Union of Pure and Applied Chemistry. For more details, follow the NZ Herald link: *www.nzherald.co.nz/technology/news/article.cfm?c_id=5&objectid=11451801*

Distinguished Professor Margaret Brimble, was also awarded a 2015 Vice-Chancellor's Commercialisation Medal at the University Research Excellence Awards in May.

Dr *Christy* ***Wang*** was awarded one of the five Vice-Chancellor's prizes for the best doctoral theses at the University of Auckland in 2014. Christy was also awarded the Briggs prize from the School for the best PhD dissertation in 2014. Congratulations to Christy, and her supervisor, Dr *Jonathon* ***Sperry***, for mentoring Christy to

PhD students who gave 15 minute talks at the Research Showcase, together with the Dean of Science, Prof John Hosking (left) and Head of School, Prof Kevin Smith (4th from the let). The winner was Matthew Calvert (2nd from right).

Members of the School of Chemical Sciences pose for the centenary celebration photo.

SCS Centenary Research Showcase Committee members with the Head of School and Vice-Chancellor. From left to right: Prof Kevin Smith (HoS), Dr Tilo Soehnel, Dr Viji Sarojini, Mr Tasdeeq Mohammed, Dr Peter Swedlund, Mrs Anoma Ratnayake, Dr Ivanho Leung, Dr Jianyong Jin (Committee Chair) and Prof Stuart McCutcheon (Vice-Chancellor).

such a high level of achievement.

Congratulations to all the students who graduated at the autumn graduation ceremony earlier in May.

After a decade of discovery and research, two University of Auckland medical oncology researchers along with their dedicated teams have developed a new anti-cancer compound that will advance to human Phase II clinical trials. The co-inventors of the compound TH-4000, Dr Adam Patterson and Dr Jeff Smaill, senior academics from the Auckland Cancer Society Research Centre and the Maurice Wilkins Centre, have collaborated with a NASDAQ-listed American biotechnology company, Threshold Pharmaceuticals (TP), to advance the compound to this stage. TH-4000 is described by Threshold as a molecular-targeted, hypoxia-activated irreversible epidermal growth factor receptor (EGFR) tyrosine kinase inhibitor (TKI) that may overcome resistance to therapy from conventional EGFR-TKI compounds. “We are grateful for the funding support from the Ministry of Business Innovation and Employment, the Health Research Council of New Zealand and the Maurice Wilkins Centre over the years,” said Drs Patterson and Smaill.

In September 2014, TP licensed exclusive worldwide rights to a clinical development programme based on TH-4000 from Auckland UniServices, the technology transfer company of the University of Auckland. “We are delighted to join forces with our friends and experts in the field of tumour hypoxia and hypoxia-activated prodrug technology at the University of Auckland, and look forward to our collaborative efforts in the development of TH-4000 as a potential new therapy that has potential to overcome the limitations of currently available EGFR-TKI therapies,” said Dr Pearce of Threshold Pharmaceuticals.

Auckland University of Technology

The Auckland University of Technology has recently appointed two Professors of Chemistry in the School of Applied Sciences. *Nicola* ***Brasch*** and *Allan* ***Blackman*** both obtained their PhD degrees under the supervision of *Dave* ***Buckingham*** and *Charles* ***Clark***. Nicola’s interests centre around the chemistry of vitamin B$_{12}$, while Allan’s research focusses on the synthesis and reactivity of complexes containing multidentate amine ligands. The school is currently renovating a large chemistry research laboratory, and has recently taken delivery of a glove box, a Cary100 UV-Vis spectrometer, a stopped-flow instrument and a microwave plasma instrument. A Bruker 400 MHz NMR and a laser flash photolysis instrument are set to arrive in the next couple of months. *John* ***Robertson*** is taking six months of sabbatical leave. He will be working on terrestrial drone technology and spending a month in North -Western Australia flying drones with an Aboriginal group mapping their traditional lands. *Mark* ***Duxbury*** is undertaking mangrove elemental analysis (which involves getting up to his knees in mud collecting mangrove leaf samples, then measuring nitrogen isotopes in the leaves). *John* ***Milligan*** has gone to a 0.6 position, where he looks after the Foundation Chemistry students. *Heather* ***Aspeling***, formerly a teacher at Howick College, has been appointed as a Chemistry Teaching Assistant for both the Foundation and First Year courses.

CANTERBURY

The annual NZIC BBQ for 2nd, 3rd and 4th year university and polytech students as well as postgraduates and NZIC members was held on 12 March at the University of Canterbury Staff Club and was well attended by hungry hoards.

University of Canterbury

PhD student *Anna* ***Farquhar*** (Downard group) had a very successful week at the Advanced Materials & Nanotechnology (AMN7) conference in Nelson, 8-12 February (*www.macdiarmid.ac.nz/event/amn-7/*). She won the best poster prize and a prize for the best dancing. Former Downard PhD student, *Dave* ***Garrett***, won the prize for the best beard. *Shane* ***Telfer*** (Massey University), a former member of the Hartshorn group, was an excellent Conference Chair.

In June of last year *Steward* ***Alexander*** was part of the UC team for a new series of University Challenge, along with *Gerald* ***Pfiefer***, *Rachel* ***Harris***, *Daniel* ***Redmond*** and *Liam* ***Boardman***. The programme has been televised on Prime at the unfortunate time of 11.30am on Saturday. Despite a shortage of science questions, Stewart gave his share of answers, ranging from T. S. Eliot, to chlorophyll, to The Proclaimers. The team secured a place in the semi-finals against the favourites – Victoria - and came away with a narrow win. Auckland was the other finalist, coming off a semi-final where they demolished Otago 300-120. There was only five points in it going into the final segment but they put the foot down and pulled away to win 210-155, taking home the trophy. It was an amazing experience for them, competing against a number of wonderful teams, and if any other chemistry students ever get the chance to take part, seize the opportunity with both hands.

If anyone wants to see the show, the most recent episodes are on SkyGo for free (you have to make an account to view them, but you don’t have to be a Sky subscriber).

Visitors

We have welcomed a number of visitors recently: *Aoife* ***Noonan*** - a student from Utrecht University in the Netherlands. Aoife is in her second year of an MSc in drug innovation and is doing a research internship at Canterbury, with Antony Fairbanks’ group. Aoife is originally from Ireland and completed her BSc in the chemistry of pharmaceutical compounds at University College Cork before moving to the Netherlands. In her spare time Aoife loves to travel and is looking forward to seeing New Zealand while she is here.

Natacha ***Massenet*** - a visiting intern student from New Caledonia. Natacha joined Ian Shaw’s Human Toxicology Research Group as part of her Master’s degree in ecotoxicology. For Natacha’s research project she will be studying the mechanisms of estrogenicity of the ubiquitous environmental pollutant, dibutylphtalate (DBP) and assessing its risk to human health.

Before coming to New Zealand Natacha was studying for her Master’s degree at the Université de Lorraine, northern France. She graduated with two diplomas: a DUT (university undergraduate degree) in biology engineering from Université de Strasbourg (2012) and a Bachelor’s degree in environmental biology with a major in environmental health and chemistry (Université de Lorraine, 2013). In her spare time Natacha would love to explore the South Island.

Florence ***Houdouin*** - an intern student from France. Florence graduated from the Institute of Technology in chemistry (IUT) and also went on to obtain a Bachelor degree in chemistry. Florence is currently in her second year of a Master’s degree in organic chemistry at the University of Maine in Le Mans, France. Florence has recently joined Peter Steel’s research group as part of her Master’s degree. Her research will focus on the synthesis of heterocyclic sulfoxides and sulfones for use as ligands in metallosupramolecular chemistry. Outside of chemistry, Florence enjoys mainly dance, and hiking from time to time. Florence is eager to discover more of New Zealand’s nature. If anyone knows of good places to go around Christchurch then she would love to hear from them.

Leyla ***Bustamante*** – working in the department with Emily Parker as a Research Associate. Leyla completed her first degree at the Universidad Nacional in Bogotá, Colombia. Following a two-year spell researching molecular markers of drug resistant malaria at the International Centre for Training and Medical Research (CIDEIM) in Cali, Colombia, she moved to Spain to undertake a PhD at the Universidad Complutense in Madrid, investigating changes in the expression of the oxidative cascade genes in malaria parasites following chloroquine exposure. Postdoctoral positions led her to the United Kingdom where she first studied mechanisms of action and resistance to antimalarials, before joining the Wellcome Trust Sanger Institute as a Scientific Manager for the malaria programme. At the Sander Institute, Leyla provided operational management to the laboratories to support the delivery of their planned goals and also undertook research focused on the study of protein-protein interactions to understand how the malaria parasites invade human erythrocytes, which resulted in the identification of a receptor that is essential for erythrocyte invasion and has a clear vaccine potential. Leyla recently moved to New Zealand, following her kiwi husband who took a position as a research scientist within the Protein Science and Engineering Team of Callaghan Innovation. Leyla enjoys cycling, travelling and cooking, and is looking forward to doing some kind of extreme sport, as she is given to believe all New Zealanders do.

*Maryne **Dubois***, a student from Paris, has recently joined Antony Fairbanks' group as part of her Master's degree in molecular chemistry majoring in organic chemistry. Maryne completed her undergraduate studies in biomedical science and during that period she completed two internships in biology and pharmacology. During her study Maryne was most interested in chemistry and so did a specialisation in chemistry in the last year of her degree. In her spare time Maryne enjoys sports and dancing. Maryne would like to go on to do a PhD in chemistry incorporating pharmacology.

*Nicole **Behme*** joined Owen Curnow's group as a research intern as part of her Master's degree in synthesising ionic liquids. Nicole is from Germany and completed research for Technische Universitat Chemnitz where she examined the self-assembly of Janus particles. In addition, Nicole was a scientific assistant involved in synthesis dyes and solvatchromatic measurements with ionic liquids. When she's not studying Nicole likes hiking, biking, painting and travel.

*Amelia **Albrett*** is working in the Department as our new instrument support person. Amelia completed her PhD in chemistry in 2009 at the University of Auckland with Penny Brothers, working on the synthesis of novel boron porphyrin derivatives. Following this, she has been a Postdoctoral Fellow at the University of Otago in Christchurch with Tony Kettle and Christine Winterbourn in the Centre for Free Radical Research. This research was concerned with investigating the role of white blood cells, free radicals and antioxidants in health and disease. Amelia enjoys travelling, dancing and spending time with family.

*Gregory **Metha*** has arrived as an Erskine Fellow. Greg is currently the Head of Chemistry at the University of Adelaide where he started as an ARC Research Fellow in 1997, transferring into academia in 2003. His research interests were initially focussed on gas phase molecular (laser) spectroscopy and this morphed into a interest in studying the fundamental properties of gas phase metal clusters, both experimentally and computationally. This has subsequently led to the exploration of metal clusters in photocatalytic systems. Greg is also actively involved in developing innovative teaching approaches to improve learing outcomes, as exemplified by his university, state and national teaching awards. When not inundated with administrative duties, he likes to travel (with his family – for pleasure), eat and imbibe local produce, and tries to balance gastronomic excesses with exercise.

MANAWATU

Massey University, Institute of Fundamental Sciences

Dr *Vyacheslav V. **Filichev*** in collaboration with Dr *Gillian E. **Norris*** has been awarded a Cancer Society grant for a project devoted to helicases, G4-DNA and drug design ($160,568 over two years).

Dr *James M. **Withers***, who successfully finished his PhD under supervision of Dr. Filichev and Associate Professor *Shane **Telfer***, has been offered a postdoc position in the laboratory of Dr *Glenn **Burley*** in the Department of Pure and Applied Chemistry at University of Strathclyde, UK. Jamie will start working on the design and preparation of modified DNA nanostructures, DNA-binding molecules and new surface immobilisation chemistries in July 2015.

Dr *Gareth J. **Rowlands*** welcomed *Leonie **McKenzie*** who joined the Massey synthetic chemists for her PhD and *Lise **Deuilhe*** as a French intern for four months.

The Institute of Fundamental Science welcomed several international guest speakers to the campus. These speakers and their talks were: Professor *Joshua J.* **Pak** from Idaho State University, *I-III Bimetallic complexes: molecular precursors for chalcogenide semiconductors*; Associate Professor *Ketul **Popat*** from Colorado State University, *Micro/Nano-engineering of material surfaces for tissue engineering and regenerative medicine*; and Professor *Greg **Metha*** from Adelaide University, *Metal nanoparticles and clusters*.

OTAGO

Professor *Larry **Overman*** (University of California, Irvine) was in New Zealand in March to give the 2015 Ferrier Lecture. He visited the University of Otago to meet with staff and presented an excellent seminar, cosponsored by the NZIC, titled *Linking chiral rings at stereocenters*.

University of Otago, Department of Chemistry

The Polymer and Supramolecular Group (Moratti and Hanton) welcomed *Eleonore **Mathis*** as a project student from France here for six weeks. *Sophie **Mills*** recently graduated from the group with a well-deserved MSc with distinction. The group's work was highlighted on *Our changing world* (Radio New Zealand National, 26 March) which gave an account of recent "experiments" in dropping our gels from a helicopter to show how tough they are. *Stephen **Moratti*** returned from Morocco where he presented the group's work on supramolecular gels at the 13th International Conference on Polymers and Advanced Materials.

The exhibition *The world of Joseph W. Mellor (1869-1938) chemist, ceramicist, & cartoonist* ran 17 December 2014 – 5 March 2015 at the De Beer Gallery, University of Otago Central Library. Notable items on display included a manuscript 'textbook' notebook compiled by Mellor in 1888-1890, testimonials from Professor James Gow Black and George M. Thomson, and Mellor's chemistry publications including his *Comprehensive treatise on inorganic and theoretical chemistry* (1922-1937). Co-curator *Lyall **Hanton*** opened the exhibition and presented a public lecture on the life Mellor in February. An online version of the exhibition is available at: *www.otago.ac.nz/library/exhibitions/mellor/*

*Bill **Hawkins*** was invited to speak at SynthCon3, a biennial conference focused on synthetic chemistry in Australia, held in the Yarra Valley in April 2015.

Jameson group PhD student *Casey **Davies*** has been awarded both a Freemasons' Postgraduate Scholarship and also a Brooker United Travel award. Concluding their PhD studies in the Brooker group, *Matthias **Fellner*** successfully defended his PhD thesis in May and *Antonia **Seidel*** recently presented a research seminar about *Kinetic studies of lactoperoxidase.*

In March, *Daniel **Killeen*** presented his PhD research *Carrots, beer and mānuka: quantitation and localisation of bioactive natural products by spectroscopic methods* co-supervised by *Nigel **Perry*** and *Keith **Gordon***. Daniel then successfully defended his thesis, which was placed on the Division of Sciences Exceptional Thesis List. He has published four papers from his thesis work including a study in *New Phytologist* which used Raman microscopy to demonstrate that mānuka sequesters herbicidal β-triketones in leaf oil glands. Daniel has accepted a position with Plant & Food Research in Nelson, where he will be performing research relating to marine natural products.

*Jeremy **Rooney*** is a recipient of a Callaghan Fellowship to undertake PhD research in the Gordon group. Jeremy will be working with NZ Steel and is co-supervised by *Steve **Moratti***. *Jonathan **Barnsley*** has been selected as a finalist for the AMP Ignite *Pitch Your PhD* competition. He will present how dye-sensitised solar cells work and why solar energy is an interesting realm of research. *Geoffrey **Smith*** is speaking at the upcoming International Conference on Advanced Vibrational Spectroscopy in Vienna about his work titled *Imaging the desolate microscopic landscape of cheese using Raman microscopy* that was conducted in conjunction with Fonterra. Keith Gordon is an invited speaker at the meeting and *Greg **Huff*** who is also attending the conference was a recipient of a travel scholarship.

Congratulations to *Chris* and *Megan **Larsen*** on the birth of their baby daughter Mia, and to *Alvie **Lo*** and Tye on the birth of their second child, daughter Aeress. Mothers and children are doing well; fathers are both writing-up.

*Matthew **Clarkson*** has joined the department to undertake postdoctoral research using metal isotope systems to investigate the de-oxygenation of the oceans during warm 'super greenhouse' climates occurring 90 million years ago, as part of a Marsden-funded project led by *Claudine **Stirling***. Matthew's PhD work at the University of Edinburgh, linking ocean acidification to widespread mass extinction 252 million years ago, has been published in *Science* (**2015**, *348*, 229–232).

WAIKATO

University of Waikato

Professor *Doug **Macfarlane***, the RSC Australasian Lecturer from Monash University, Australia, recently visited and gave a very well attended lecture on *Ionic liquids for sustainable chemistry: applications in the chemical-, materials-, electro- and bio-sciences*.

We welcomed Blair Munro as a new first-year tutor in chemistry and farewelled Pat Gread who retired recently after 26 years of service as a technician in the department. Pat was in charge of the first-year laboratory when she started at Waikato, but for many years was in charge of the second- and third-year organic and inorganic laboratories. Her experience and dedication to that role was absolutely invaluable. She was the "go to" person for any problems in the lab and many students, demonstrators and staff have benefitted from her wisdom and experience in these lab classes. Outside of these classes, Pat was always a very willing helper in other areas. As the technician in charge of the Micro-ToF mass spectrometer, she has been invaluable to many research projects, training students and running samples, including those for chemical services. Pat could always be relied upon to assist capably with school visits, university open days and after hours publicity events such as Chemquest. Pat's talents extend well beyond chemistry. She is an enthusiastic cyclist, walker and bridge player, and an excellent cake baker and decorator, baking cakes for staff morning teas and for grandson Aidan's birthday parties. We wish Pat all the very best in her well-deserved retirement.

Recently submitted theses in the department include:

PhD:

Megan Grainger: Kinetics of conversion of dihydroxyacetone to methylglyoxal in honey (supervisors Merilyn Manley-Harris, Jo Lane and Emeritus Professor Richard J. Field (University of Montana, Missoula, USA).

John McDonald-Wharry: Carbonisation of harakeke (Phormium tenax) biomass for potential application as composite reinforcement (supervisors Merilyn Manley-Harris and Kim Pickering).

MSc:

Daniel Bernstein: Development of a method for trace analysis of dioctyl sodium sulfosuccinate by liquid chromatography mass spectrometry and its application to samples from the MV Rena incident (supervisor Merilyn Manley-Harris).

Alicia Lloyd: Analysis of amino acids in manuka honey (supervisor Merilyn Manley-Harris).

Steven Salmon: An estimation of the concentration of atmospheric nitrous oxide containing complexes (supervisor Jo Lane).

Alice Wang: Elucidating the modes of action of the antitumour New Zealand marine natural product pterocellin A (supervisor Michèle Prinsep).

Megan Wyllie: Applications of hydroxymethylphosphines (supervisor Bill Henderson).

BSc (Hons):

Richard Brunton: *The extraction, quantification and characterisation of kavalactones from Piper methysticum (Kava)* (supervisor Merilyn Manley-Harris).

Geoffrey Tait: *Natural products from Malaysian fungi* (supervisor *Michèle Prinsep*).

Hayden Thomas: *Synthesis & characterisation of mercury and rhodium NHC complexes containing polyfluoroaryl substituents* (supervisor *Graham Saunders*).

New students include Huma Saeed who is doing an environmental chemistry PhD with Adam Hartland

and *Michael* ***Mucalo*** on lakes and phosphorus, Hayden Thomas who is undertaking a PhD with Graham Saunders on synthesis and reactions of metal complexes of fluoroaryl-substituted *N*-heterocycle carbenes, Hannah Lowry who is undertaking a Masters project with *Michael Mucalo* on controlled release delivery of bio-actives/nutrients of relevance to the agritech sector, Jacob Shrubsall who is undertaking a Masters project with Michèle Prinsep on bioactive natural products from marine bryozoans, Lewis Dean who is carrying out his Honours project with Michèle Prinsep on peptides from nudibranchs and their bryozoan prey and Connor Haisley-Bossard who is carrying out his Honours project with Merilyn Manley-Harris studying the nectar of *Dactylanthus taylorii*.

WELLINGTON

W.E. (*Bunt*) ***Dasent***, a longstanding member of the Branch, former VUW senior lecturer in Chemistry, Bursar and eventually its Pro-Vice-Chancellor died on July 11.

The first meeting of 2015 was the March meeting addressed by Dr Rhian Salmon (Victoria University of Wellington) on *Adventures and opportunities made possible by studying chemistry* in which she described the opportunities available after taking a science degree because we want to *make a difference*. This could be as true in medicine, new technologies, psychology and physics as environmental sciences such as conservation biology or climate change research. But what aspects of our science really do make a difference? Is it the doing, or the understanding? Is it the results or the communication of those results? She took us on a journey through different aspects of her career – from a BSc in chemistry and PhD in atmospheric chemistry – to becoming an Antarctic research scientist and climate science communicator. She took a critical look at how (or indeed if) we can make a difference with our science, and how chemistry in particular influenced her life and career. Rhian is a senior lecturer in the Science in Context group at Victoria University and has designed and co-ordinated a wide range of public engagement activities related to environmental science. Her research now focuses on communication activities by scientists.

Dr Alexander Maxwell of Victoria's History Department provided the April seminar and gave a fascinating and illuminating discourse *From alchemy to Moseley: a history of the elements*. He began by pointing out that elemental theories of matter have a long history and illustrated the four-element theory from ancient times to the beginning of modern history. He then pointed out that Marie-Anne and Antoine Lavoisier together first provided the beginnings of our current understanding of elements in the late eighteenth century. During the nineteenth century, various discoveries enabled Mendeleev to devise his periodic system. Then the great discoveries of quantum mechanics enabled scientists to construct a complete table of elements in the early twentieth century culminating in Moseley's completion and prediction of the missing long-lived elements.

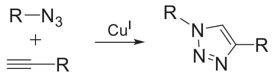
May saw Dr Bridget Ingham of Callaghan Innovation speak on *Shining synchrotron light on materials science*. She discussed the nature of synchrotron facilities - large X-ray light sources, producing intensely focused beams six or more orders of magnitude brighter than laboratory instruments. The increased flux thus available offers better signal to noise ratios and reduced measurement time, to the point where performing real-time studies is possible. The X-ray wavelength is also tuneable, allowing element-specific information to be obtained. She went on to give an introduction to synchrotron radiation and illustrate how it can be used by way of case studies, including *in situ* electrochemical corrosion experiments, nanoparticle formation, amorphous metal carbide fuel cell electrode materials, structural transitions in polymers, and the mimicking of calcium-binding to protein micelles in milk. Bridget is now a senior researcher at Callaghan Innovation. She gained her physics PhD at VUW and undertook postdoctoral studies at Imperial College (London) and the Stanford Synchrotron Radiation Light source where she developed her expertise in the use of synchrotron techniques. She has been a member of the powder diffraction and small angle X-ray scattering proposal advisory committees at the Australian Synchrotron, and represented New Zealand synchrotron users on the user advisory committee. Her current role is to provide synchrotron advice and expertise to the NZ science community.

Victoria University – SCPS

The 2014 Ferrier lecture was delivered by Professor Larry Overman (Chemistry Department, University of California-Irvine) on March 3. He visited the Ferrier Institute and gave a research lecture the previous afternoon and then delivered the more general named lecture in the evening in Rutherford House on the VUW Pipitea campus. The Overman group has developed an amazing ability to design and synthesise new molecules for molecular level investigations in many areas of science. The research centres on the invention of new transformations and strategies in organic synthesis, and the total synthesis of complex organic molecules having promising biological properties. The named lecture was entitled: *Natural products synthesis: insights into chemical reactivity and inspiration for new antitumor agents* in which Larry described two of his recent natural products total synthesis projects, one that led to new strategies for coupling complex molecular fragments and another to a new class of preclinical epigenetic antitumor agents. His more 'hard core' Monday lecture at Gracefield covered aspects of the epipolythiodiketopiperazine (ETP) alkaloids. These are described as highly complex natural products with potent anticancer activity; gliotoxin and sporidesmin are examples.

Professor *Peter* ***Schwerdtfeger***, 2014 Rutherford Medallist (Centre for Theoretical Chemistry and Physics, Massey University, Auckland) visited the School on March 6 and gave his lecture: *The topology of fullerenes*. He pointed out that fullerenes are three-connected cubic planar graphs consisting of pentagons and hexagons only. He outlined the great progress over the last two decades describing the topological and graph theoretical properties of fullerenes, and then pointed out the many unsolved and interesting mathematical (and chemical) problems open in this field. A few examples he discussed included *i*) how to generate all possible non-isomorphic graphs for a fixed vertex count, *ii*) whether fullerenes are Hamiltonian (Barnette's conjecture) and what is the number of distinct Hamiltonian cycles, *iii*) the Pauling bond order and the number of perfect matchings and *iv*) the search for suitable topological indices to find the most stable fullerene structure out of the many (N^9) possibilities, or how to pack fullerene cages in 3D space (Hilbert problem). His research group in Albany is now developing a general-purpose program (*Program Fullerene*) that creates 2D graphs and accurate 3D structures for any fullerene isomer through various different graph-theoretical methods and algorithms, and subsequently performs a topological analysis.

Associate Professor *James D.* ***Crowley*** (Otago University) visited and gave an excellent well attended seminar entitled *Functional (supramolecular) molecular architectures and machines: It's as easy as 1,2,3 'click'* in late March. The cycloaddition of an organic azide with a terminal alkyne catalysed by Cu(I) readily provides 1,4-disubstriuted 1,2,3-triazoles (**1**) and it is this reaction that has led the Crowley group to much success in area of functionalised molecular architectures.



1

The lecture concentrated on the metallo-macrocycles and cages generated this way and diverged to discuss their potential use as antibacterial, anti-cancer and drug delivery agents. Dr Kelling Donald (Department of Chemistry, University of Richmond, Virginia) visited at the end of March and gave a seminar entitled: *The ionic switch - chemical bonding and relativistic effects in binary metal dihalides*. He gained his PhD at the University of The West Indies, had postdoctoral experience at Cornell and Darmsadt T.U., and is currently an Associate Professor at Richmond. Although it was a select audience, he gave a fascinating lecture. Dr Gregory F. Metha (Department of Chemistry, University of Adelaide) gave a seminar entitled *Combining theory and experiment to understand the photocatalytic potential of metal clusters on titania* and met with relevant staff members. His June 5 seminar covered the background to the knowledge that gold nanoparticles of less than 2 nm in size are catalytically active. He went on to show that strong evidence is emerging showing that very small gold clusters, comprising only a dozen or so gold atoms, are responsible for most of the activity of catalysts prepared by crude methods, even though such small clusters constitute <1% of the total gold content on the surface. He then went on to discuss his current studies exploring the potential of a range of metal clusters such as Au_8, Au_9, Au_6Pd, Ru_3, Ru_4 and $AuRu_3$, that are ligand stabilised and experimentally confirmed to have precisely defined metal cores for use as co-catalysts in photo-catalytic processes involving various TiO_2 substrates.

Prof Kate McGrath and Lia van den Kirkhof

Dr *Ben* ***Clark***, a former VUW chemistry honours graduate (with *Peter* ***Northcote***) visited, met with colleagues and gave a lecture that summarised some of his work entitled: *Assorted natural products – metabolomics, chemotaxonomy, and drug discovery.* This knitted together his doctoral and postdoctoral studies over the past few years and provided a summary of his areas of operation.

Among the students who graduated in May was Pauline Calloch, supervised jointly by Dr *Ian* ***Brown*** of Callaghan Innovation and Professor *Ken* ***MacKenzie*** (VUW). Dr Calloch's research was on *New reaction paths for advanced SiAlON/TiN composites*. *Lia* ***van den Kerkhof***, one of the staunch student representatives on the 2014 Branch Committee, graduated with her MSc degree from joint supervision by *Justin* ***Hodgkiss***, *Kate* ***McGrath*** and *John* ***Spencer.*** Her work encompassed the synthesis of anthracene-based liquid crystals as photon up-converters for solar cells.

Others who have completed their PhD degrees recently include *Matthias* ***Herzog*** (*Jim* ***Johnston***), *Teresa* ***Vaughan*** and *Melanie* ***Nelson*** (both *John* ***Spencer***). *Ben* ***McVey*** and *Lucy* ***Gloag*** have left Victoria University to complete their PhD studies with Professor *Richard* ***Tilley*** now at the University of New South Wales.

On 8 June, *Ken* ***McKenzie*** hosted a visit by Professor Ivar Reimanis (Metallurgy and Materials Department, Colorado School of Mines). He works on the development of energy conversion devices and transparent armour from waste materials and gave a seminar entitled: *A taste of ceramics research at Colorado School of Mines*, which highlighted the mechanical behaviour of an unusual ceramic.

Electrospray ionisation — a simple prelude to the understanding of other mass spectrometry techniques

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Keywords: *mass spectrometry, electrospray ionisation, review, applications*

Introduction

Mass spectrometry (MS) is a powerful analytical technique used in the characterisation of a wide range of chemical and biochemical substances. The technique is extensively used in research, across a wide range of disciplines. One of the main strengths of mass spectrometry is that miniscule amounts of sample are typically needed, in the order of micrograms or less. While the study of spectroscopic techniques has been a part of qualifications such as the International Baccalaureate Diploma for some time,[1] a new Achievement Standard on Spectroscopy has been introduced relatively recently into the New Zealand Chemistry Curriculum, which includes the technique of electron ionisation (EI) mass spectrometry.[2] This article aims to provide, for those perhaps encountering mass spectrometry for the very first time, a short discussion on electrospray ionisation mass spectrometry as an alternative introduction to this important analytical technique.*

Mass spectrometry

In essence, mass spectrometry separates gas phase ions according to their mass-to-charge ratios (*m/z*), which is simply the mass of an ion *m* divided by its charge *z*. There are two main processes involved in mass spectrometry – ion generation, and ion detection – and this article will focus on the former, of which electrospray ionisation is but one example. Electrospray ionisation is conceptually simple, and its beauty lies in the simple and easily interpreted spectra which are often obtained. The technique can also be used to illustrate the concept of isotopes.

Ionisation techniques

An ionisation technique is the physical process by which a sample of the substance being investigated – the *analyte* – is converted into gas phase ions. Depending on the chemical and physical nature of the sample, the choice of an appropriate ionisation technique is absolutely crucial; an ionisation technique might work beautifully for one type of substance, but be completely useless for another. A good example of this is electron ionisation (EI). In this technique, a sample of the substance is heated under vacuum, causing some of the substance to volatilise. The volatilised substance is then bombarded with high energy electrons; these cause the neutral gas-phase molecules to become positively-charged ions by loss of an electron, and the resulting ions are separated and detected. This technique is ideal for analysis of non-polar but volatile substances such as hydrocarbons, and as an illustrative example, University of Waikato researchers have used electron ionisation mass spectrometry to provide analytical data on oils recovered from the 2011 Rena marine disaster.[3] Because electron ionisation typically requires the compound to be volatile (and therefore of low molecular weight, and uncharged) it finds most use in the analysis of small organic molecules. It cannot be used to *directly* analyse polar, involatile substances such as sugars or proteins, which typically degrade rather than volatilising when heated.† Until the advent of electrospray ionisation, many types of chemical substances were effectively inaccessible to MS analysis.

Electron ionisation is also rather 'harsh', the mass spectrometry equivalent of using a sledgehammer to crack open a walnut; it works, but what is formed can sometimes pay little resemblance to the original nut. The consequence of this is that the *molecular ion* – the original starting molecule which has ionised by losing a single electron – is typically of low intensity, or in some cases unobservable. This is because the high energy of the electron ionisation process imparts excess energy to the ions formed, causing their fragmentation. This results in the formation of various fragment ions. Although this can provide a lot of very useful structural information, to the mass spectrometry beginner it can be somewhat daunting to be faced with an array of peaks. Furthermore, if it is molecular weight information which is desired, a weak or unobservable molecular ion can complicate matters. Electrospray ionisation provides a useful and simple alternative in many cases.

Electrospray ionisation

Today, electrospray ionisation (ESI) mass spectrometry is one of the most important analytical techniques used by chemists, biochemists and materials scientists; its importance was recognised by the co-award of the 2002 Nobel Prize in Chemistry to John Fenn, the inventor of the technique.[4]

Fig. 1 shows a schematic diagram of an electrospray capillary, and a typical modern mass spectrometer is shown in Fig. 2. Electrospray ionisation is conceptually quite simple, and involves forming a very fine spray of droplets of an analyte solution, using an inert nebulising gas (typically nitrogen); this is the spray part of electro**spray**. The solution is sprayed from a fine metal capillary tube, which is held at a high voltage (hence, the electro part of the word **electro**spray). The effect of this is that the droplets which are formed are enriched in positive ions (if the capillary is positive), or negative ions (if the capillary is negative). These droplets are then evaporated using more nitrogen gas, which has the effect of converting the original analyte solution into the gas phase (effectively, it has nowhere else to go!). Solubility in a suitable solvent, rather than volatility, becomes the most important factor in determining the likely success of the technique in generating ions that can be subsequently detected.

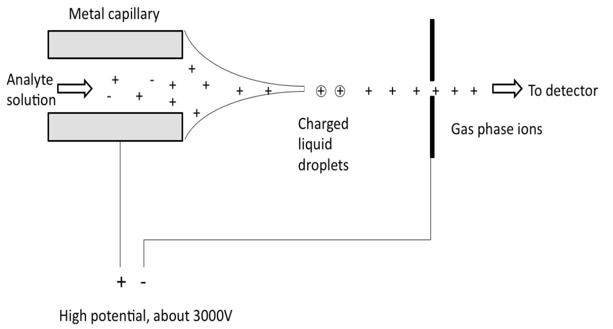

Fig. 1. A schematic diagram of an electrospray capillary, showing the ionisation process

How does it work in practice? Imagine the electrospray process applied to the analysis of a solution of sodium chloride in water. Of course, when sodium chloride is dissolved in water, Na^+(aq) and Cl^-(aq) ions are formed; spraying this solution through a positively-charged capillary produces droplets that have an excess of Na^+(aq) ions. Evaporation of these droplets forms Na^+(g) ions which can then be analysed. If the capillary is negatively-charged, the resulting droplets are enriched in negatively-charged chloride ions, so the electrospray technique can be used to study both the cations and/or the anions of salts very easily. As stated earlier, lack of volatility is not an issue – large cations such as cetylpyridinium (as its chloride salt, used as an antibacterial agent in mouthwash) can be analysed very easily, and produces the mass spectrum shown in Fig. 3.

Applications of electrospray ionisation mass spectrometry are not restricted to salts; neutral compounds can also be characterised, providing that a charge can be attached to the molecule in solution. In practice this means that the molecule should contain an atom which has at least one lone pair of electrons, for example most (but not all) of the common functionalised organic molecules (alcohols, ketones, esters, amines, amides, carbohydrates, proteins...). Protonation of the analyte molecule can commonly occur [from the small concentration of H^+(aq) ions which arise from the self-dissociation of water through $H_2O \rightarrow H^+(aq) + OH^-(aq)$], but other cations such as Na^+ (and K^+) can also form adducts[5] water stored in glass bottles will invariably contain sufficiently high concentrations of dissolved sodium ions from the glass. A neutral analyte molecule M will therefore typically give a protonated ion $[M + H]^+$, and/or a sodium adduct $[M + Na]^+$, and it is normally a very simple process to determine the molecular mass of M from the observed ions.

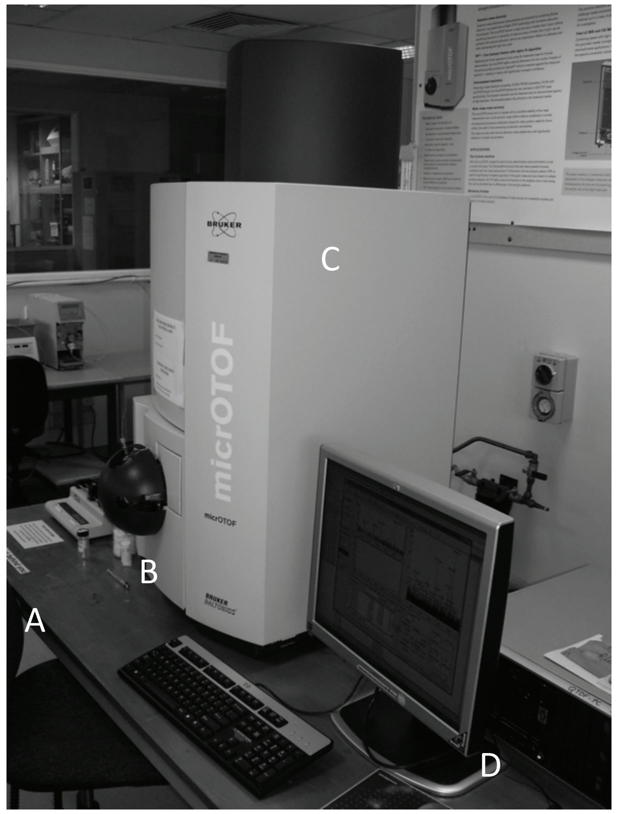

Fig. 2. A typical modern electrospray ionisation mass spectrometer (Bruker MicrOTOF); the sample is introduced *via* a syringe and a syringe pump (A) to the instrument's spray chamber (B). The ion detector in this instrument is a time-of-flight detector (C), which accurately determines the time for ions of differing *m/z* to travel the length of a long tube under vacuum. Data collection and processing is controlled by a PC (D)

Non-polar organic molecules such as alkanes cannot be analysed by ESI directly because they cannot be protonated; electron ionisation MS remains the technique of choice for these substances.

Obtaining isotope information

Many elements exist as a single stable isotope, but other elements can exist as two or more isotopes.[6] Electrospray ionisation mass spectrometry can be used to demonstrate isotopic composition very easily – indeed the power of mass spectrometry was realised in the very early days of the technique around 100 years ago, when J.J. Thomson showed that neon existed as two isotopes having atomic masses 20 and 22, in the ratio of 10:1, consistent with the average atomic mass of neon being 20.2. Since then, mass spectrometry has been extensively developed as a way of providing isotopic information, in applications that range from the nuclear industry (the first separation of uranium-235 for an atomic bomb was determined by mass spectrometry), to archaeological and geological dating techniques.

The power of the technique in providing isotope information is best illustrated by an example. Consider the analysis of an aqueous solution of silver nitrate. The ESI process simply transfers Ag^+(aq) ions to the gas phase, and removes their associated water molecules, giving 'bare' Ag^+(g) ions. Two peaks are observed, corresponding to the two isotopes of silver (^{107}Ag, 51.8% and ^{109}Ag, 48.2%)

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* This article was originally written for the general readership of *ChemEd NZ*, but with the demise of this publication, is now published in *Chemistry in New Zealand* as a gentle introduction to mass spectrometry (especially electrospray ionisation) for those unfamiliar with the technique.

† Substances such as sugars can, however, be converted into more volatile derivatives by suitably modifying them, typically by converting polar –OH groups into less polar groups such as $–OSiMe_3$, by reaction with a suitable derivatisation reagent.

as shown in Fig. 4.

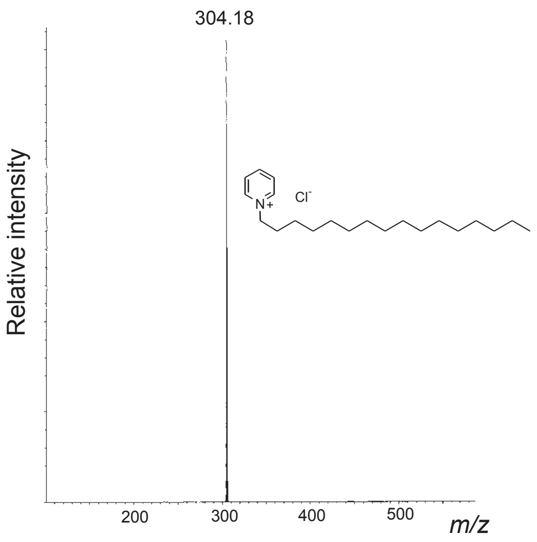

Fig. 3. Positive ion electrospray ionisation mass spectrum of cetylpyridinium chloride (structure shown as inset)

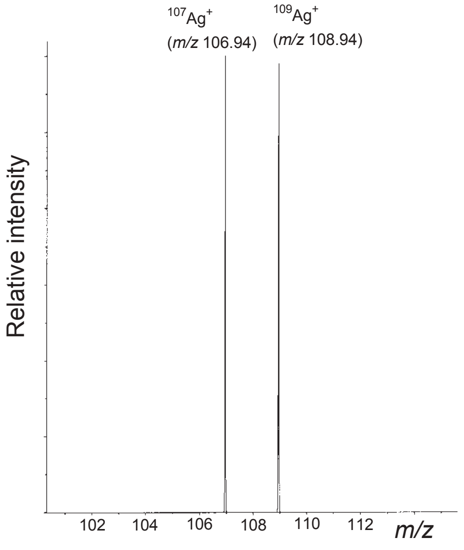

Fig. 4. Positive-ion electrospray mass spectrum of a solution of $AgNO_3$ showing the two isotopes of silver through the ions $^{107}Ag^+$ and $^{109}Ag^+$

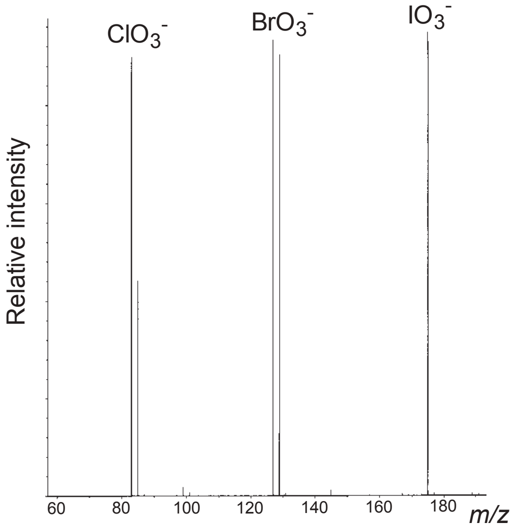

Fig. 5. Negative-ion electrospray mass spectrum of a solution containing a mixture of $KClO_3$, $KBrO_3$ and KIO_3 showing the different appearance of the ClO_3^-, BrO_3^- and IO_3^- ions arising from the elemental isotopic compositions of chlorine, bromine and iodine

A second example illustrates the ESI MS analysis of the salts $KClO_3$ (potassium chlorate), $KBrO_3$ (potassium bromate) and KIO_3 (potassium iodate). The EO_3^- ions are easily observed in the negative-ion mass spectrum. As an approximation we will assume that oxygen exists as a single stable isotope, ^{16}O.[7] The mass spectrum of a mixture of the three ions ClO_3^- + BrO_3^- + IO_3^- (Fig. 5) shows all three ions at their expected *m/z* values, but the appearance of the peaks is different for each one. This is due to the different elemental isotopic composition of the three halogens chlorine, bromine and iodine. For IO_3^-, a single peak is seen, because iodine exists as a single isotope (^{127}I), and a single peak at the expected *m/z* (127 + 3x16 = 175) is seen (charge *z* =1). However, for BrO_3^- two approximately equal intensity peaks are seen, at *m/z* 127 and 129, which are a consequence of the presence of two isotopes of bromine (^{79}Br, 50.7% and ^{81}Br, 49.3%). For ClO_3^-, two peaks are also seen at *m/z* 83 and *m/z* 85, but the intensities are now in a 3:1 ratio because of the two chlorine isotopes in unequal proportions (^{35}Cl, 75.8% and ^{37}Cl, 24.2%).

Fragmentation

Inspection of any electron ionisation mass spectrum will typically show a plethora of fragment ions, which can provide substantial structural information. Ions generated by electrospray ionisation can also be fragmented, to different extents, at will, by causing them to collide with residual nitrogen gas molecules from the ionisation process.[8] The effect of this can be seen on the negative-ion electrospray mass spectra of BrO_3^- in Fig. 6. Under low fragmentation conditions (Fig. 6a) the parent ion is observed, but under more fragmenting conditions (Fig. 6b) ions formed by loss of oxygen atoms are seen, giving sequentially BrO_2^- (bromite), BrO^- (hypobromite) and finally Br^- (bromide). Unlike electron ionisation, ESI inherently produces relatively 'intact' ions, which can be subjected to fragmentation if this is desired.

Applications of ESI MS to the analysis of polymers and biomolecules

Given that there is no requirement for an analyte to be volatile in order to be analysed by electrospray ionisation mass spectrometry, it is not surprising that the very earliest studies on the technique demonstrated its successful use in obtaining mass spectra of large, involatile and sometimes heat-sensitive molecules such as polymers and proteins. This is important because it allows the molecular weight (or in the case of a polymer, the molecular weight distribution arising from individual polymer molecules having different chain lengths) to be measured. Again, the behaviour can be illustrated by an example, in this case the polyether-amine Jeffamine® D-2000. Polyether-amines find widespread technological applications, including the formation of polymers, and as a fuel additive, for example Techron®.[9] Jeffamine® D-2000 has the structure shown in Fig. 7; it is based on the $CH(CH_3)CH_2O$ repeat unit, with NH_2 groups at each end of the chain. These amine groups are basic and provide a site for protonation in electrospray mass spectrometry analysis. The material is not a pure substance, but instead exists as a range of chain lengths, with an average of 33 $CH(CH_3)CH_2O$ repeat units in the polymer chain.[10] The ESI mass spectrum of Jeffamine® D-2000 is shown in Fig. 7. The spectrum shows two main groups of peaks; the set centred around *m/z* 1700 are due to the monoprotonated ions $[M + H]^+$, where M represents an individual polymer molecule. The separation between adjacent peaks is 59 mass units, corresponding to the mass of a $-CH(CH_3)CH_2O-$ repeat unit, and the mass of an individual polymer molecule can easily be obtained, as the mass of the ion minus 1 (for the mass of the added proton). The second set of peaks centred around *m/z* 1054 is due to the doubly protonated ions $[M + 2H]^{2+}$. It is easily seen that adjacent peaks in this set are more closely spaced together (by 29.5 *m/z* units, i.e. half of 59). For these ions the smaller *m/z* values arise because the charge *z* on these ions is now 2.

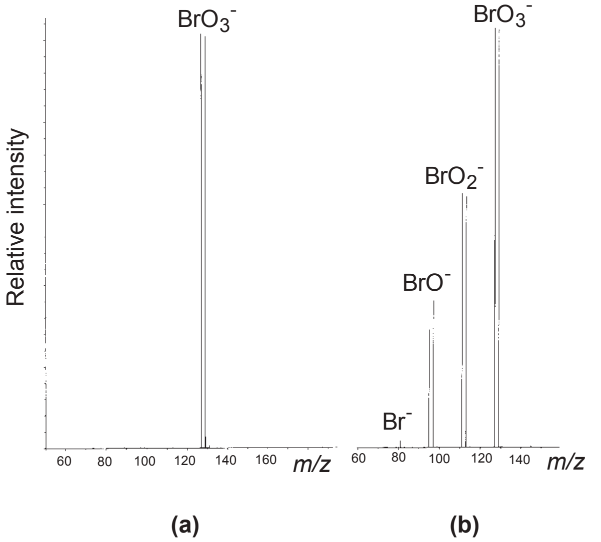

Fig. 6. Negative-ion electrospray mass spectrum of a solution of $KBrO_3$ at capillary exit voltages of (a) 70 V (non-fragmenting conditions) and (b) 180 V (fragmenting conditions) showing the formation of BrO_2^-, BrO^- and Br^- fragment ions; in each ion the distinctive isotope pattern from ^{79}Br and ^{81}Br isotopes is observed

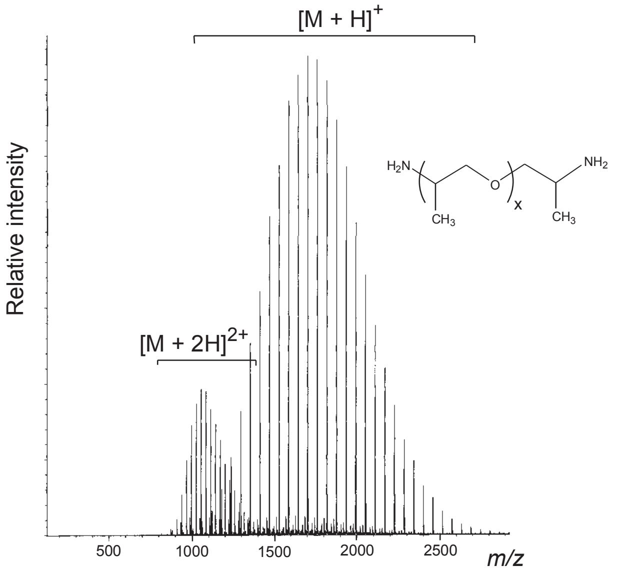

Fig. 7. Positive-ion electrospray mass spectrum of a solution of Jeffamine$^{\grave{O}}$ D-2000 showing the sets of monoprotonated $[M + H]^+$ and diprotonated $[M + 2H]^{2+}$ ions, and the structure of Jeffamine$^{\grave{O}}$ D-2000

Applications of ESI MS in inorganic chemistry

Although perhaps not immediately obvious, many inorganic substances have features in common with biological molecules such as proteins. For example, inorganic salts, and many coordination compounds are water soluble, ionic, and involatile compounds that decompose (rather than volatilise) on strong heating. Not surprisingly, ESI MS can often be usefully applied to the characterisation of many inorganic compounds, providing of course the substance is soluble in some suitable solvent, and can generate ions (if not already charged). Figs. 5 and 6 (*vide supra*) have already demonstrated the ability of ESI MS to analyse simple salts, and the reader is refereed to more comprehensive texts for a full discussion of this topic.[11]

Conclusions

Electrospray ionisation mass spectrometry (ESI MS) is a powerful analytical technique, which can be applied to almost any compound, providing it is soluble in a suitable solvent, and providing it is either charged, or can become charged by a suitable, gentle, solution-based process (protonation, addition of alkali metal cations such as Na^+, and others). ESI MS has revolutionised the characterisation of many types of substances that were previously relatively inaccessible to mass spectrometry techniques, in particular polymers, bio-molecules such as proteins, as well as involatile inorganic compounds. The beauty of the technique lies in its gentle ionisation (which causes minimum fragmentation), and the simplicity of the spectra which are often obtained. However, as with any analytical technique, it has its limitations, and electron ionisation mass spectrometry – the technique which has been chosen to represent mass spectrometry in the Chemistry curriculum – retains an important role for the analysis of volatile, and in particular, non-polar organic molecules.

References and notes

1. See for example: Brown, C.; Ford, M.; *Standard Level Chemistry developed specifically for the IB Diploma*, Pearson Education, Harlow, Essex, 2008.
2. Achievement Standard AS91388 Chemistry 3.2: *Demonstrate understanding of spectroscopic data in chemistry*, December 2012, available at http://www.nzqa.govt.nz/qualifications-standards/qualifications/ncea/ (accessed 10/03/2015).
3. See: http://sci.waikato.ac.nz/research/projects-and-case-studies/rena-research (accessed 10/03/2015).
4. See: http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2002/illpres/mass.html (accessed 10/03/2015).
5. Sodium and potassium ions are invariably present in low concentrations when solvents such as water and alcohols are stored in glass bottles (glass contains considerable amounts of sodium ions).
6. Information on the isotopic composition of the elements can be obtained from books, for example *Aylward and Findlay's SI Chemical Data*, A. Blackman and L. Gahan, John Wiley & Sons, 7th edition 2013 (or earlier editions). Alternatively, reputable online data sources such as from the Royal Society of Chemistry (http://www.rsc.org/periodic-table) and tools such as the University of Sheffield's Chemputer (http://winter.group.shef.ac.uk/chemputer/isotopes.html) provide easily-accessed data.

Continued on page 136

Carbon sequestration chemistry

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Keywords: *carbon sequestration, carbon dioxide, photosynthesis, carbonisation, carbonation, charcoal*

The amount of carbon dioxide in the earth's atmosphere has increased by approximately 40% between 1850 and 2015. The cause of this increase is largely attributed to the industrial-scale combustion of coal, petroleum and natural gas.[1] Cement production, deforestation and other land-use changes are also regarded as making significant contribution to this massive transfer of carbon to the atmosphere. Reducing additional emissions of carbon dioxide in an effort to reduce risk of global warming and ocean acidification has been widely discussed for many decades. Even if global carbon dioxide emissions are drastically reduced during the course of this century, hundreds of gigatonnes (1 gigatonne is 1,000,000,000 tonnes or 10^{12} kg) of excess carbon may need to be actively removed from the atmosphere and then stored or sequestered for a long period of time. Practices which can result in net transfer of carbon from the atmosphere into solid materials or geological/marine reservoirs are referred to by a number of terms including "carbon sequestration", "carbon dioxide removal" (CDR) and "negative emissions technologies" (NETs).[1] Such practices are sometimes given the more controversial labels of "geoengineering", "climate engineering" or "climate intervention" depending on the definition being used and often the intentions of those proposing (or carrying out) practices which could sequester carbon.[1a] This article will briefly cover the industrial production of carbon dioxide and the major approaches that have been proposed for carbon sequestration. The proposed approaches will be grouped according to the chemical form of the stored carbon (carbon dioxide, cellulosic biomass, chars, carbonates, and bicarbonates).

The industrial production of carbon dioxide

The combustion of coal, petroleum and natural gas are regarded as making the largest contribution to increasing atmospheric CO_2 levels over the last few centuries. The combustion of coals is represented in a generalised way in equation 1 (based on a middle of the range bituminous coal while ignoring the ash and sulfur components[2]). The combustion of the major component of natural gas (methane) is represented in equation 2. Complete combustion reactions for the various hydrocarbons in petroleum would fall between the coal and methane examples with lighter hydrocarbon producing more water relative to carbon dioxide.

$$\text{(Coal) } CH_{0.66}O_{0.07} + 1.13O_2 \rightarrow CO_2 + 0.33H_2O \qquad \text{(Eq. 1)}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \text{(Eq. 2)}$$

Other industrial processes also add large quantities of carbon dioxide to the atmosphere, chief among these are ones which involve calcination of calcium carbonates such as the manufacture of Portland cement clinker from limestone and sand (equation 3).[3]

$$5CaCO_3 + 2SiO_2 \rightarrow 3CaO.SiO_2 + 2CaO.SiO_2 + 5CO_2 \quad \text{(Eq. 3)}$$

Capture or collection of carbon dioxide

As the carbon dioxide concentration in flue gas from industrial facilities such as thermal power stations are around 350 times higher than the atmosphere it makes sense where practical to collect/capture carbon dioxide at these emission sources.[4]

The two main approaches to collecting carbon dioxide from the atmosphere are direct air capture (DAC) and biological photosynthesis. DAC proposals usually involve large devices to scrub carbon dioxide from the atmosphere using alkaline solutions or amine resins with a regeneration cycle,[1b,4a] which are currently considered both expensive and having large energy requirements.[5] The biological photosynthesis approach instead involves growing trees, crops, or algae which are naturally solar powered. Most of the proposed approaches to sequester carbon dioxide as carbonates discussed later in this article have been initially targeted towards the high concentration industrial emission point sources, though in principle could use carbon dioxide recovered from the atmosphere by DAC proposals.

Carbon sequestration through geological storage of carbon dioxide

In the case of geological storage, the plan is to store carbon by pumping compressed carbon dioxide into underground reservoirs. Geological formations such as depleted oils wells and deep saline aquifers are the commonly proposed reservoirs. In some situations the carbon dioxide is expected to react with brines of minerals to form solid carbonates otherwise it is hoped that impermeable rock layers will hold the carbon dioxide underground. Geological storage is often proposed as part of carbon capture and storage (CCS) proposals where carbon dioxide is to be scrubbed from the flue gas from thermal power stations, compressed and then injected into geological formations.[1b,4a]

One type of proposal gaining prominence is bioenergy with CCS, where the thermal power station is burning biomass. As the carbon in biomass was relatively recently removed from the atmosphere by photosynthesis, storing the post-combustion carbon dioxide underground should in principle be able to reduce atmospheric carbon dioxide concentrations.[4a,6]

Carbon sequestration in cellulosic biomass

Globally, photosynthesis by organisms such as plants is estimated to remove around 120 gigatonnes of carbon from the atmosphere each year. However, plants are estimated to quickly return around half this carbon back to the atmosphere as CO_2 due to respiration.[1b] Large amounts of carbon go into building polymers such as cellulose and lignin to be used in structures such as leaves and wood (Eq. 4) which allows living biomass to store a considerable amount of carbon (estimated at around 560 gigatonnes of carbon). However, ecosystems can release almost as much carbon as they remove from the atmosphere on an annual basis since much of the biomass will eventually be eaten, burnt or decomposed.[1b, 7]

$$CO_2 + 0.85H_2O \rightarrow \text{(wood) } CH_{1.70}O_{0.59} + 1.13O_2 \qquad \text{(Eq. 4)}$$

Planting forests and letting arable land revert to woodland is known to cause an accumulation of carbon in living tree biomass, as well as leaf litter and soil carbon, with the majority of carbon accumulated in above ground biomass.[8] If protected from decomposition, biomass can sequester carbon by keeping it out of the atmosphere for longer periods of time. A number of approaches have been proposed based on collecting and storing biomass for carbon sequestration including the sinking of crop residues into the anoxic deep ocean[7a] and increased wood harvest with the burial of logs in abandoned mines.[7b]

Carbon sequestration in chars and carbonised biomass

Heating wood and other biomass material and converting them into carbon-rich chars is a very old practice with the resulting chars often used as charcoal for fuels and smelting metals. Another old practice, that of adding chars to cultivated soils as a soil conditioner, has recently seen a considerable revival of interest in using these so-called biochars to both sequester carbon and improve soil fertility.[9]

The pyrolysis and carbonisation of biomass is complicated with complex mix of reactions taking place as the biomass is heated. Equation 5 is based on the approximate stoichiometric equation for cellulose pyrolysis at 400 °C proposed by Klason *et al.* in 1909 and shows the formation of char along with a mixture of pyrolysis tars.[10]

$$\text{(Cellulose) } C_{1.6}H_{2.67}O_{1.33} \rightarrow \text{(char) } CH_{0.60}O_{0.13} + \text{(tars) } C_{0.40}H_{0.33}O_{0.10} + 0.13CO_2 + 0.07CO + 0.77H_2O \quad \text{(Eq. 5)}$$

Most biomass contains other polymers such as lignin and hemicellulose which adds complexity to the charring reaction . The resulting char is also often carbonised further at temperatures well above 400 °C, resulting in further enrichment in carbon with the preferential removal of hydrogen and oxygen. Chars produced at higher carbonisation temperatures are generally considered more stable and resistant to decay than those produced at lower temperatures.[9b,11]

In many cases, the tars, oils, carbon monoxide and hydrogen formed during biomass pyrolysis are combusted to supply heat or electricity, although there is considerable interest collecting some these products for uses such as liquid fuels.[9a, 12] A stoichiometric equation which approximates the preparation of a char carbonised at ~700 °C from a pine wood precursor[13] and assuming the complete combustion of the non-char pyrolysis products is approximated in equation 6. Combined with the photosynthesis chemistry which formed the wood in the first place, a simplified equation for the net conversion of carbon dioxide into char is represented in equation 7. Well-carbonised chars often contain more than 80% carbon by weight when dry, making them one of the more concentrated forms of carbon sequestration.

$$\text{(Wood) } C_{1.96}H_{3.33}O_{1.16} + 1.2O_2 \rightarrow \text{(char) } CH_{0.18}O_{0.06} + 0.96CO_2 + 1.573H_2O \qquad \text{(Eq. 6)}$$

$$CO_2 + 0.09\ H_2O \rightarrow \text{(char) } CH_{0.18}O_{0.06} + 1.015\ O_2 \qquad (7)$$

There is also scope to sequester carbon in construction materials which contain biomass-derived chars. Like soil conditioner applications, the use of charred and carbonised biomass in construction is also an ancient practice with the Roman engineer Vitruvius recommending the use of charred wooden stakes and charcoal especially in the construction of foundations owing to their resistance to decay.[14] Evidence of the use of chars in ancient Chinese and Japanese construction is also reported.[15] Recently, char-plaster and char-concrete composites have been developed at the Ithaki institute.[16] At the University of Waikato, char-resin composites have been under research and development since 2010, with the latest formulations having over 80% of the carbon content sourced from recent photosynthesis with scope to sequester over a kilogram of carbon per litre of material. Early char-resin composite research appears to have been focused toward dental implants and the last few years have seen a large increase in papers featuring various types of composite materials containing charred/carbonised biomass.[17]

Carbon sequestration in carbonates

Many proposed approaches to carbon sequestration involve the formation of magnesium carbonates and/or calcium carbonates using carbon dioxide as a feedstock (sourced either from the atmosphere or directly from emission sources). Carbonate formation takes place when some metal silicates, metal oxides or metal hydroxides react with carbon dioxide. These reactions are exothermic and occur naturally during the weathering of some minerals.[1b,18] Calcium silicate and carbon dioxide forming calcium carbonate and silica is shown in Reaction 8.[18]

$$\text{(Wollastonite) } CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 \qquad \text{(Eq. 8)}$$

Because silicate weathering reactions are regarded as slow at lower temperatures and atmospheric concentrations of carbon dioxide, research effort has been devoted to accelerating this carbonisation process by carrying out the reaction using elevated temperatures, higher carbon dioxide pressures and catalysts.[18-19] Olivine and serpentine are magnesium silicate minerals commonly proposed to be mined for carbon sequestration reactants. Equation 9 represents the net reaction commonly proposed for olivine and carbon dioxide reacting to form magnesium carbonate (magnesite) and silica.[1b, 18-19] In a patent concerning silicate-to-carbonate processes for carbon sequestration, Blencoe *et al.* used sodium hydroxide to form metal (calcium, magnesium or iron) hydroxides and then regenerate the sodium hydroxide at the end of the process as the metal carbonates are precipitated from an aqueous solution. The use of resulting carbonates as materials for road construction, amendment of acidic soils and cement-like products has also been proposed.[19]

$$\text{(Olivine) } 0.5Mg_2SiO_4 + CO_2 \rightarrow MgCO_3 + 0.5SiO_2 \qquad \text{(Eq. 9)}$$

The Calera Corporation also proposed a means of capturing carbon dioxide from industrial sources and converting it into carbonate minerals for carbon sequestration and construction materials.[20] Equations 10 and 11 are the reported overall reactions for Calera processes which proceed through bicarbonate and carbonate ions formed by reactions with the hydroxide ions. These reactions require a supply of calcium and/or magnesium cations along with a source of alkalinity which appears to be consumed in the overall process.[21] Alkalinity was proposed to be sourced through electrolysis of sodium chloride to produce sodium hydroxide and HCl. The magnesium and calcium were at one stage proposed to be sourced from brines (either natural or residue from seawater desalinisation) or fly ash.[21] The high costs associated with electrochemistry in the Calera process were reported to have led to the founder of Calera Corporation leaving and starting a new company (Blue Planet) with the same goal of sequestering carbon in carbonate construction materials made using seawater, while claiming to have overcome the limitations of the Calera processes using an osmotic process rather than electrolysis to supply the alkalinity.[22]

$$Ca^{2+} + CO_2 + 2OH^- \rightarrow CaCO_3 + H_2O \qquad \text{(Eq. 10)}$$

$$Mg^{2+} + CO_2 + 2OH^- \rightarrow MgCO_3 + H_2O \qquad \text{(Eq. 11)}$$

Metal oxides found in slags, cement manufacturing waste and fly ash from coal burning can be reacted with CO_2 to form carbonate minerals. If the metal oxide reactants are formed originally from carbonates, then equation 12 and equation 13 will overall only be replacing (to some extent) the carbon dioxide released when the original carbonates were calcinated. Precipitated calcium carbonate formed in equation 13 (although going through a slaked lime, calcium hydroxide step) is reported to be produced industrially at several million tonnes per year to be used in the paper industry[23].

$$MgO + CO_2 \rightarrow MgCO_3 \qquad \text{(Eq. 12)}$$

$$CaO + CO_2 \rightarrow CaCO_3 \qquad \text{(Eq. 13)}$$

In a similar carbonation process, some calcium species in cement will react with carbon dioxide to form carbonates. These cementitious carbonation reactions have been estimated to recover ~8% of the carbon dioxide released during the calcination of limestone as part of the cement manufacturing process over the lifetime of a building. The grinding of demolition concrete and exposing it to air for 30 years has also been estimated to increase this re-carbonation up to 57%.[24] Curing concrete using carbon dioxide instead of water has also been proposed as a way of sequestering carbon, rapidly re-carbonising a large proportion of the cement and reducing the net amount of carbon dioxide released during cement manufacture.[25]

Carbon sequestration in dissolved bicarbonates

Instead of storing sequestered carbon in solid carbonate minerals, a number of proposals aim to store the carbon as bicarbonate anions dissolved in water. A source of magnesium, calcium or other metal is required and a number of factors in the water chemistry can affect the bicarbonate formation.[4b,26] Due to the difference in charge between the bicarbonate and carbonate ions, bicarbonate ions could theoretically sequester twice as much carbon per atom of calcium or magnesium when compared to carbonate ions based on stoichiometry. This is shown in equation 14 from a proposal which involves the accelerated weathering of olivine-containing rock by grinding it into a fine powder before spreading it on land, large river systems or the ocean, although in practice it is unlikely to reach this theoretical maximum.[26a]

$$\text{(Olivine) } Mg_2SiO_4 + 4CO_2 + 4H_2O \rightarrow 2Mg^{2+} + 4HCO_3^- + H_4SiO_4 \qquad \text{(Eq. 14)}$$

Another proposal, often called "ocean liming",[4a] involves the addition of calcium oxide into the upper ocean where it is expected to dissolve, react with carbon dioxide and then store the carbon as bicarbonate ions. Equation 15 is the net reaction proposed by Kheshgi with the minor species not listed said to account for the discrepancy in hydrogen stoichiometry.[26b] Since the calcium oxide of equation 15 will likely be produced from calcium carbonate which releases carbon dioxide, this will in effect reduce the net carbon dioxide sequestered by ~56% (without including extra emissions if coal or gas are used to supply energy to the calcination kilns). This ocean liming approach is often combined in proposals with collection and geological storage of the carbon dioxide emission from the calcination kilns.[4a,26b]

$$CaO + 1.79CO_2 + 0.79H_2O + \ldots \rightarrow Ca^{2+} + 1.62HCO_3^- + 0.17CO_3^{2-} + \ldots \qquad \text{(Eq. 15)}$$

A proposal intended to avoid the need for calcium carbonate calcination was put forth by Rau and Calderia. It involves the reaction of carbon dioxide in flue gas with a wet bed or slurry of calcium carbonate. The reaction involves the formation of carbonic acid when the carbon dioxide and water react, with the net reaction shown as equation 16.[4b] The bicarbonate solution is then proposed to be dumped in the ocean.

$$\text{(Limestone, calcite) } CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \qquad \text{(Eq. 16)}$$

Questions of scale and feasibility

With global carbon dioxide emissions from human activity estimated to total around 10 gigatonnes of carbon per year,[5] important questions arise concerning whether carbon sequestration proposals are feasible on a scale sufficient to make a significant difference to the carbon dioxide concentration in the atmosphere.

The case of mineral carbonation converting the mineral olivine into magnesium carbonate provides an example of the massive material requirements for carbon sequestration proposals in general. Pure magnesium carbonate is just over 14% carbon by mass, therefore it would take approximately 7 gigatonnes of magnesium carbonate to store 1 gigatonne of carbon. Based on its density,[27] this quantity of magnesium carbonate would take up at least 2260 million cubic metres and this volume is hypothetically represented as a cube in Fig. 1. In practice, quantities of material involved would be considerably larger, since rocks containing olivine are not purely magnesium minerals and silica is also formed in the carbonation reactions mixed with the carbonates. Unreacted olivine will often be present if the olivine is not ground finely enough for it to completely react, which could increase the amount of material required. Calcium carbonate is only 12% carbon by mass, meaning that a greater volume and mass of material would be needed to sequester a given amount of carbon as calcium carbonate. Calcium and magnesium silicates are abundant minerals so in principle there is more than enough mineral feedstocks to potentially sequester many thousands of gigatonnes worth of carbon emissions as carbonates.[18] The feasibility is more a question of handling and processing materials at these massive scales. Portland cement production is one of the few industrial processes conducted at the scale of a few gigatonnes per year[3,20] and current production is estimated to exceed 3.4 gigatonnes per year.[4a] The global cement industry is an important example of the reality of what is involved in mining, processing, handling and utilisation of materials on the scale of gigatonnes. Carbon sequestration potential of carbonate and bicarbonate-based proposals are often estimated at between 0.5 and 2.7 gigatonnes of carbon per year.[4a,26a] Although it is theoretically possible that they could be implemented at far larger scales, it is difficult to assess the plausibility of activities at a scale much larger than contemporary cement manufacture.

Sequestering carbon in wood (~ 50% carbon by dry mass) or well-carbonised chars (>80% carbon by dry mass) requires less mass of material per tonne of carbon sequestered when compared to the use of carbonates. However, such sequestration is reliant on biological photosynthesis and at the scale of gigatonnes such carbon sequestration activity would consume a few percent of total net primary production of the entire planet's ecosystems. For biochar, the extremely ambitious estimates for the amount of carbon that could be sequestered globally range between[12a] 3.25 and 9.5 gigatonnes of carbon per year by the end of the century[9a,12a] with lower estimates of 0.6-1 gigatonnes per year considered more credible. Wood harvest and storage proposals have reported that a rough theoretical potential of 10±5 gigatonnes of carbon could be sequestered per year, although these estimates were reduced to 1-3 gigatonnes per year once large land areas were removed from the calculations to account for existing uses, biodiversity/ecosystem protection and food production.[7b] In the proposal for sinking crop residues into the deep ocean, it was estimated that ~0.6 gigatonnes of carbon per year could potentially be sunk into the ocean as part of such a sequestration method.[7a]

Energy requirements and economics have not been covered in this article. Currently these estimates of energy requirements and cost vary greatly in the literature, even within the same type of proposed process. This reflects the fact that many proposals are often still based largely on back-of-the-envelope type calculations at larger scales.

Conclusions

This article has provided a brief overview of the build-up of carbon dioxide levels in the atmosphere and the chemistry behind a number of proposals to actively reduce these levels by carbon sequestration. The various approaches have different requirements in terms of reagents and the storage of the carbon in different chemical forms. Implementation of any of these potential carbon sequestration proposals at the scale of gigatonnes will involve massive quantities of materials and will require an immense, concerted effort.

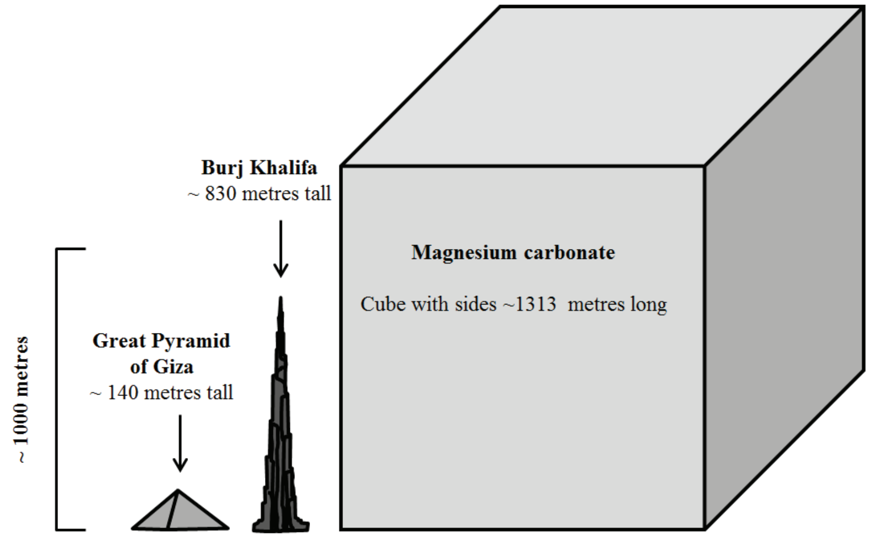

Fig. 1. The minimum volume of magnesium carbonate required to sequester a gigatonne of carbon (or 3667 million tonnes of CO_2). The Great pyramid of Giza and the world largest skyscraper (Burj Khalifa) depicted at the same scale.

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7. Oxygen actually has trace amounts of 17O (0.038% abundance) and 18O (0.205% abundance).
8. The ions are accelerated by means of a potential difference; the higher the accelerating potential, the greater the acceleration of the ions, producing higher energy impacts resulting in more extensive fragmentation.
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Corrigendum

The article published in *Chemistry in New Zealand* vol 79, no. 1, Jan 2015, pp36-41 authored by Grant J. McIntosh *et al.* erroneously referred to alumina as an adsorbate in the title and elsewhere in the text. Alumina is in fact the adsorbent.

The chemistry and metallurgy of beryllium

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Keywords: *beryllium, ligands, chronic beryllium disease, coordination chemistry*

Introduction

Beryllium (Be), the first of the group 2 alkali-earth elements, is a silver-gray metal possessing an unmatched combination of physical and mechanical properties, which are vital for a variety of applications that offer tremendous benefits to society. It is the lightest workable metal, only two-thirds the weight of aluminium, yet it has six times the stiffness of steel, making it an ideal material for stiffness-dependent and weight-limited applications. The chart in Fig. 1 illustrates how much beryllium outclasses other engineering materials with respect to thermal conductivity and dimensional stability (ability of a material to retain its uniformity under stress measured as the Young’s modulus to density ratio). These unique properties of beryllium translate into performance enhancement in the end product, for instance the James Webb Space Telescope (JWST: see Fig. 2). The next generation James Webb Space Telescope, scheduled to be launched in 2018 as NASA’s replacement for the Hubble telescope, will utilise a 6.5 meter wide beryllium mirror to reveal images of distant galaxies 200 times beyond what has ever been sighted.

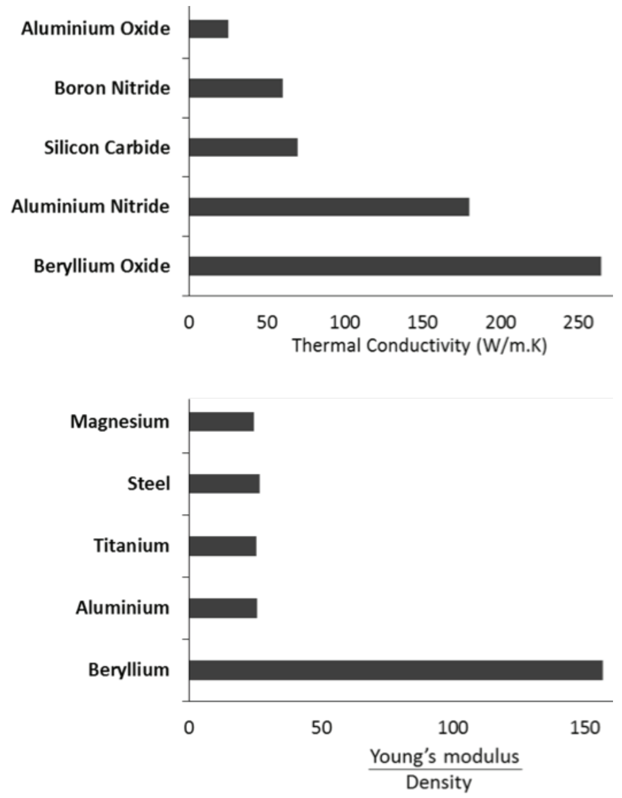


Fig. 1. Some properties of beryllium and beryllium oxide as compared with alternatives (thermal conductivities used with permission from American Beryllia Inc.)

Unfortunately, beryllium is also problematic. It is brittle, hard to machine, expensive and extremely toxic. It is a suspected human carcinogen, an initiator of chronic beryllium disease (CBD) and is regarded as the most toxic non-radioactive element in the periodic table. Surprisingly, this has not deterred its production and usage, making it imperative to gain a better understanding of this element. This review surveys aspects of beryllium metallurgy within a New Zealand context, including applications and toxicity. The coordination chemistry of beryllium is also discussed with an emphasis on the trends amongst ligands that exhibit strong interactions with beryllium as well as research activities within our group to identify suitable chelators for beryllium.

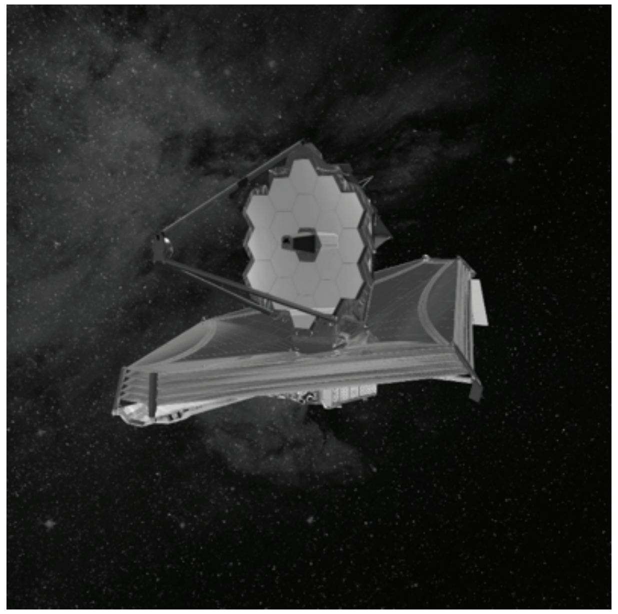


Fig. 2. The James Webb Space Telescope scheduled to be launched in 2018 will utilise a 6.5 m (21 ft) wide beryllium mirror to reveal images 200 times beyond what has ever been sighted. (Picture credit: NASA; used with permission)

Sources and production

Beryllium is the 44th most abundant element and occurs naturally in the earth’s crust, fossil fuels, air, and water. It is also found in trace quantities in foods although it has no known biological function in the human body. Beryllium was discovered in 1724 by Vauquelin, and later isolated independently by Bussy and Wöhler in 1828. Originally, it was named glucinium (Gl) after its sweet tasting oxide but in 1957, IUPAC adopted its present name. Commercial outlets for beryllium began in the 1920s, but its usage has increased over the years and its annual demand is estimated to approach 500 tonnes by 2018.[1] Mining of beryllium is only viable from a few of its minerals including beryl ($Be_3Al_2Si_6O_{18}$, 5 % by weight beryllium) and bertrandite [$Be_4(OH)_2Si_2O_7$, 15% by weight beryllium] in the United States, China, Kazakhstan, Mozambique, Brazil, Australia and Madagascar. Beryl also occurs naturally in New Zealand in pegmatite on the West Coast and Hawks Crag Breccia in the Buller Gorge.[2] However, over two-thirds of the world's beryllium is produced by the US while the rest comes from China, Kazakhstan and Russia. To extract beryllium, its minerals are first crushed and leached with acid to produce a beryllium salt solution from which the metal hydroxide is precipitated. Since the beryl crystals are more resistant to acid attack, it must first be melted at a high temperature. The stability of these minerals and their low beryllium content require expensive extraction techniques, making beryllium an expensive metal. The resultant hydroxide is further processed into beryllium's three most useful forms namely the pure metal, beryllium oxide, and its alloys with metals such as copper, nickel and aluminium.

Properties and uses

Beryllium is vital and indispensable in many of its applications. An understanding of the relevance of beryllium is best illustrated in its regard as a critical and strategic metal in the US and Europe. This is to highlight the impact its shortage or substitution could have on the economy, national security and defence. Interestingly, while the usage of beryllium in certain applications has been discontinued for safety reasons, new and crucial applications have emerged leading to its continuous demand and production.

The application of beryllium in aerospace and military equipment has been the most extensive. It is found in missiles, sensors, jet fighters, helicopters, landing gear, heat shielding and brakes for military and commercial aircrafts. Components made from beryllium are essential in spacecraft or military equipment because of its high strength which can sustain various structures without adding weight or losing strength from vibrations, thereby ensuring safety, precision and reliability in the end product. The high infra-red reflectivity of beryllium also makes it an ideal optical material for military, navigation and communication satellites, for instance, in the James Webb Telescope and Galileo Navigation Satellite System.

Besides aerospace and military applications, beryllium components have gained prominence in telecommunications, consumer and automobile electronics which now account for 45% of beryllium usage. The exceptional thermal conductivity and electrical insulation of beryllium ceramics makes it an excellent heat sink for electronic devices to support miniaturisation and the design of compact components. Furthermore, alloys containing beryllium in various proportions exhibits highly enhanced properties utilised for air bag sensors, electrical relays in automobiles, non-spark tools for oil and gas exploration, fatigue resistant springs and housing for undersea cables. In comparison with other metals, beryllium is very transparent to X-rays due to its low atomic number and is applied in X-ray windows for medical and scientific equipment.

Beryllium also possesses interesting nuclear properties. It is has a high neutron scattering cross section and is applied as a neutron moderator, reflector, and blast shields. In construction of nuclear fusion reactors, beryllium is a superior material for the lining of interior walls as it erodes more slowly and retains less of the plasma while the inclusion of beryllium oxide in fuels for nuclear fission can speed up cooling, thereby offering significant improvements to safety and efficiency of nuclear power plants.

Toxicity

Although beryllium possesses highly attractive properties and a variety of applications, it is also necessary to consider its toxicity and the hazards involved with the continual production and usage of the metal, its oxide and alloys. Beryllium is extremely toxic, both as a carcinogen and as an initiator of acute and chronic beryllium disease (CBD).[3-5] Although beryllium is considered a carcinogen, its carcinogenicity has only been established in animals while carcinogenicity in humans is still a subject of debate with recent studies questioning beryllium cytotoxicity.[3] Nevertheless, exposure to beryllium fumes or dust particles by inhalation and possibly dermal contact in certain individuals (1-15%) can lead to beryllium sensitisation and further progress into CBD. Chronic beryllium disease (CBD) is a debilitating granulomatous lung disorder resulting from an uncontrolled cell-mediated immune response marked by the proliferation of the $CD4^+$ T cells.[4] The dissolution, speciation and exact mechanism by which beryllium particles trigger CBD is not clearly understood. Current molecular understanding of the disease proposes that inhaled beryllium is detected by antigen-presenting cells which trigger the body's immune system into producing blood cells that engulf the particles forming granulomas that eventually harden the lungs causing respiratory abnormalities.[4] The onset of CBD can be delayed for over 20 years after exposure and there is no strong correlation between levels of exposure and CBD development, suggesting that a change in the beryllium speciation could be culpable. Interestingly, there is a genetic correlation to the disease as research evidences suggest that the risk of CBD is increased by the presence a specific gene- the HLA-DPB1.[5] Based on this, a beryllium lymphocyte proliferation test (BLPT) has been developed for routine use in diagnosis and workplace screening to predict susceptibility towards the disease. Another interesting correlation with CBD is that it is associated only with the processed forms of beryllium, such as beryllium metal and the oxide. Beryl and other ores of beryllium do not trigger a similar immune response possibly due to the lack of bioavailability of beryllium from these ore as they are insoluble in aqueous solution. It has also been observed that there is no beryllium oxo cluster (Be-O-Be) in the beryl structure ($Be_3Al_2Si_6O_{18}$), but rather silicon oxide units bridge beryllium and aluminium atoms.[4]

Beryllium in New Zealand

Beryllium is neither mined nor processed in New Zealand and although beryllium components are found in electronic devices and other consumer products, they are well encased and offer no hazard to general users. However, appropriate disposal via the segregation of these components is recommended considering the imminent increase of beryllium in electronic waste. Exposure to beryllium can also result from the combustion of fossil fuels, especially coal which can contain significant amounts of beryllium. The main concern for beryllium exposure involves occupational related activities with beryllium components. The occupational exposure limit for beryllium in New Zealand is 2 μg m^{-3} for an 8 hour time-weighted average but it remains unclear if this limit actually excludes the development of CBD. No CBD case has been documented in New Zealand but a single beryllium sensitisation case was reported among aircraft maintenance staff in Air New Zealand.[6,7] The company thereafter set up a copper beryllium project in 2006, sampling work areas to identify and manage potential health risks to its workers involved in beryllium work areas. Noteworthy in their findings was the uncharted occupational hazards associated with beryllium-related operations in New Zealand.

The chemistry of beryllium

Beryllium is an s-block element with a relative atomic mass of u = 9.01218307(8) and an atomic number of z = 4. Its only naturally occurring isotope is ^{9}Be making it the only element having an even atomic number with one stable isotope. Beryllium has a density of 1.84 g cm^{-3} and is one of the lightest metals, second only to lithium, yet it has one of the highest melting points (1287 °C) amongst the light metals.

In comparison with its periodic table neighbours the coordination chemistry of beryllium has been relatively understudied due to its toxicity and a strong tendency towards hydrolysis. Solution techniques such as potentiometry and NMR are often utilised in the investigation of the coordination chemistry of the Be^{2+} cation and its interaction with ligands. ^{9}Be NMR has a narrow range of chemical shifts and suffers line broadening as a result of the quadrupolar beryllium nucleus ($S = 3/2$) and aqueous beryllium sulfate is used as the reference peak. Computational techniques are also invaluable and by the correlation of experimental and theoretical NMR chemical shifts, coordination to the Be^{2+} cation can be identified without isolating the resulting complex. This safe method for beryllium investigation has been pioneered by an author in our group.[8] Further research in our group utilises electrospray ionisation mass spectrometry (ESI-MS) as a solution technique for the cross validation of beryllium speciation. ESI-MS could be the technique of choice for the investigation of beryllium speciation in solutions, being able to transfer pre-existing solution species into the gas phase where they are analysed by the mass spectrometer. Importantly, this technique is sensitive, requiring only miniscule amounts of sample in solution thereby minimising any exposure to beryllium dust and allowing rich information on beryllium speciation to be gained from a study utilising only tiny quantities of beryllium compounds.

The coordination chemistry of beryllium is largely governed by its small size and high charge density. Its ground state electron configuration is $1s^2\ 2s^2$ and the loss of the $2s^2$ electrons leads to its only stable ion Be^{2+}. The small beryllium cation (31 pm) has a charge to size ratio (Z/r) of 6.45, which is comparable to the Al^{3+} cation (6.0) hence these two elements illustrate the typical periodic table diagonal relationship observed among the main group elements. Indeed, the chemistry of beryllium shows more similarities to aluminium rather than its heavier alkali earth metal congeners such as magnesium and calcium. For instance both elements exhibit a tendency to form strong covalent bonds, and form strongly solvated cations that are acidic and prone to hydrolysis. They also dissolve in non-oxidising acids or alkalis with the liberation of hydrogen. This striking similarity between the two metals resulted in beryllium being overlooked as a constituent of beryl until 1724. In fact even after beryllium's discovery, scientists presumed beryllium to have an oxidation state of +3 and placed it above aluminium in group 13 of the periodic table. However, aluminium still exhibits some differences from beryllium. Aluminium is a larger sized cation, therefore it prefers an octahedral geometry and is effectively complexed by EDTA while beryllium maintains a four-coordinate tetrahedral geometry and shows poor binding with EDTA.

Interaction with simple inorganic ligands

Generally, only a few inorganic ligands can compete with the hydroxyl ligand for a binding site with beryllium because in aqueous solution the Be^{2+} ion is strongly solvated. It also exhibits complex pH- and concentration-dependent aqueous speciation. In very acidic solution (pH < 3.5), without any ligand present, beryllium exists as the tetra-hydrated ion $[Be(H_2O)_4]^{2+}$. The high charge density of the Be^{2+} cation polarises the water molecules causing the negative end of their dipole to align toward itself while the protons are strongly repelled such that they are easily transferred, leaving the hydroxyl ion OH^- in contact with the beryllium ion. Subsequent increases in pH or concentration yield several polynuclear hydroxo cluster species in varying degrees of abundance (Fig. 3). The trimer is the predominant hydroxo species and it exists as a cyclic six-membered ring structure with the four-coordination of the beryllium ion preserved by water molecules. NMR and potentiometric measurements[9,10] have characterised the $[Be(H_2O)_4]^{2+}$, $[Be_2(OH)]^{3+}$, and $[Be_3(OH)_3]^{3+}$ species while crystal structures of the picrate salt $[Be_3(\mu\text{-}OH)_3(H_2O)_6](picrate)_3 \cdot 6H_2O$ have confirmed the stability

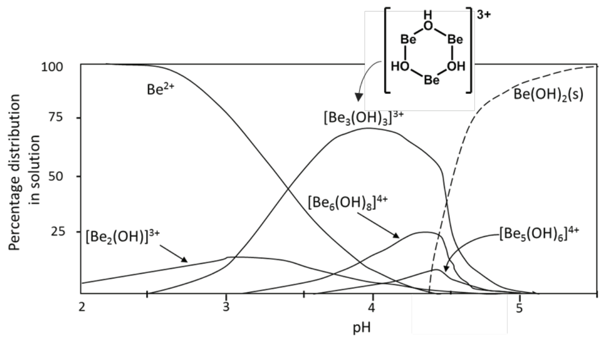


Fig. 3. Beryllium hydroxo species distribution diagram in acidic solutions. Tetra-coordination of beryllium is maintained by aqua ligands removed for clarity (adapted from reference 10 with permission from the Royal Society of Chemistry)

and cyclic nature of the trimeric species (Fig. 3).[11] The equilibrium is further complicated by other minor species in solution of which the $[Be_5(OH)_6]^{4+}$ and $[Be_6(OH)_8]^{4+}$ species offer the best fit for speciation data.[10] Between pH 5.5-12.0, insoluble beryllium hydroxide $Be(OH)_2$ precipitates. In solutions of higher alkalinity (pH > 12), this amphoteric $Be(OH)_2$ precipitate begins to dissolve, giving rise firstly to $[Be(OH)_3]^-$ and then, at even higher alkalinity, the tetrahydroxoberyllate dianion $[Be(OH)_4]^{2-}$ is formed. This occurs in the ^{9}Be NMR spectrum as a narrow peak at 2 ppm.[12] IR spectroscopy also proved the existence of this species with a characteristic IR band in the range of 700-750 cm^{-1}.[13] Several $M[Be(OH)_4]$ salts have been isolated[12] where M = Ca, Sr or Ba but a later attempt to resynthesise the $Ca[Be(OH)_4]$ complex (at pH 13.5-14) resulted in the isolation of a crystal whose structural investigation showed that it contained the hydroxoberyllate trianion, $[Be_2(OH)_7]^{3-}$, instead of the expected $[Be(OH)_4]^{2-}$ as previously assumed.[14] The $[Be_2(OH)_7]^{3-}$ anion was found to be associated with two calcium cations and a Z-shaped hydroxide hydrate anion $[HO\text{-}H\text{-}OH]^-$ which resulted in the $Ca_2[Be_2(OH)_7](HOHOH)(H_2O)_2$ complex.[14] The presence of yet another hydroxoberyllate anion $[Be_4(OH)_{10}]^{2-}$ was further identified by Schmidbaur *et al.* as crystals obtained from aqueous sodium beryllate solutions at high pH (13.2) result in the hydrated species $Na_2[Be_4(OH)_{10}](H_2O)_5$.[15] The tetraberylliumdecahydroxide dianion species was found to have a highly symmetrical adamantane structure where four beryllium atoms occupy the vertices of a regular tetrahedron with a terminal hydroxyl group at each metal centre while the remaining six bridging hydroxyl groups completed the tetra coordination to beryllium atoms.[15] The energetics for the existence of the $[Be_4(OH)_{10}]^{2-}$ anion can be explained by the condensation of the species $[Be(OH)_4]^{2-}$ with the extrusion of OH^- anions (Eq 1).

$$4[Be(OH)_4]^{2-} \underset{+2OH^-}{\overset{-2OH^-}{\rightleftharpoons}} 2[Be_2(OH)_7]^{3-} \underset{+4OH^-}{\overset{-4OH^-}{\rightleftharpoons}} [Be_4(OH)_{10}]^{2-} \qquad \text{(Eq. 1)}$$

The fluoride ion similarly exhibits high affinity for beryllium and was found to be the only inorganic ligand to form all four substitution products with water, $[Be(H_2O)_{4-n}F_n]^{(2-n)+}$ where n = 1-4. Based on equilibrium measurements,[16] it was found that the fluoride ion effectively competes with the hydroxo ligand up to pH 8, at which point $Be(OH)_2$ precipitates and species such as $[BeF_2(H_2O)_2]$ and $[BeF_3(H_2O)]^-$ exist in solution at a pH ranging from 0.5-8 in varying concentrations. The ^{19}F NMR spectra of these beryllium species give rise to signals of 1:1:1:1 quartet splitting due to coupling to the ^{9}Be nuclei.[12] In the ^{9}Be NMR spectrum, a mixture of species containing $[BeF(H_2O)_3]^+$, $[BeF_2(H_2O)_2]$ and $[BeF_3(H_2O)]^-$ can be distinguished as separate signals from an overall multiplet of a 1:1 doublet, a 1:2:1 triplet and a 1:3:3:1 quartet. The observation of the quartet in ^{19}F NMR suggests that the fluoride anions are attached to a single beryllium and that they do not form bridges between two beryllium atoms while the relative intensity of the signals shows that some of the hydrated BeF_2 species undergo ligand dissociation and redistribution in solution (Eq 2, 3).[12]

$$BeF_2 + 2H_2O \longrightarrow [BeF_2(H_2O)_2] \qquad \text{(Eq. 2)}$$

$$2BeF_2(H_2O)_2 \rightleftharpoons [BeF(H_2O)_3]^+ + [BeF_3(H_2O)]^- \qquad \text{(Eq. 3)}$$

Beryllium halides of the structure BeX_2 (X = F, Cl, Br, I) are not easily formed in the presence of water and often lead to different hydrolysis products. In most cases, in order to overcome this, harsh conditions of high temperatures and liquid ammonia are employed to form the halides by way of thermal decomposition. The dihydrogen phosphate ion $H_2PO_4^-$ is also known to replace water and results in the complexes $[Be_2(OH)(H_2PO_4)]^{2+}$ and $Be_3(OH)_3(H_2PO_4)_3$. NMR results further suggest the existence of another complex with the formula $[Be_3O(H_2PO_4)_6]^{2-}$ containing a 'beryllium acetate' type structure (see next section) where three beryllium ions are bound to a central oxygen atom with three phosphate units bridging the metals and the tetrahedral arrangement of the beryllium is completed by terminal phosphate ligands.[17]

Interaction with organic ligands

Recent research efforts have focused on beryllium speciation by ligands of interest with the objective of identifying suitable sequestering agents[18-21] as well as to obtain a clearer picture of the "mystic beryllium species" guilty of triggering an uncontrolled immune response in beryllium sensitisation and CBD.[4,22-25] Beryllium is highly oxophilic and a hard Lewis acid; therefore, it binds preferentially to hard donor atoms such as oxygen in carboxylates, hydroxyl and phosphate groups as well as nitrogen donors but to a lesser extent. Three themes have been central in studies of the interaction of beryllium with organic ligands, namely functional groups, chelate ring size and ligand geometry.

The significance of the chelate effect in beryllium's interaction with ligands is highlighted by the fact that bidentate dicarboxylate ligands have increased binding to beryllium compared to the monocarboxylate ligands, while dicarboxylate ligands possessing rigid structures that prevent chelation show poor binding with the beryllium ion.[12] Acetate, a typical monocarboxylate ligand, forms a polynuclear beryllium complex species $Be_4O(O_2CCH_3)_6$ where six acetates act as bridging ligands for four beryllium atoms.[16] In contrast to this, the dicarboxylate ligands reveal beryllium species of the types $[Be(H_2O)_2L]$, $[BeL_2]^{2-}$ and $[Be_3(OH)_3(L)_3]^{3-}$.[16] The trimeric hydroxo/dicarboxylate species $[Be_3(OH)_3(L)_3]^{3-}$ was further crystallised, highlighting the stability of the hydroxo trimer and the competing hydrolytic tendency in the presence of other ligands in aqueous solution.[17] Further support for enhanced interaction and stability of beryllium with ligands that form suitable chelate rings can be shown by a survey of formation constants (log *k* values) among analogous ligands of varying chelated ring size (Fig. 4). Ligands that form six-membered rings with beryllium are the most stable for the binding of beryllium since they offer the most compatibility for a tetrahedral geometry with the small sized Be^{2+} cation. Consequently, malonate which forms a six-membered ring binds beryllium more strongly than oxalate which forms a five-membered ring, while succinic and maleic acids which form seven-membered chelate rings also reveal weaker binding. Chromotropic acid, the strongest bidentate ligand for beryllium, forms a six-membered chelate ring.

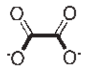
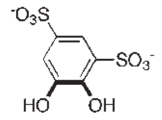
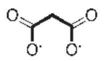
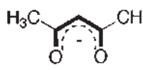
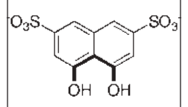
Chelate ring size	Dicarboxylate	Diketonate	Dihydroxy
Five	 Oxalate (4.08)	 Tropolonate (8.40)	 Tiron (13.50)
Six	 Malonate (5.91)	 Acetylacetonate (12.36)	 Chromotropic acid (16.34)

Fig. 4. Formation constant (log *k*) of beryllium complex among analogous ligands of 5 and 6 membered chelate rings (Log *k* values from reference 13)

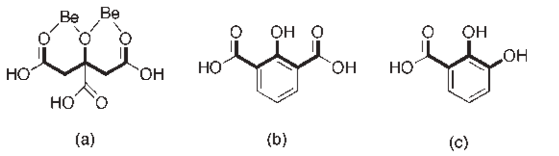


Fig. 5. 2:1 Be-citric acid complex (a) and similar ligands (2-hydroxyisophthalic acid (b) and 2, 3-dihydroxybenzoic acid (c)), possessing polynuclear binding pocket for beryllium via a carboxylate and a bridging hydroxyl group

The interactions of the beryllium ion with hydroxycarboxylate ligands have been extensively investigated because they exhibit significant binding with beryllium and can serve as models for ligands of biological interest. In fact, the aromatic hydroxycarboxylate aurin tricarboxylate (aluminon) was earlier developed for chelation therapy in beryllium poisoning.[13] In a remarkable contrast, aliphatic hydroxycarboxylates generally show a weaker interaction with beryllium with the exception of citric acid. Citric acid is an excellent ligand for beryllium capable of solubilising beryllium at molar concentrations across the entire pH range.[23] It binds beryllium in a polynuclear fashion with a metal to ligand ratio of 2:1 (Fig. 5a). To further understand the strong binding of citric acid with beryllium, six other aliphatic hydroxylcarboxylic acids have been studied, each chosen to highlight the relevance of the hydroxyl or carboxylate functionality toward a strong beryllium chelation. Competition experiments have shown that the significant binding of beryllium to citric acid could be attributed to the formation of a five- and six-membered ring Be-O-Be motif via a bridging hydroxyl group.[23] In agreement with this, two aromatic analogues, 2-hydroxyisophthalic acid (Fig. 5b) and 2,3-dihydroxybenzoic acid (Fig. 5c), which offer a similar polynuclear binding pocket for beryllium via a carboxylate and a bridging hydroxyl group, revealed an even stronger interaction with beryllium as well as excellent selectivity in the presence of other metal ions.[22] This development is of particular interest considering the abundance of similar functionalities in the major histocompatibility complex (MHC) class II receptor gene implicated for the genetic susceptibility in CBD cases.

However, other ligands lacking the characteristic polynuclear binding pocket of citric acid have equally been observed to bind beryllium strongly (Fig. 6). An example is 10-hydroxybenzo[*h*]quinoline-7-sulfonate (HBQS) (Fig. 6a) which binds beryllium extremely well and is now part of a commercial beryllium detection system.[26] This has led to the proposition that the beryllium cation actually interacts strongly and is bonded by ligands possessing a hydrogen bonded proton that can easily be displaced by the similarly small but tetrahedral Be^{2+} cation.[25] These ligands also possess high pKa values and Fig. 6 shows some examples. This concept was further explored in identifying the tri-dentate ligand 2,6-bis(2-hydroxyphenyl)pyridine (BHPP) (Fig. 6b) as a fluorescent Be indicator for cellular studies as it is able to detect and solubilise beryllium in phosphate media under physiological conditions.[27] X-ray crystal structure of the Be(BHPP) complex revealed that the metal is coordinated in a tetrahedral geometry by the pyridine nitrogen and the two oxygen donors of the phenolic groups while the fourth coordination site is taken up by a water molecule. This understanding of beryllium's interaction with ligands possessing suitable sites of strong hydrogen bonding offers new insight into the binding of beryllium to proteins and other biomolecules relevant for the biomolecular understanding of how beryllium triggers CBD.[24]

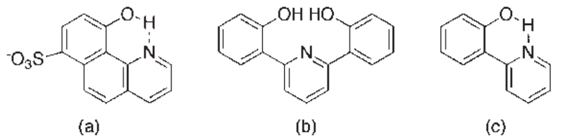


Fig. 6. Ligands possessing strongly bonded hydrogen sites suitable for beryllium binding: (a) 10-hydrobenzo(h)quinolone-7-sulfonate (HBQS), (b) 2,6-bis(2-hydroxyphenyl)pyridine (BHPP), (c) 2-(2-hydroxyphenyl) pyridine

An alternative geometry for beryllium binding which forms the central theme of research in our group involves tetra-dentate ligands which potentially encapsulate the Be^{2+} cation (Fig. 7). This is illustrated in the binding of nitrilotripropionic acid to beryllium (Fig. 7a). Nitrilotripropionic acid binds beryllium through the central amine and the three carboxylate groups which wrap round the Be^{2+} cation creating six-membered chelate rings with appropriate tetrahedral geometry.[28] Ligands such as phthalocyanine (Fig. 7b), although tetradentate, do not provide a tetrahedral arrangement of donor atoms however, a chiral binapthyldiimine- Be(II) complex (Fig. 7c) analysed in solution by Plieger *et al.* have revealed a tetrahedral coordination with the Be^{2+} cation suggesting that selective uptake of Be^{2+} could possibly be attained by incorporating mixed N/O donor atoms as in polyaminocarboxylic acids.[13,19] Potentiometry and NMR spectroscopy[28] have further supported the selectivity of a mixed N/O donor ligand and the ligands nitrilotripropionic acid and nitriloaceticdipropionic acid revealed selective uptake of Be^{2+} in the presence of Mg^{2+}. However, the flexibility afforded by the alkyl arms used for encapsulation cannot effectively preclude the ligand binding to larger metal cations.[21] Therefore, nitrilotripropionic acid-type ligands have further been investigated in a study which incorporated the rigidity of aromatic groups to enhance selectivity (Fig. 8).[20,21] Full encapsulation of the beryllium cation by these ligands was validated by correlating experimental and theoretical Be NMR chemical shifts, while the synthetic variation of the chelate ring size and the donor atom in one of the encapsulation arms (Fig. 8) reiterated beryllium's binding preferences. Significantly, this study revealed that the combination of unfavourable features in ligands such as weakly coordinating donors and five-membered chelate rings results in weaker binding with the Be^{2+} cation. For instance, the calculated ^{9}Be NMR chemical shifts for the beryllium complexes with ligands shown in Fig. 8a and 8b did not correlate well with the experimental shifts, suggesting that they might not be able to fully encapsulate the Be^{2+} cation like the ligands in Figs. 8c-f, which offer either a strongly coordinating oxygen donor or an unstrained six-membered chelate ring .[20,21]

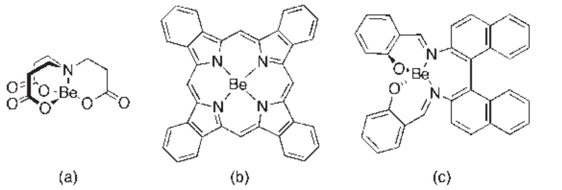


Fig. 7. Tetradentate coordination of beryllium to (a) phthalocyanine (b) nitrilotripropionic acid (c) chiral binaphthyldiimine ligand

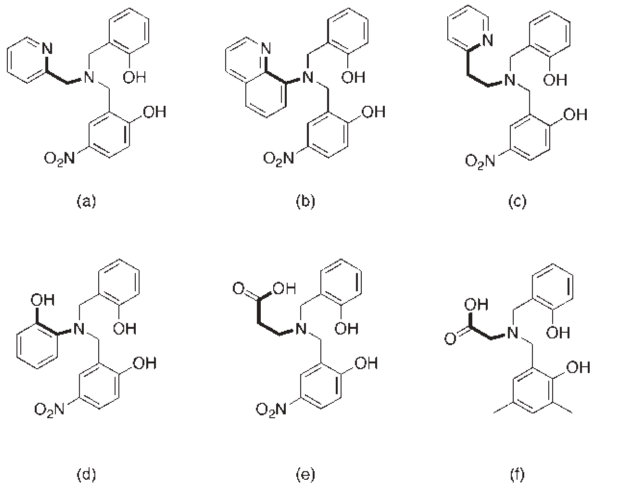


Fig. 8. Nitrilotripropionic acid-type ligands for the full encapsulation of beryllium

Another functional group relevant for beryllium binding is the phosphonate group but fewer studies have investigated the solution chemistry of beryllium phosphonate complexes despite the fact that phosphonate ligands (PO moiety) form stronger complexes than carboxylate/hydroxyl ligands (CO moiety). For instance, methylphosphonate, a monodentate ligand, forms a stronger complex than the malonate ligand while methylenediphosphonate, which offers a similar six-member chelate ring as malonate, reveals a much stronger interaction with beryllium.[29] Using potentiometric and multinuclear NMR methods, the interaction of beryllium with some phosphonate ligands have been ordered as malonate<methylphosphonate<phosphonopropionate<phosphonoacetate<methylenediphosphonate. The structures and chelate ring sizes of these ligands are shown in Fig. 9. The superior interaction of the PO moiety with beryllium is again revealed in the stronger interaction of methylenediphosphonate over phosphonoacetate. Both ligands differ only in a second donor site. Methylenediphosphonate possesses two phosphonate groups while the phosphonoacetate coordinates via a phosphonate and carboxylate group. The stronger binding of methylenediphosphonate and phosphonoacetate over phosphonopropionate is presumably due to the latter forming a seven membered chelate ring.[30] Accordingly, all the bidentate ligands in Fig. 9 containing phosphonate groups exhibit superior binding with beryllium compared to the monodentate methylphosphonate. This is relevant since metal complexes of nucleotides containing the phosphate groups such as adenosine 5-monophosphate, -diphosphate (ADP) and –triphosphate (ATP) play a fundamental role in biological processes. Potentiometric titrations[31] have revealed higher stability constants for the $[Be(ATP)]^{2-}$ species (log k = 6.52) compared with the corresponding $[Mg(ATP)]^{2-}$ species (log k = 4.10) and beryllium is also known to inhibit alkaline phosphatase and DNA replication.[32] Using a competitive fluorimetric approach, it was further observed that the decrease in the number of phosphate groups from ATP to ADP resulted in a remarkable decrease in binding affinity confirming that the Be^{2+} cation is chelated by adjacent phosphate groups in ATP.[33] Ferritin is also another phosphate binding biomolecule. It is an iron storage protein that reveals significant binding with beryllium and is likely to provide binding sites that allow beryllium to pass through cellular systems.[4,33]

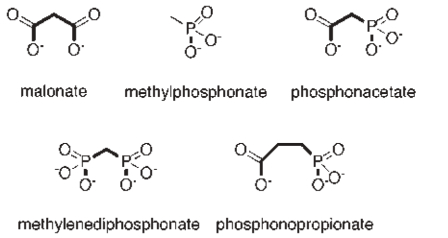


Fig. 9. Malonate and ligands with the phosphonate functionality

Conclusions

Beryllium is a very useful speciality metal and is indispensable in several of its applications. However, its usage should be limited considering its toxicity and strict industrial and government controls should be administered to reduce future potential exposure of beryllium in New Zealand workplaces. Substitutes for beryllium metal and alloys include titanium and pyrolytic graphite, while beryllium oxide can be replaced by aluminium nitride. Unfortunately, these substitutes often result in a notable reduction in the performance of the end product and this has led to a sustained usage of beryllium. It is important, therefore, to identify selective and tight binding ligands with suitable functional groups and arrangement of donor atoms for applications in the area of beryllium detection, remediation and chelation therapy. Research in our group is building a greater understanding of the coordination chemistry of the Be^{2+} cation for the development of sequestering agents that will potentially encapsulate beryllium for selective uptake. Meanwhile, other studies on the bioinorganic chemistry of beryllium hold the key to unravelling the mystery of the uncontrolled immune system's response to beryllium particles.

Acknowledgements

We appreciate financial support from the Marsden Fund (contract MAU1204) of the New Zealand Government, administered by the Royal Society of New Zealand.

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Heroes and plots in chemistry storytelling

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Keywords: *storytelling*, *plots*, *heroes*, *chemical processes*, *chemical elements*

In recent years there has been an explosion in the publication of 'popular' books written about various disciplines, including scientific ones. While some of these have been collaborative efforts – as for example the book *Are Angels OK?*,[1] where discussions with scientists provided a feedstock for creative writers to exploit, others such as *The Elegant Universe of Albert Einstein* are a compilation of science tales,[2] possibly motivated by discussions with creative writers, but not unduly influenced by them. In the preface to *As Far as We Know: Conversations About Science, Life and the Universe*,[3] Professor Sir Paul Callaghan opined, "… it is the responsibility of science to tell its own story, and to communicate as widely and clearly as possible why the scientific view enriches human understanding. The last decade has seen a steady stream of science communication literature through books of remarkable quality aimed at a general audience." The time trend of publication of such books is demonstrated in Fig. 1, but it is interesting that fewer than 5% of the topics in the *Conversations* between Callaghan and broadcaster Kim Hall were chemistry related.[4]

Such books are of a type that can be considered to "… restate the triumphal status of science in contemporary society… These accounts allow us to see the prevalence of a scientific world view, an 'ideology' – scientism – that is a commonly shared perspective on the world around us. The public are presented with and assimilate a range of resources in constructing their understanding of science, and given the composition of much of this material, it is unsurprising that we see a societal understanding of science that reflects aspects of popular science accounts."[5]

The NZ Institute of Chemistry has been involved with several compilations of chemistry 'stories'. The editor of one of these books indicated, as befits its title – *Chemical Processes in New Zealand*,[6] that "we have tried to keep the emphasis on chemical processes occurring in New Zealand", while admitting that "the level of chemistry varies from article to article, and a lot of non-chemical descriptive material is included". The cover and title page of this book include a graphic with the theme "Life is Chemistry" (Fig. 2), and yet a striking feature of the compilation is the minimal reference to the scientists actually involved in either the development or the application of the processes described. Providing anonymity to scientists was perhaps more understandable in the Institute's pollution report in the 1970s,[7] being closer in time to the publication of *Silent Spring*, perhaps the first book to demonise science.[8] In an earlier book published in 1940, which was presumably targeted at a general audience, *Chemistry in the Development of New Zealand Industry*,[9] and rather later in *A History of Chemistry Division* (published in 1981),[10] the chemists undertaking the research described are specifically identified.

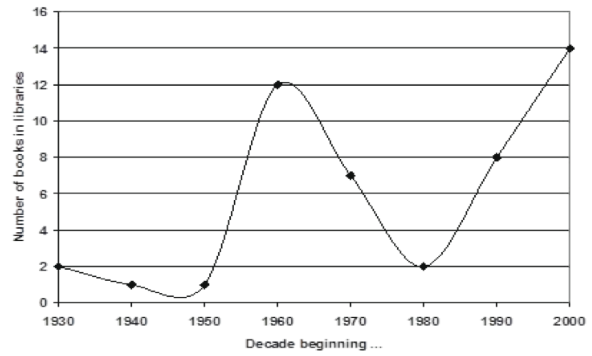

Fig. 1. The combined holdings in 2010 of 'popular' science books in the libraries of Auckland University of Technology, University of Waikato, Victoria University of Wellington and University of Otago, by the decade in which the books were published. There is a clear post-Second World War 'spike' before a minimum in the 1980s followed by a more recent revival in publication of this type of book. (The plot can only be indicative because it takes no account of book purchasing policies of the libraries or any culling of books since acquisition).

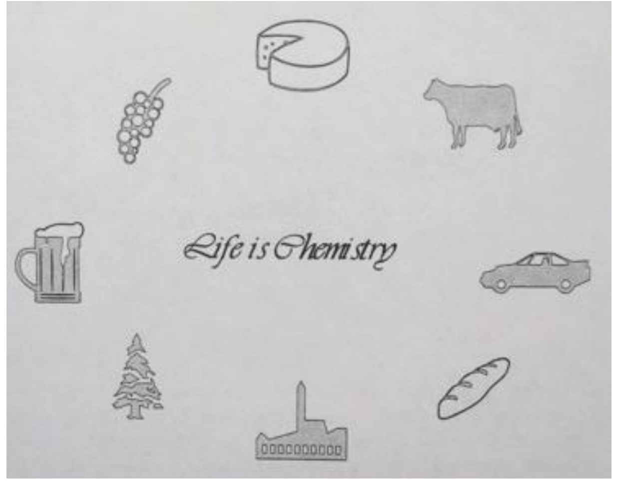

Fig. 2. "Life is Chemistry" image used on the cover and title page of *Chemical Processes in New Zealand* (reference 6). No people feature in the image.

In the 1999 book, *New Zealand is Different*, the cover blurb notes that the essays

> "… are a testament to the dedication and skill of New Zealand chemists and engineers as well as to the effectiveness of government research establishments. More importantly, this volume conveys something of the human activity behind the achievements, since most of the authors were personally involved in the events they described".[11]

Indeed, each essay is prefaced by biographical details and a photograph of its author. There is a certain 'heroic' character to all the stories told, in which the 'heroes' are either the chemical processes themselves or the people involved.

The typology of storytelling in Table 1[12] suggests that most stories comprise five stages: the call, the dream, frustration, ordeal, and resolution.[13] Such an analysis of fiction has inevitably attracted criticism, one critic noting that "Booker's framework ends up less a source of enlightenment than a straitjacket, leaving whole areas of literature and storytelling fundamentally either inexplicable, or reduced to an uninteresting 'essence'".[14] However a number of contemporary novelists find merit in the approach.[15]

On the basis of this reductionist approach to stories, many stories in *New Zealand is Different* and other similar compilations seem likely to take the form of a 'quest', in which a group of scientists undertake a research journey with a successful outcome, albeit with setbacks and failures along with the way (see Table 1), although one essay in *New Zealand is Different* is considered by its author to represent a 'tragi-comedy'.[16]

In the preface to Eric Scerri's book *A Tale of Seven Elements*,[17] Oliver Sacks notes that Scerri's storytelling "allows us to see chemistry, and science generally, as an essentially historical enterprise – a human adventure that shows the best, and sometimes the worst, of human nature".[18] From such a statement it can be inferred that the process of discovery of at least these chemical elements did not run smoothly; Scerri's narratives show that the scientific endeavours are disrupted either by personality issues affecting the heroes or by external influences, in particular war and politics. As a result, rather than all being 'quests', some of the seven tales have characteristics of other types of plot, as shown in Table 2 and detailed below.

As told by Screrri, the discovery of francium by Marguerite Perey has the hallmarks of a 'rags to riches' story. Perey was initially a technician in Curie's laboratory in 1929, working on concentrating actinium. The 'call' and 'initial success' stages related to her observation that the half-life of the decay of actinium could not be attributed to actinium's daughter isotopes alone, but to actinium itself. She deduced that actinium decayed to another element – element-87. There is not much of a 'central crisis' in this instance; rather than everything going wrong, Perey was simply cautious in announcing her discovery. With respect to the fourth stage – 'independence and the final ordeal' – Perey had kept her two mentors independently advised of her success, but the mentors could not agree which of them should share the credit for the discovery, so, as Scerri puts it, Perey was "permitted to keep the discovery to herself". The final stage – 'comple-

Table 1. Summary of stages of Booker's seven basic plots*

Type of plot	**Stages**				
The Monster	1, The Call (or Anticipation)	2, Initial success (or Dream)	3, Confrontation (Frustration)	4, Final Ordeal (Nightmare)	Miraculous Escape (and Death of Monster)
Rags to Riches	1, Initial wretchedness and 'call' to activity	2, Out into the world – initial success	3, Central crisis – "everything goes wrong"	4, Independence and final ordeal	5, Completion and fulfilment
The Quest	1, The Call: rectification of intolerable oppression requires a journey	2, Journey across hostile terrain with monsters and temptations to overcome†	3, Arrival and frustration	4, The Final Ordeals – a last series of tests	5, After a 'last thrilling escape from death', the kingdom or life-transforming treasure is won
Voyage and Return	1, Anticipation and 'fall into another world	2, Initial fascination, which may exhilarate because of unfamiliarity	3, Frustration stage, with intruding shadow	4, Nightmare; shadow‡ dominates and threatens survival	5, Thrilling escape and return
Comedy	1, A 'little world' in which people are confused, frustrated and shut off from one another		2, Worsening confusion and darkness;‡ a nightmarish tangle		3, Previously unrecognized things come to light, changing perceptions and dispersing shadows, 'little world' becomes happy
Tragedy	1, Anticipation; hero incomplete, hoping for unfilled gratification, nut finds a focus for action	2, Dream stage: hero becomes committed to a course of action in which things initially go improbably well	3, Although initially imperceptible, frustration sets in, with dark acts performed and threats from shadowy figures‡	4, Nightmare – matters out of hero's control, there is an increase of fear and despair	5, Destruction or death of hero, by forces hero has roused, or a final act of violence
Rebirth	1, Hero influenced by 'shadow of dark power'‡	2, All seems well, the threat apparently receding	3, Threat returns forcefully	4, Continuation of threat to its perception of the dark power being triumphant	5, A miraculous redemption

*See Reference 12
†Quests always have more than one hero, to ensure that mistakes can be shared and the hero survives
‡Shadow or darkness may be physical or psychological

Table 2. Mapping of Scerri's seven elements to Booker's seven basic plots

Type of plot	Scerri's seven elements						
	Proactinium	Hafnium	Rhenium	Technetium	Francium	Astatine	Promethium
The Monster							
Rags to Riches					●		
The Quest	●		○				
Voyage and Return							
Comedy		●				●	●
Tragedy	○	○	●	●			
Rebirth							

● Dominant type
○ Subordinate type

tion and fulfilment' – is amply demonstrated by Perey being invited by the International Union of Pure and Applied Chemistry to suggest a name for her discovered element (she chose 'francium' to honour her homeland and to recognise the contribution of French scientists to radiochemistry), by her being invited to submit research for a doctorate (despite having no undergraduate degree), and by her being appointed to a chair in nuclear chemistry at the University of Strasbourg.

Although other researchers are mentioned, Scerri's story of the discovery of protactinium focuses on "[Lisa] Meitner and [Otto] Hahn's path to protactinium", in essence a 'quest'. The good progress that Meitner makes during the First World War is described by Scerri as providing "increasing confirmation that she was succeeding in finding the mother substance of actinium". The 'frustration' stage comprises the other potential claims to discovery, even though they were relatively easily discounted, principally because the alleged discoveries were of short-lived isotopes. The story could have ended in 1918 with the discovery of protactinium, but Scerri chose to continue Meitner and Hahn's 'quest' by including their continued work on uranium through which they discovered nuclear fission. Doing so introduces the 'ordeal' of Meitner being an Austrian Jew at the time of the Second World War, with Hahn, although publicly opposed to Nazi policies, bowing to their pressure and asking Meitner to resign her research post in Berlin. Meitner and her nephew then recognise the prospect of uranium fission to barium, later cited by a science historian thus: "Sixty years old and officially retired, Meitner had explained one of the greatest discoveries of the century".[19] Meitner may not have received a Nobel prize, and Hahn's claim "that physics had actually hampered the discovery of nuclear fission and that it had been a triumph for chemistry alone", in an obvious slur to Meitner's contribution (Scerri, reference 17, p. 79) could be inferred to make this story a tragedy, but it is countered by an affirmation of the quest's success in the final paragraph in a section of the chapter entitled "But Why No Nobel Prize for Meitner":

> "But by what is perhaps a nice touch of irony, an element that had been provisionally called hahnium was eventually named meitnerium, albeit several years after Meitner's death in 1968. Hahn had effectively been deprived of having an element named after him. Too little too late perhaps, but quite significantly the suggestion came from a German…" (Scerri, ref. 17, p. 79).

Three of the stories – those for hafnium, astatine and promethium – fit the stages for comedy. Each opens with a 'little world' of protagonists separated from each other, with worsening confusion, and ultimately resolved through changed perceptions of reality.

Scerri's introduction to his story of the discovery of promethium sets it up as a comedy, referring to two sides of a priority debate, both of which "appealed to X-ray data and Moseley's law", yet "… neither side was correct. In their own way each side was working in complete delusion, since element 61 [promethium] is highly radioactive and unstable, does not occur naturally on Earth and could only be isolated in minute quantities by artificial means when such methods became sufficiently developed in the 1940s" (Scerri, reference 17, p.176). In fact, the actual discovery in 1949 was not a deliberate attempt at synthesis, but came about as a result of interpretation of an unexplained peak on an elution curve from ion exchange chromatography of isotopes. This is the classic end to a comedy, with a "coming to light of things not previously recognised [by which] perceptions are dramatically changed" (see Booker, reference 12, p. 128).

A similar little world of people closed off from each other sets the scene for the discovery of astatine. Confusion reigns through the 1940s, made worse by the isolation of some of the protagonists from each other during World War 2. By the end of the chapter one group appears to have succeeded (although the accolade of discovery may yet be shared[20]) in part because an influential contribution to *Nature*[21] clarified the rules for naming rights of elements, thereby changing previously held perceptions.

An element of atomic weight 180 was predicted by Dmitri Mendeleev as a homologue of zirconium, but there was prolonged confusion as to whether the new element was a transition element (provisionally named hafnium) or a rare earth element (provisionally named celtium). Theoretical physics evidence suggested the former was correct, while initial X-ray data appeared to favour the latter. The scientific differences of opinion were further complicated by nationalistic fervour, leading to "one of the most bitter and acrimonious priority disputes in twentieth century science" (see Scerri, reference 17, p. 91). In Scerri's narrative, the hafnium supporters won the day, perhaps in part because the celtium supporters unsuccessfully tried to change the rules in respect of the relative importance of determination of the element's properties and the priority of its detection. In a sense, then, for the hafnium 'side' the story is a comedy, while for the celtium 'side', it might be considered a tragedy.

The chapter on rhenium could be considered a combination of a quest in respect of the actual discovery of the element, and a tragedy in respect of the activities of Japanese scientists to rehabilitate an earlier claim by Masataka Ogawa of the discovery of an element he thought was element 43, but which others subsequently inferred was probably rhenium. Scerri's description of the "arduously long extraction" by which the rhenium discoverers Walter Noddack, Ida Tacke (later Ida Noddack) and Otto Berg "obtained just one gram of rhenium after processing about 660 kg of the ore molybdenite" may be considered in the nature of a quest. However, in Scerri's narrative this quest pales by comparison with the tragedy revealed by the 'frustration' of the Japanese in attempting to replicate Ogawa's work, the 'nightmare' of their reinterpretation of spectroscopic and X-ray data, and Scerri's ultimate destruction of the claim by drawing attention to the implausibility of cultural excuses made by the claimants.

Scerri's story of technetium is to some extent bound up with that of rhenium. Walter and Ida Noddack's claim for element 43 was never formally retracted, even though the claim is unjustified "for the simple reason that the discovery of this element had to await its artificial synthesis following the discovery of nuclear fission" (Scerri, reference 17, p. 124), something only achieved much later than the Noddacks' work. The actual discovery by Emilio Segrè is said by Scerri (reference 17, p. 132) to be serendipitous, leaving him, as the storyteller, to focus on the tragedy of the unsuccessful rehabilitation of the Noddocks' claim.

Scerri admits to his stories being "revealing of the often frail humanity of the scientists involved or perhaps of the scientific method as a whole and the pressures it places on scientists", and that they are "dominated by nationalistic drives" which sometimes "comes from the scientists themselves while in other cases it is supporters of these scientists or perhaps even the press in the countries involved that fuel the nationalism" (Scerri, reference 17, p. xxxii). In essence, he has woven his narrative around some facts and around his and others' interpretations of those facts to create stories that are his own.

In a similar way, Primo Levi's autobiographical use of selected chemical elements in *The Periodic Table – Il Sistema Periodico*[22] can be interpreted in terms of the relative emphasis of his life, his work as a chemist and his development as a writer. As the book progresses the relative emphasis 'swings' between each of these aspects.[23] Such variation resembles that found by Matthew Jockers in his plots of 'emotional valence' versus 'narrative time' for Irish fiction, including that for James Joyce's *Portrait of the Artist as a Young Man* (see Fig. 3).[24] Of his method for determining 'emotional valence', Jockers notes that the process involves two major components: "a controlled vocabulary of positive and negative sentiment markers …. and a machine model that [he] trained to identify and score passages as positive or negative." A simple version of the same approach can be applied to non-fiction, as described below for Brian Halton's autobiography.[25]

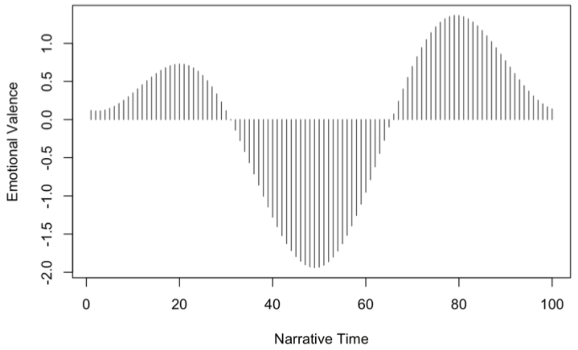

Fig. 3. 'Emotional valence' versus narrative time compiled by Matthew Jockers for James Joyce's *Portrait of the Artist as a Young Man* (http://motherboard.vice.com/read/computers-find-that-there-are-six-plots).

Brian Halton's career, as revealed by his annual research publication record is probably typical of many scientists: a dominance of peer-reviewed papers, interspersed with chapters, books, and edited books, and with contributions to professional – rather than scholarly – journals comprising a greater proportion of annual outputs as his career draws to a close (Fig. 4).

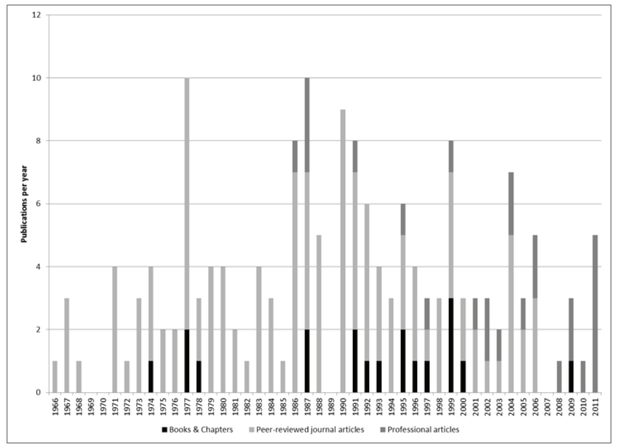

Fig. 4. Distribution of selected types of publication over Brian Halton's career in chemistry (compiled from reference 25, Appendix 2).

The peaks in such a distribution would be expected to correspond with times of a greater sense of career fulfilment, but their precise cause is difficult to determine. Peaks and troughs are also apparent in a plot of 'sentiment' versus time (Fig. 5), where 'sentiment' is determined from the difference between the number of times selected 'positive' words are mentioned and the number of times selected 'negative' words are mentioned on each page of Halton's autobiography. Often-repeated words deemed 'positive' for an academic scientist such as Halton were: 'research', 'teaching', 'conference' and the name of his wife (Margaret). On reading the autobiography, the most negative influences were those related to Halton's being unwell: 'health', 'heart' and 'hospital'. These measures are also compiled for each chapter of the book (Table 3).

Table 3. Sentiment by chapter of Brian Halton's autobiography

Chapter in *From Coronation Street to Consummate Chemist*	**Pages**	**Sentiment***							Aggregate sentiment†
		Positive				Negative			
		A	***B***	***C***	***D***	***E***	***F***	***G***	
The Early Years – Lancashire and London	1-9		1						0.11
University Years - Southampton	10-20	9			1	1		2	0.64
Florida in the Mid-1960s	21-31	6	6						1.09
A New life, a New Place, and an Emerging Career	32-58	32	14	3	24		1	1	2.63
A Young Family, a Career, and Momentum	59-76	15	3	8	8	3	2	4	1.39
Chemistry and Service	77-93	8	4	5	4				1.24
From Recognition to Retirement	94-128	47	21	8	8	4	8	15	1.63
The Joys of Emeritus Professor – What Better Role?	129-139	27	14		1	2	1		3.55

*Positive 'sentiments': ***A***, Research; ***B***, Teaching; ***C***, Conferences; ***D***, Margaret (Brian Halton's wife); Negative 'sentiments': ***E***, Health; ***F***, Heart; ***G***, Hospital

†The aggregate sentiment for each chapter is $(N_A + N_B + N_C + N_D - N_E - N_F - N_G)/N_P$, where N_A is the number of times sentiment ***A*** is mentioned; N_B, the number of times sentiment ***B*** *i*s mentioned, etc.; and N_P is the number of pages in the chapter

Table 3 shows the hallmarks of 'the quest' type of story: building to initial success (a high value of aggregate sentiment – 2.63 – in the fourth chapter), followed by darker times (reaching the nadir with a value of the aggregate sentiment of 1.24 in the sixth chapter), with all coming right at the end (with the highest value of aggregate sentiment – 3.55). The stages of an idealised story are less clear from Fig. 5, indicating that even with the same facts, a different story could have been told, and with a different emphasis a story here classified as a quest could be a tragedy, or a tragedy could be a comedy. Storytelling is unashamedly an art, and if (as is often said) art imitates life,[26] then storytelling also imitates life, of which the conduct of science is a component (Fig. 6).

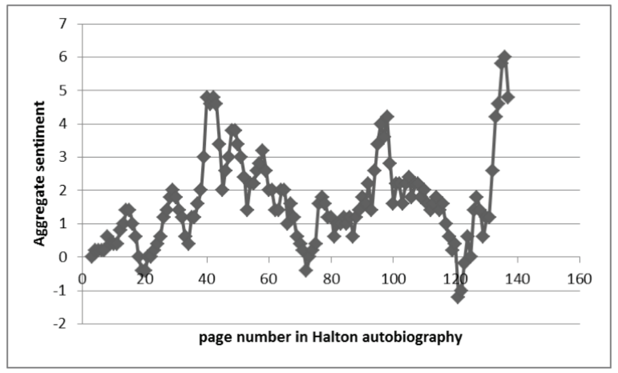

Fig. 5. Sentiment analysis of Brian Halton's autobiography. From the number of times the positive sentiments (research, teaching, conferences, Margaret (Brian Halton's wife)) less the number of times the negative sentiments (health, heart, hospital) feature on each page, five-page moving averages of the aggregated sentiments are calculated and plotted against the page number.

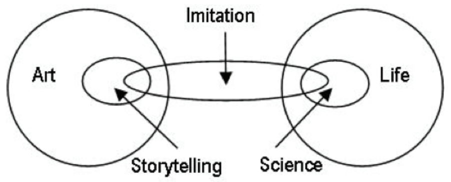

Fig. 6. Inter-relationship between art, storytelling, science and life. The central oval is "art imitating life" – or "life imitating art" (see ref. 26)

Acknowledgements

I am grateful to Eric Scerri for providing a review copy of *A Tale of Seven Elements*, which has been a cornerstone in the development of this paper, and to Brian Halton for his agreement – albeit with some skepticism – for his autobiography *From Coronation Street to Consummate Chemist* to be used in a more quantitative way than he would have ever imagined.

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Continued on page 153

Metals: ancient and modern

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Introduction

Lavoisier's 18th century table of elements was based on the distinction between Sb, Au, As, Bi, Co, Cu, Sn, Fe, Mn, Hg, Mo, Ni, Au, Pt, Pb, W, Zn and the non-metals S, P, C, Cl, F, B.[1] Earlier than this, alchemists generally distinguished metals, which they connected with the seven wandering stars of antiquity (Fe/Mars, Cu/Venus, Ag/Moon, Au/Sun, Hg/Mercury, Sn/Jupiter, Pb/Saturn), from non metals (C, S) and semi-metals (As, Sb), which were not so connected. Mercury seemed to be different, but was still associated with silver and the other metals, e.g. "quicksilver" or "hydrargyrum (Hg)". Alchemists generally viewed mercury as the metallic principle, e.g. Paracelsus' "three primes" – his other two being sulfur and salt.[2,3]

There are many properties of metals listed in old chemistry books, such as being shiny, malleable, ductile, conducting heat and electricity well, etc. These are mostly a consequence of having reasonably free electrons – electrons which are not bound to one atom, or a few atoms, but are free to move throughout the crystal, or put another way, they contain electron bands which are partially filled.

One property of metals that is useful for distinguishing them from other substances is that they conduct electricity less well hot than cold. Semiconductors and ionic conductors are usually better conductors hot than cold. For example, the lodestone, magnetite (Fe_3O_4) is a low bandgap (0.1 eV) semiconductor, not a metallic conductor. Its electrical resistance (100-1000 Ω cm) is close to the metallic range, but decreases with temperature. Below 120 K, it changes structure and becomes an insulator .[4]

Metals on the edge

Whether an element is metallic or not depends on the crystal structure and on the temperature and pressure. One famous example is the behaviour of tin at low temperatures ("Tin pest").[5] Articles made of tin have been observed to crumble into dust when kept at low temperatures for long periods, e.g. church organ pipes in mediaeval Europe.[5] The transition temperature is 13.2 °C for pure tin. This is supposed to have affected Captain RF Scott's 1912 expedition in the Antarctic when leaks developed in soldered kerosene tins and Napoleon's troops during the Russian Campaign when tin uniform buttons crumbled. Both examples are disputed.[5] The low temperature form (α-Sn) is a grey powder, has the same crystal structure as silicon and diamond and is a semiconductor. The band gap of α-Sn is quite small (0.08 eV) and it seems possible that under high pressures the band gap of α-Sn would be zero or negative. α-Sn has a lower density (5.77 g/ml) than β-Sn (7.31 g/ml), so would not be stable at high pressures, but the transition might be slow. Germanium has a high pressure form (β-Ge) which has the same structure as β-Sn and should be metallic. Indium has a tetragonal crystal structure like tin, and it may be that non-metallic crystals of In could also be made with a less dense crystal structure.

The calculations concerning copernicium being a semiconductor rather than a metal[6] are likely to remain theoretical for some time to come. Assuming that the band gap is also a function of cluster size, as many physical properties are for Hg, it would seem to require several hundred copernicium atoms at least to be prepared, and assembled in the same crystal.

Effect of high pressures

It may be that most elements will have metallic forms at extremely high pressures. Arsenic has a high pressure form with a simple cubic structure which is metallic.[7] Sulfur is metallic at high pressures >100 GPa.[7] Iodine is metallic at pressures of 16-18 GPa and greater.[7] Argon, krypton and xenon have been calculated to be metallic at pressures > 132 GPa.[8] Possibly astatine will show metallic properties if enough of it can be made to study. Apart from the old speculation about metallic hydrogen,[9] there has also been some speculation that ammonium might be metallic at very high pressures.[10]

Apart from the approximately 90 metallic elements, there are many more metallic alloys and metallic compounds.

Metallic alloys

Some alloys, e.g. brass, have been known since ancient times. Brass was known before zinc was isolated, at least in Europe. As a material, it has retained its separate identity, being listed in many tables of physical properties.

The properties of brass are quite different from those of a linear combination of copper and zinc properties, as shown in Table 1.

Table 1. Properties of copper, zinc and brass

	Copper	**α-Brass**	**Zinc**
% Cu	100	70	0
% Zn	0	30	100
Crystal structure	fcc	fcc	hcp
Melting point ºC	1083	900	420
Density (kg/m^3)	8.9	8.5	7.1
Electrode potential (V)	0.34	-0.35	-0.76
Electrical conductivity (S/m)	59×10^6	16×10^6	17×10^6
Thermal conductivity (W/m/K)	400	-150	116

The traditional ways of making alloys by mixing the elements and melting them together, or by mixing and reducing their compounds together, tends to produce only the alloys which are stable at the melting temperature. Other alloys, which are not stable under these conditions, can often be made by electrolysis. It is possible to electroplate an equimolar tin-nickel alloy,[11,12] which cannot be made by heating, as it is unstable above 350 °C. Similarly, iron amalgam, which cannot be made directly, can be made by electrolysing a ferrous sulfate solution using an iron anode and a mercury cathode.[13a] It is also possible to make iron amalgam by reducing ferrous sulfate solution with sodium amalgam.[13b]

Whether different metal atoms readily substitute for each other and form alloys or not depends mainly on the atomic radius, but also on the crystal structures, the valency of the metals (a metal with low valency is more likely to dissolve in a metal with high valency than vice versa) and their electronegativities (Hume-Rothery rules[14]). About ±15% difference in atomic radius is about the limit. For instance, iron (metallic radius 126 pm) forms substitutional alloys with other elements with an atomic radius of between 105 pm and 145 pm.

Most non-metallic elements can also form metallic alloys with metals. For example, antimony is usually considered at most a semi-metal, but it forms many metallic alloys. Sb alloys (such as type metal) often expand on freezing which is useful for good quality impressions when casting type. This expansion on freezing is also seen with indium and bismuth alloys.

It is hard to predict which elements will, or will not, form alloys together. Atomic size is one factor but there are many anomalies. For instance, why do copper, silver, gold, aluminium, tin and many other elements readily form amalgams with mercury, but iron, platinum, tungsten and tantalum do not readily form amalgams?

The Hume-Rothery rules do not apply very well to mercury, as can been seen in Table 2. Mercury is a much better solvent than predicted by these rules. Perhaps this is another relativistic effect?

Table 2. Hume-Rothery limits for mercury and properties of selected elements which do and do not form mercury amalgams

Element	**Atomic radius (metallic) (pm)** [15]	**Electronegativity**	**Valency***
Mercury	151	2	2
Hume-Rothery limits for mercury	128-174	1.6-2.4	≤ 2
Elements which readily form amalgams:			
Sodium	186	0.93	1
Potassium	227	0.82	1
Copper	128	1.9	2
Silver	144	1.93	1
Gold	144	2.54	3
Calcium	197	1	2
Aluminium	143	1.61	3
Tin	145 [20]	1.96	4
Elements which do not readily form amalgams:			
Iron	126	1.83	3
Platinum	139	2.28	4 ?
Tungsten	139	2.36	6
Tantalum	146	1.5	5

* It is not clear in what sense Hume-Rothery used the term "valency". It has been taken here to mean maximum common oxidation state.

Metallic compounds

Oxides

Vanadium (II) oxide, VO, was mistaken for the element itself by Berzelius in 1831.[16] It is a metallic conductor,[17] so this should not be surprising. Titanium(II) oxide, TiO, and niobium(II) oxide, NbO, are also metallic conductors, as are CrO_2 and MoO_2. There are other oxides which may be metallic conductors when non-stoichiometric, e.g. ~SnO_2, ~EuO, ~In_2O_3, etc.[17]

VO_2 is a metallic conductor at room temperature and changes to a semiconductor/insulator at 340 K.[18] A number of these oxides are superconductors at low temperatures.

The perovskites $CaVO_3$[19] and $SrVO_3$[20] are also metallic conductors.[21, 22]

The high temperature superconductors discovered in the late 1980s are also mixed oxides, e.g. "BSCO": $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+x}$ (n=1, 2, 3) and "YBCO": $YBa_2Cu_3O_{7-x}$.

The tungsten bronzes - $M_x WO_3$ ($0<x<1$) - are prepared by inserting hydrogen, alkali metals, alkaline earth metals, lanthanides, Cu, Ag, Tl, Sn or Pb, into WO_3 under reducing conditions. $NaWO_3$ was the first to be discovered, by Wöhler in 1824.[23] They have WO_3 octahedra sharing vertices and a perovskite type cubic structure for $0.3<x<1$ which shows metallic conductivity. For $x<0.3$, they have a hexagonal crystal structure and are low temperature superconductors (T_c <10 K). Mo(VI), V(V), Nb(V) and Ti(IV) form similar bronzes.[24]

Sulfides

There are many metal sulfides that look shiny and metallic. This may have given support to the mercury-sulfur-salt 3-element alchemical theory, as the properties of sulfides are quite variable and can be adjusted by varying the proportion of sulfur. However, most of the shiny, metallic looking sulfides are low or medium band-gap semiconductors.

Sulfides of the main group elements are semiconductors or insulators. Transition metal sulfides and lanthanide and actinide sulfides can be semiconductors, insulators or metals.

CoS_2 and CuS_2 are metallic conductors.[25] CeS is a metallic conductor, as is ThS.[26] The higher sulfides of thorium (Th_2S_3, ThS_2, etc.) are semiconductors.[27]

Some interesting semiconducting metal sulfides include FeS_2, iron pyrite or fool's gold; PbS, galena, which is dark and shiny; bornite, Cu_5FeS_4 (red-brown fresh and iridescent purplish blue when exposed to air) and CuS, covellite. These, and many others, were used for making cats whisker detectors (Schottky barrier diodes) and Perikon detectors[28] (p-n hetero-junction diodes) in the early days of radio. The first three are semiconductors and may be n-type or p-type depending on their impurities, defects and stoichiometry. CuS is automatically p-type because of its structure $(Cu^+)_3(S^-)(S_2^{2-})$ and is a very good electrical conductor. CuS is sometimes listed in reference books as a "p-type metal". It was used for the first field effect transistors (FETs) constructed in the late 1920s.[29]

Other compounds with metallic conduction

When lithium, sodium, calcium or a number of other metals are dissolved in liquid ammonia, a blue solution is formed with solvated metal cations and solvated electrons. The dilute solutions have the electrical properties expected from electrolytes. If more metal is added, a bronze phase is formed (for lithium, above a mole fraction of 0.1) which conducts electricity very well, in the range of metallic conductors.[30a] Solutions of this type are known for other solvents such as amines and ethers,[30b] but are less stable.

The preparation of potassium by electrolysis of molten KOH or KCl is more difficult than the corresponding preparations of sodium, because potassium is distinctly soluble in molten KOH or KCl. Rubidium metal is more soluble in molten rubidium salts than potassium is in its molten salts, and caesium is completely miscible with molten caesium halides. These solutions appear to be metallic solutions with free electrons, similar to the liquid ammonia solutions.[31] According to the latter reference, some earlier researchers had noticed blue or bronze colours in these solutions. This may mean that these solutions closely parallel the liquid ammonia solutions, with blue and bronze phases.

Ammonium amalgam (NH_4/Hg, CAS 26497-91-6) was discovered by T. J. Seebeck[32] (of thermoelectric effect fame) in 1808, and independently by Berzelius and Pontin[33] the same year. It appears to be a true metallic solution of ammonium in Hg, but it is unstable except at low temperatures.[33] Above 0 °C, a brown foam of NH_3, H_2 and Hg is formed.

Tetramethylammonium amalgam and other 'onium amalgams have been reported.[34,35] There has been a patent granted for hydrazinium amalgam.[36]

The lanthanide dihydrides are also metallic conductors, with delocalised electrons[37]: $Ln^{3+} (H^-)_2 (e^-)$. Some but not all of the lanthanide dihalides are metallic conductors[37]: $Ln^{3+} (X^-)_2 (e^-)$. Lanthanum also forms a metallic monoiodide LaI with a NiAs structure[38]: $La^{3+} (I^-) (e^-)_2$.

Anisotropy of metallic properties

Most metals and alloys crystallise in cubic crystal structures, so the physical properties are the same in three dimensions. It is a similar case for metals that crystallise in hexagonal crystals. There should be slight differences between the properties in the x, y, z directions and on the diagonals. Metals that crystallise in orthorhombic crystals (Ga) or tetragonal crystals (In, Sn) should show some more directionality of electric conductivity and other properties.

The metal oxide conductors BSCO and YBCO have crystal structures with elongated unit cells and they should show marked anisotropy as normal metallic conductors. When using them for making electrical wires, great care needs to be taken to have the crystals lining up at the boundaries, otherwise the wire will not exhibit superconductivity.

Antimony and grey arsenic have layer structures and should conduct electricity better in the plane of the layers. This is well-known for graphite (which has the electrical properties of a semiconductor rather than a metal).

It could also be possible for a crystal to show metallic properties in one or two directions and non-metallic properties in the others. This could be useful for making electronic devices.

The elements in the p-group near Ga, In and Sn would be a good place to look for this sort of behaviour. The elements in this zone of the periodic table are close to the border between metals and non-metals, and they can crystallise in crystals of less than cubic symmetry.

The alchemical quest, or the philosopher's stone

One objective of the alchemists was to find the "philosopher's stone", a means of converting base metals to gold. The modern industrial equivalent of the philosopher's stone is the corrosion inhibitor, which turns iron (or another base metal) into a noble metal, resisting corrosion. The physical properties of metals are not entirely fixed: they are capable of considerable variation, depending on crystal size, impurities, defects, internal stress, surface treatment, etc. This is also true to some extent of chemical properties – for instance, many metals become more easily corroded when stressed, an effect often seen with stainless steel.

When meals are electroplated, the internal stress in the metal is often very high, and this varies depending on the plating bath conditions (electrodes, temperature, chemical form, concentration and presence of additives). The chemical resistance of electroplated metals does differ depending on the type of plating bath used, and stress may be part of the explanation. Some alloys have unexpected properties e.g. electroplated tin-nickel, which looks like silver, and is relatively unreactive compared with either tin or nickel.[12]

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Correspondence

In Peter Hodder's article in the April issue of *Chemistry in NZ*, p107-109, there seem to be a couple of errors with the conductivity units. In Table 1 and elsewhere, conductivities are given as ranging from 750 to 7500 mS/cm, but this is much too high. The units should probably read microSiemens per centimetre.

In Table 5 (*Editor: Fig. 5)*, most of the increasing conductivity at pH<3 could be attributed to the hydrogen ions themselves. The equivalent conductivity of hydrogen ions in water is much more than that of other ions, and a conductivity of about 400 microSiemens/cm at pH 3, or 4000 at pH 2 is to be expected.

The electrical conductivity of water probably isn't very relevant to the bathing experience, as it isn't sensed by the skin (as far as I know). The density and osmotic pressure might be more interesting.

Robert Bennett

Author's Response:

The correspondent is correct in respect of the conductivity units – they should indeed be microSiemens cm^{-1}, i.e. mS cm^{-1}, as shown in the Thousand Springs database, from which the data were derived, rather than mS cm^{-1}.

In respect of the correspondent's comments on Fig. 5 of the article, the clarification is helpful. The near-surface oxidation processes yield waters of low pH which are highly conducting for the reason the correspondent cites.

The conductivity of these waters is a proxy for the combination of chloride ions, bicarbonate ions, sulfate ions, etc., which balneologists claimed, not always convincingly, to contribute to the waters' therapeutic properties, and presumably thereby to the bathing experience. However, Table 1 of the article shows a poor correlation of visitor rating with conductivity, much lower than with pH or turbidity, for example, so the correspondent's assertion that "electrical conductivity probably isn't very relevant to the bathing experience" is confirmed by the data. The density of the geothermal water is related to its chemical composition, and the osmotic pressure is a function of the concentration of the solute. Both parameters are thus related to the water's conductivity, so, even had the data been available, the correlation between density or osmotic pressure and the bathing experience, might not, in fact, be any more 'interesting' than those already shown in Table 1, and its associated figures.

I remain rather surprised that there was not a better correlation between water temperature and visitor rating (Table 1), but of course, other factors may contribute to visitors' willingness to 'take the waters' (Fig. 1 of this response).

Finally, the correspondent's reference to osmotic pressure caused me to wonder whether subjecting the skin – a semi-permeable membrane – to relatively high-pressure geothermal waters, as in the 'Aix douche' shown in Fig.2 of this response, would really constitute an enhancement of the bathing experience.

Fig. 1. "A Labour supporter stares in amazement at Prime Minister Helen Clark, apparently enjoying the extreme heat of a Rotorua hot pool. The Prime Minister languishes in boiling mud and is surrounded by clouds of steam. She shouts at him that compared with the last six months this is nothing. She refers to the heat generated in the House over election overspending and the saga of Taito Philip Field in particular."

Credit: DANGER! Boiling hot pool, Rotorua Council. "Compared to the last six months, this is nothing..." 28 October, 2006. Scott, Thomas, 1947- :[Digital cartoons published from 2003 onward in the Dominion Post]. Ref: DCDL-0002575. Alexander Turnbull Library, Wellington, New Zealand; see: http://natlib.govt.nz/records/22761857.

Fig. 2. "Interior view of a therapy room in the Government Sanatorium, Rotorua, New Zealand. The view shows one man on a raised bed under a shower while another man administers a massage. Two hoses on the floor are spraying both with water. A caption states that the therapy in progress is an `AIX massage douch.' Photographed by an unknown photographer in about 1926.

Credit: Aix massage douche, Sanatorium, Rotorua, New Zealand. Railways album 2. Ref: PA1-f-051-26-3. Alexander Turnbull Library, Wellington, New Zealand; see: http://natlib.govt.nz/records/22830728.

Patent Searching

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Picture this scenario: you are a researcher and you invent a new process for the extraction of gold from seawater. You're pretty excited to say the least. You take great care to avoid public disclosure, engage a patent attorney to draft and file a provisional patent application and set up a company to commercialise the process. You obtain some funding from friends and family and refine the process over the next twelve months. You file a Patent Cooperation Treaty (PCT) application funded by Angel investors. You engage project partners to help with commercialisation – a business development consultant, a chemical engineer, an accountant. The PCT application is examined by an international examiner and the examiner says that your invention is neither novel nor inventive based on the disclosure of document D1. You look at document D1. It discloses the exact same method that you invented. You check the Intellectual Property Office of New Zealand (IPONZ) patents database. A patent was granted five years ago which covers the exact same process that you believed you invented. You realise that not only is your invention not novel, but if you carry out your process, you will be infringing the existing NZ patent.

While somewhat uncommon, this scenario does demonstrate the importance of considering the *patentability* of your invention and whether you have *freedom to operate*, i.e. will you infringe someone else's patent rights.

Patentability search

The most fundamental patentability criterion is whether the invention is novel, i.e. has the invention been disclosed publicly anywhere in the world before the filing date of the patent application? A novelty search involves assessing the invention and searching for documents which disclose the invention (referred to as prior art documents). A patentability search is somewhat wider in that it also considers other patentability criteria. For example whether your invention is *inventive*, i.e. non-obvious.

The first step in a novelty search is for the searcher to intimately understand the invention and its context. For this reason it is preferable that a specialist in the particular technology field carries out the search. Once the searcher understands the technology, the invention's context in that area and the objectives of the search, they can formulate a search strategy. One part of this is choosing appropriate keywords (including common synonyms) which describe the invention. Those keywords are then used to query online databases. For some keyword combinations a large number of search hits are returned.

Since it is unpractical to trawl through thousands of documents, patent search databases typically allow you to filter by technology classification. The most common classification system is the International Patent Classification (IPC). Searching using classifications enables more focussed searching but has the downside that the classifications could be incorrect, or obscure to the non-specialist.

Scope of the search

The databases queried in a patentability search will include patent databases and may also include academic publication databases and general web searches. Some useful patent search databases include the following:

- PatentScope – developed by the World Intellectual Property Office (WIPO). Enables full-text searching of PCT applications as well as patent collections from a number of countries (USA, European Patent Office, Canada, China among others).
- Espacenet – developed by the European Patent Office (EPO), this database provides full-text searching of patent documents from multiple collections in multiple languages.
- United States Patent and Trademark Office (USPTO) Patent Databases – The USPTO was the first patent office to launch an online patent database (back in 1994). However, it suffers from usability issues and only searches US issued patents (PatFT) or published US patent applications (AppFT).
- The Lens – Open source search and patent analytics covering multiple collections.
- Google Patents – easy to use, but somewhat limited in scope, search options and analytics.

For particular inventions, specialist databases may also be searched. For example to determine the novelty of compounds, chemical formulae databases may be searched, e.g. UniChem, ChemSpider, Reaxys, SciFinder, PubChem. To determine the novelty of gene or protein sequences, sequence databases may be searched, e.g. Genbank, EMBL-EBI, Swissprot, PIR. In addition to the search providers above, there are also a number of proprietary databases that provide access and advanced search/analytics/reporting on a commercial basis.

Following initial review of the search results, the searcher will typically refine the search and search again in an iterative process. Refinements may include amending keywords/classifications, or searching by a particular company or inventor of interest.

Interpretation and analysis

Once a manageable number of search results has been obtained, the next step is to review and analyse those documents to see if the invention is novel. This involves carrying out a detailed review of the prior art document to see if it discloses *all* of the features of the invention. Going back to the example of extraction of gold from seawater, does the prior art document disclose each step of the extraction process? And does it disclose each parameter of each step? Essentially, if the document discloses all features of the invention then the invention lacks novelty.

One common issue that arises during novelty searching is the use of different terms to describe a similar concept. This can mean that the keyword combinations do not find relevant documents. Other issues include where only part of a step is disclosed (although the other part may be inherent in how the step is described), or where a slightly different process step is disclosed yet the same result is achieved.

Absence of evidence ≠ evidence of absence

Novelty searching is an essential part of the patent process and we recommend that all new inventors familiarise themselves with the prior art. An appreciation of the prior art helps the inventor and patent attorney to understand the context of the invention and the scope of protection that the applicant might ultimately be able to obtain. It can also avoid wasting time and money on pursuing patent applications for inventions that are later found to lack novelty. However, be aware that the old adage applies: *absence of evidence is not evidence of absence*. In other words, failure to find an invention after a quick google search does not guarantee novelty and that a patent will be granted. Although searching relevant databases with carefully formulated keywords is to be encouraged, it is quite common for inventors to search and find nothing when a professional searcher would find relevant prior art.

It is important to understand that there is no such thing as an exhaustive patent search. For example a prior art document published in a different language or in an obscure journal will rarely be found by an English-language search. Although a high quality novelty search will give a good idea of the prior art relevant to an invention, there is always the risk of a prior art document surfacing to torpedo your patent rights in the future. Searching simply reduces that risk. For this reason, a novelty search with a favourable opinion on patentability is a valuable tool to show to investors to reduce their perceived investment risk.

Freedom to operate (FTO) searching

This involves answering the question: Do I risk infringing another party's patent rights if I make, use or sell my product in a particular country? The key difference from patentability searching is that an FTO search is restricted to examining existing patent rights in a particular country. In contrast, a patentability search looks at the entire body of human knowledge published before the filing date. Therefore FTO searching generally provides a more definitive answer because the body of knowledge being searched is limited.

A typical FTO search strategy involves understanding the technology in question and identifying all features that may present an infringement risk. The relevant Patent Office database is then searched using selected keywords. Some Patent Office databases allow full-text searching of patent documents. Others, e.g. the Intellectual Property Office of New Zealand (IPONZ) only allow searching of the title and abstract of the patent. Full-text searching allows deeper analysis but can provide unmanageable numbers of search results. On the other hand, title/abstract searches are more focussed but can miss documents with undescriptive titles or terms in the abstract. FTO searching can be refined by searching for particular companies or individuals known to be active in the tech area being considered.

If relevant documents are found in the FTO search, the patent *claims* should be analysed in detail. It is the claims that define the exact scope of monopoly of the patent and therefore what a party must do to infringe the patent. Claim interpretation and infringement analysis requires a good understanding of the patent law and practice of the country in question and should only be undertaken by an experienced patent attorney.

A major limitation of FTO searches is that they only provide accurate information on granted patents. In most countries the specification of a pending patent application is not even published until 18 months after the date the application is first filed. These unpublished applications will not be uncovered by an FTO search. Pending patent applications may be in the patent pipeline for a number of years and their ultimate scope of protection (and the associated infringement risk) only becomes known close to the patent being granted.

Freedom to operate searching is a risk management strategy that should be employed before entering a new market. Even where no infringement risk is found, targeted FTO searching can provide valuable market intelligence on technology trends and emerging key players.

The bottom line

The most important fact to consider about patent searching is that one can never be certain that every relevant patent has been located. Therefore, a balance needs to be struck between the thoroughness of a search and the cost involved. For novelty searching, where this balance lies often depends on the value of obtaining patent rights and the consequences of uncovering relevant prior art down the line. For FTO searching factors to consider include the total value of the project, and the consequences of having to remove the product/service from the market (or negotiate with the patentee). In both cases it is advisable to conduct searching early on to avoid setbacks later.

If you have any queries regarding intellectual property related matters (including patents, trademarks, copyright or licensing), please contact: tim.stirrup@baldwins.com Baldwins Intellectual Property, PO Box 5999, Wellesley Street, Auckland. www.baldwins.com

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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.

Henry Edward Armstrong, FRS (1848-1937)

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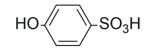
Henry Edward Armstrong was born on May 6, 1848 in Lewisham, then a part of Kent but now South-East London.[1] He was the first of seven children to Richard and Mary (née Biddle) Armstrong. His parents had eloped and married before they were 21 years of age in 1847 and Henry is cited as a 'seven-months child'.[2] The Armstrong family saw Henry's parents remain in Lewisham for the rest of their lives, while Henry lived there for his entire life, except when overseas.[1,2] The mid-nineteenth century had Lewisham as a country village beginning to provide homes for London businessmen who liked the country air. Although the Armstrong home was always there, they moved houses as Richard's fortunes rose and fell from his position as a commission agent and importer of Mark Lane in the city of London. Thus, Richard Armstrong was a businessman with sufficient income to support his wife and increasing number of children in fair comfort. Sadly, only four of the seven children survived childhood.

Henry's home in Lewisham was on Avenue Road, a street that now has disappeared and is replaced by what is the main entrance to The Lewisham Centre. After attending a number of small schools, Henry moved to Colfe's Grammar School on Lewisham Hill bordering on Greenwich, to which he walked from home. It remains one of the oldest established schools in London. He left there at age 16 years with 'no particular interest, but observant and an experimentalist' and was thought to be 'delicate'.[1] Because of this, he spent the following winter in Gibraltar with his uncle, likely on the recommendation of his grandfather who had been Governor of the Convict Prison there. He returned to Lewisham in the spring of 1865 and 'just slid into chemistry' as his father let him attend the Royal School of Chemistry (RSC) on Oxford Street.[1] That was for the summer term of 1865 just before the noted August Wilhelm von Hofmann returned to Berlin and Henry was taught by Edward Frankland.[3] Chemistry was the only subject available at the RSC and so Armstrong took other courses at the affiliated Royal School of Mines given by Tyndall, Huxley and Ramsay. Keeble[2] also tells us that Henry attended the operating theatre of St. Bartholomew's Hospital regularly on Saturdays, a factor in his subsequent career.

After 18 months of study, Frankland took Henry Armstrong into his private laboratory as his personal assistant and it was there that Henry began his first research. Frankland had been appointed as one of three to a Royal Commission tasked with enquiry into the pollution of England's rivers and waterways.[3] Armstrong's task was to devise ways of estimating the organic impurities in sewage and of sewage matter in drinking water. For this Armstrong and Frankland established a successful combustion method in vacuum that led to Frankland's analysis of the British water supply. Not surprisingly, after about one year, Armstrong left to study for his PhD. Kolbe, in Leipzig, had been mentor to Frankland and it was to him that Frankland sent Henry. There, in October 1867, Henry was introduced to the sulfonic acids and the interest enkindled in Henry by this class of compounds remained with him throughout his life. In fact,[2] the day that Henry arrived was spent nitrating 4-hydroxyphenylsulfonate (**1**). He spent the next five semesters studying under Kolbe, the beginning of his lifelong study of aromatic compounds. The master's, '*Try it, Try it*' had a lasting impact on Henry, who gained his PhD in 1869 for a thesis the essence of which was published in the *Proceedings* of the Royal Society that year.[4] Armstrong returned to London in 1870 taking up residence back in his parents' home, though in another house on Belmont Hill. There, living next door but one in her parents' home, he met Frances Louise Lavers, who he subsequently married on August 30, 1877.



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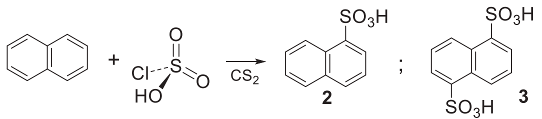
On his return to London, Henry gained a position as assistant to Dr Matthesson at St. Bartholomew's Hospital, teaching chemistry to the medical students. He held this post for 12 years until Matthesson died. Then, in 1871, he gained another part-time appointment as Professor of Chemistry at the London Institution where he taught classes from 6-8 pm on 'analytical chemistry and methods of original investigation'.[1,2] The salary for this was low (£50 pa) but he had a private laboratory though no allowance for it or the necessary supplies! The lab, little more than a coal-hole, was close to the lecture theatre and it was there that Henry Armstrong began his extensive studies of the constituents of coal-tar. The rather unpleasant odours from the higher boiling fractions had a lasting impact on the pupils and teachers using the lecture room. The income from his two posts was insufficient to maintain a professional scientist, let alone the prospects of house and family. Thus, Henry supplemented his income by writing, examining, abstracting (for the Chemical Society *Journal*) and as a professional witness in legal chemical technology cases. It was from the exposure to examination and cross-examination protocols and the need for precision in speaking, which, when coupled with Kolbe's incisive style, made Armstrong the unpleasant critic that he described himself to be.[1,2] The various part-time occupations resulted in Armstrong regarding himself as a 'free-lance and iconoclast'.[1]

Armstrong's life work began in 1879, some 16 months after his marriage. At age 31, he was appointed by the City and Guilds (of London Institute for the Advancement of Technical Education) with William Edward Aryton, a physicist and electrical engineer, to organise classes in chemistry and physics. The appointments stemmed from lengthy discussions after the 1851 Exhibition and a definite 1876 decision to explore *Technical Education* by the City Livery Companies of London. It led to the establishment of the City and Guilds Institute in 1878 and Henry's appointment. The classes by Armstrong and Ayrton in Cowper Street, Finsbury, were, in essence, a trial to see how their subjects could best be taught. The fact is they became so popular that a separate specially adapted building was needed. The Finsbury Technical College was created as the first institution of its kind in the city. However, the focus of the City and Guilds was the establishment of the Central Institution (later the Central Technical College) and the expertise of Armstrong and Ayrton was utilised to the full in realising this. The pair went on a tour of laboratories in Germany during the autumn of 1881, each to study the nature of those for his subject. It was from these times that Armstrong's lifelong interest and impact on the teaching of chemistry is dated.

Following the Armstrong-Ayrton report to the City and Guilds, changes were made to the Central Institute, and then the Central Institution for more advanced study (in Exhibition Road, South Kensington) was opened by the Prince of Wales in 1884. Henry Armstrong was appointed as inaugural Professor of Chemistry and, after some persuasion, William Edward Aryton the inaugural Professor of Physics. There were two other professors, namely W.C. Unwin (Engineering) and O. Henrici (Mathematics). Henry Armstrong remained at the Central until it became a part of the Imperial College of Science and Technology in 1911. By then, 27 years later, Armstrong was 63 years old and required to retire upon the closure. He was given the title of Emeritus and the use of a private laboratory; all his students had left by 1914.

Armstrong's work falls into three categories, the chemical research that started at the London Institution, his interest in and impact on chemical education, and his other activities almost always related to chemistry. It was from Armstrong's chemical researches that his name was recognised far beyond England. His studies, the most substantial covering the chemistry of naphthalene, started in the mid-1870s and provided some 60 short papers, mostly published in the *Proceedings* of the Chemical Society. At its inception, little was known about naphthalene, its derivatives or its chemistry, and industrialists in the dyestuffs industry were only just beginning to see the potential of its compounds. Conceived when Henry was intimately involved in establishing technical education for students in industry, the very extensive and analytically detailed examinations of sulfonation and other reactions, delineated the nature of the ring and the orientation of substitution, results that were of immense value to the dyestuffs industries.[1] The difficulties experienced in separating mixtures of sulfonic acids led Armstrong and Wynne to use chlorosulfonic (chlorosulfuric) acid as their sulfonating agent for naphthalene; they obtained a single product, naphthalene-1-sulfonic acid (**2**; Scheme 1). When **1** was treated with slightly in excess of two molar equivalents of chlorosulfonic acid, diacid 3 was obtained and identified as the 1,-5-derivative.



Scheme 1

In order to complete this series of studies accurately, Armstrong chose to settle a series of reference compounds and, in so doing, he prepared and characterised all ten theoretically possible dichloronaphthalenes (Chart 1), eliminating two that had been proposed incorrectly.[5] The study was experimentally demanding, requiring high experimental accuracy. Many of the compounds were confirmed by synthesising them from different starting compounds of known configuration, a masterpiece of synthetic and analytical accuracy from the late 19th century. The studies led to explanations for the speeds (rates) of certain reactions that included the industrially important diazotisations. By the end of 1895, Armstrong and Wynne had prepared and characterised all 14 of the trichloronaphthalenes, four of which melt over the narrow 90-92 °C range. Each was synthesised in a quantity of between 35 g and 50 g. All of his work on the naphthalenes was geared to establishing the factors that govern substitution in the nucleus.

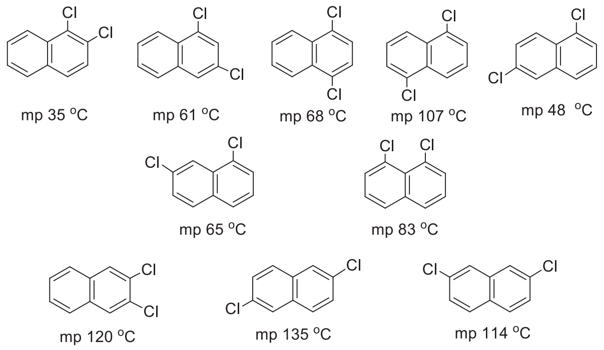


Chart 1. The ten dichloronaphthalenes with their 1888 mp data - see ref. 5

Armstrong was just as interested in the benzene series of compounds and, although much of the nature of substitution had been established by the time he was able to contribute, his study of the sulfonation of aniline and its derivatives had impact as it established that *meta*-directing groups have no *ortho/para*-directing influence and actually inhibit it. By way of example, Armstrong and his students showed that when amines are converted into salts their *o/p* effect is negated and that, in strong fuming sulfuric acid, metanilic acid (3-aminobenzenesulfonic acid) is obtained. With Miss Evans, he showed that *N.N*-dimethylaniline affords the *p*-sulfonic acid with chlorosulfonic acid, but the *m*-acid is formed only with increasing difficulty and then only when fuming sulfuric acid is the sulfonating agent. However, it is Armstrong's concepts of the benzene nucleus and his extension to the benzo-fused derivatives

that gained attention and it has an element of satisfaction associated with it. Armstrong found that the Kekulé formula for benzene did not provide him with an adequate mental picture of the molecule free from the ambiguity of formal p–bond character. In 1887, he suggested that the molecule was better represented by a 'centric' representation as had been proposed[6] by Lothar Meyer in 1872. Here Armstrong suggested that the fourth valency of each carbon atom was directed towards the centre of the molecule resulting in increased centric density. The six central affinities were assumed to neutralise each other without implying any cross-linking within the ring. Remember that the electron was neither named nor discovered until the 1890s and Armstrong's 'affinity' was, in essence, the electron. The centric form was independently proposed by Baeyer in 1892 as the Armstrong-Baeyer centric formula and it was extended satisfyingly by Armstrong to the annulated derivatives, naphthalene, anthracene and 9,10-anthraquinone as shown in Chart 2. Henry essentially invented the concept of delocalisation when he said that any one atom has an influence on other atoms not contiguous to it in the ring.[7] These late 1880 ideas were so close to the modern theory of chemistry that it is surprising he never drew the appropriate conclusions once the electron was known.[7]

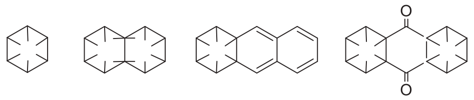


Chart 2. Centric formulae proposed by Armstrong

Another important aspect of Armstrong's legacy is his inclusion of crystallography in teaching. He instilled into his students the need to think not just in one but in three-dimensions. He took crystal properties to the chemist and showed that it did not belong solely in the realm of the mineralogist. His own classes at the Central Technical College were the first to impart the ideas and subsequently he arranged for courses on crystallography to be taught from 1886. His publications invariably include a detailed description of the crystals of each new compound reported.

Armstrong made significant contributions to the dyestuffs industry as has already been alluded to. He also instigated the quinone theory of colour, which became a guiding principle to the industry.[8] Although his experimental work in this area was minimal, he proposed that "*the unsaturated hydrocarbons are not only more reactive than the paraffins but the beginnings of colour are manifest in them if examination be made in the regions above and below the visible spectrum*" and that "*the quinonoid origin of visible colour appeared so general that if a coloured compound was not quinonoid its formula was suspect*". More importantly, he claimed that "*ultimately colour would be traced to that peculiar condition represented conventionally by a double bond, the atoms being regarded as altogether subordinate*". All this before the electron was known or conjugation recognised!

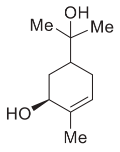
Other inspirational insights from Armstrong can be given by way of snippets from his 19th century writings that predate chemical discovery of the facts. Thus, he believed that in water, HCl interacted with the solvent in the same way as did ammonia, that all chemical change was electrical in nature (a forethought to reaction mechanism?), that mixtures of pure hydrogen and pure oxygen would not be explosive, and that atmospheric corrosion (rusting) would be impossible even in the presence of air and water if an electrolyte were absent.

The educational impact of Henry Edward Armstrong was especially significant to chemistry in the last 20 years of the 19th century and laid the foundation for teaching in the first half of the 20th century. Henry concluded early in his career that the deficiencies in the knowledge of the average boy coming into advanced classes were a result of bad elementary education. He was convinced that higher education in technical subjects could only succeed from a sound educational basis. Thus, in 1884 he proposed teaching the general science of daily life at school by having students perform simple practical experiments. This formulated his heuristic approach to teaching – learn from doing, not simply from a static dogmatic collection of facts – a revolutionary concept at the time. Henry led his students through experiment to self-discovery. He was quoted as saying: "*If the Almighty were in the one hand to offer me Truth and in the other the Search after Truth, I would humbly but firmly choose the Search after Truth*". He was among the first to base instruction and writing in chemistry upon Mendeleev's periodic table and, early on, he emphasised that molecules must have spatial configurations that determine crystal structures.

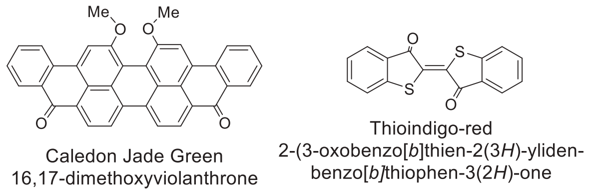
From 1887 Armstrong served on two important education committees - that of the British Association charged with reporting on teaching methods, the other on the teaching of chemistry. The reports were influential[9] in bringing about the changes that Armstrong saw as vital for science (and chemistry) but it took many years before the recommendations had any real effect. Nevertheless, it was Armstrong who had the foresight to see what was needed and it is he to whom science education is much indebted. Henry fought the conservative spirit that pervaded much of society all of his life. That his views were still not fully accepted, even after his death, is nicely illustrated[1] by a 1940 letter from Plymouth school teacher A.G. Lowndes in *Nature*. Lowndes states:[10] "*As pointed out by the Editors of NATURE a large majority of the boys complete their 'formal' education at the School Certificate stage and for this 'formal' education practical work is unnecessary. Had I my own way, ….. I would make every boy in a public school learn Latin until he were either fifteen or had passed the School Certificate. Two good science lectures weekly with demonstrations are all that are required*"!

At the Central Institution in South Kensington, Henry lectured only to the first-year students espousing the view that the ground-work was the most important, a feature common in Commonwealth Universities until the latter part of the 20th century. His lectures covered much ground and were filled with demonstrations that almost always worked. For the senior levels he led discussions rather than held formal lectures (the modern tutorial!). Armstrong was a Governor of St. Dunstan's College in Catford, neighbouring on to Lewisham, and Christ's Hospital, a co-educational school established in 1552 for the orphan children of poor Londoners in the old Grey Friars buildings on Newgate Street in the City. To this latter school he gave great service, especially after its removal to West Horsham in Sussex in 1902 when he designed and equipped its laboratories. It was the best school for science teaching in England. Henry also set up workshops for manual training and revolutionised art training. Armstrong was deputy chairman of Christ's education committee for 14 years from 1926 and its Chairman until 1937. There can be no doubt that significant changes did take place in the 50+ years after Armstrong began his educational campaign. That they happened at all are in very great measure due to him.

Henry Armstrong also had much interest in agriculture that likely started with his upbringing in rural Lewisham. This impacted on his chemistry with his major contributions to terpene and camphor research that date from 1878 and involved the isolation of the D- and L-forms of sobrerol (**4**), which he named after Ascanio Sobrero, its 1851 discoverer. He became associated with the Rothamstead Experimental Station in Harpenden, Hertfordshire. He served as the Chemical Society representative of the Lawes Agricultural Trust Committee from its establishment in 1889 until shortly before his death in 1937. It was his efforts that persuaded the Indian Government to set up a research institute for the cultivation of indigo in 1915. His strong support of the British Dyestuffs industry extended to his personal proffering of its wares. He wore brightly dyed waistcoats at formal evening functions. One such piece of clothing, a Caledon Jade Green, has been described as the most becoming, but another of indigo-blue with thioindigo-red (Chart 3) facings was the most striking. Both are Vat Dyes that had to be reduced to make them inert and water soluble prior to the dyeing process, then oxidised to regenerate the original colour.



4, sobrerol



Caledon Jade Green
16,17-dimethoxyviolanthrone

Thioindigo-red
2-(3-oxobenzo[*b*]thien-2(3*H*)-ylidenbenzo[*b*]thiophen-3(2*H*)-one

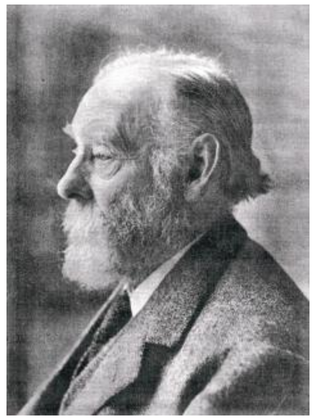
Chart 3. Dyes used in Armstrong's waistcoats

Henry Armstrong was a strong supporter of the Royal Society of Arts.[11] The first meeting that he presided at was in 1883 and he occupied the chair seven times. He provided lectures on *Problems of food and our economic policy* in 1919, and two courses of Juvenile Lectures entitled: *How chemists work* (1889) and *Alice in Wonderland at the breakfast table* (1926). He was awarded the Society's silver medal for a lecture on *the indigo situation in India* and its Albert Medal for his discoveries in chemistry and his services to education.

Much of what Henry Edward Armstrong foresaw has come true and many of his beliefs of what should be studied formed the basis of much late 20th century research. Several remain current areas of intense activity and include dyes and dying (now nano-particle involvement), agricultural chemistry, diet and nutrition, and collaborations and joint interdisciplinary publication. In many respects, Henry Armstrong was a man before his time. His educational writings are listed for completion.[12]

Armstrong was awarded a Hon. LLD from St. Andrews, Hon. DSc degrees from Melbourne and Madrid, the Davy medal of the Royal Society, the Messel medal of the Society of Chemical Industry, the Albert medal (see above), and the Horace Brown medal of the Society of Brewing. He served the Chemical Society for many years ruling it with 'an iron rod'[1] as Secretary from 1875-1893 and serving as President from then until 1895. Following this tenure, he took the role of Vice-President until his death save for two short breaks. He was, in essence, a member of the Council almost continuously from 1873 until 1937.

Upon marriage to Frances Lavers in 1877, Armstrong purchased his own home in Lewisham – one that his father had previously owned! The couple had seven children, four boys of whom industrial chemist Edward Frankland Armstrong (1878-1945) was the eldest, and three daughters. In 1882 the family moved to Granville Park in the same town and that was their permanent home. Their youngest daughter Nora never married but looked after her parents until their deaths, Frances in 1935 and Henry some two years later on July 13, 1937.



H.E. Armstrong in later life from ref. 2; source unknown

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Dates of Note

July

21 ***Henri-Victor Regnault***, the French chemist and physicist noted for his work on the properties of gases, was born in 1810. This day in 2000 an international collaboration of scientists at the Department of Energy's Fermi National Accelerator Laboratory announced direct evidence for the subatomic particle, the tau neutrino, the third kind of neutrino known to particle physicists.

25 ***Rosalind Franklin***, the English crystallographer who contributed to the discovery of the molecular structure of DNA, was born this day in 1920, the day that ***Herbert Calhoun Reed***, the American chemist noted internationally as an analytical and consulting chemist to the leather industry and allied trades, died in 1940.

26 1895 saw the day that ***Pierre Curie*** married ***Marie Sklodowska*** (Curie) in Sceaux, France. It was the following year that she decided to investigate Henri Becquerel's discovery of radioactivity in uranium for her doctoral thesis.

27 ***Bertram Borden Boltwood***, the American chemist and physicist whose work on the radioactive decay of uranium and thorium was important in the development of the theory of isotopes, was born in1880.

29 ***Heinz L. Fraenkel-Conrat***, the German-American biochemist who first showed that reproduction of a virus is controlled by genetic information within its RNA core, was born in 1910.

31 ***Friedrich Wöhler***, the German chemist who co-discovered vanadium but is best known for his 1828 synthesis of urea from ammonium cyanate to create an organic compound from an inorganic one, was born in 1800.

August

1 ***Georg von Hevesy***, the Hungarian-Danish-Swedish chemist awarded the 1943 Nobel Prize for his isotopic tracer techniques, was born in 1885, the day that ***Otto Warburg***, the a German biochemist who was awarded the 1931 Nobel Prize for Physiology or Medicine for his research on cellular respiration, died in 1970.

3 ***Guillaume François Rouelle***, the French apothecary and chemist who first proposed the modern definition of salts and distinguished acid, basic and neutral salts, died in 1770.

6 ***Joseph-Achille Le Bel***, the French chemist who presented a theory on the relationship between molecules and how they absorb or reflect light, and predicted that optical activity is due to an asymmetric carbon atom bound to four different groups, died in 1930.

8 1955 saw the opening of the Geneva Conference on the Peaceful Uses of Atomic Energy - known as the atoms for peace conference.

10 ***Henry Gwyn-Jeffreys Mosely***, the English physicist who experimentally demonstrated that the major properties of an element are determined by the atomic number and not by the atomic weight, died 100 years ago.

11 ***Erwin Chargaff***, the Austrian-American biochemist who studied the nucleic acids chromatographically and enunciated two rules that helped determine the double helix, was born in 1905.

12 ***James Batcheller Sumner***, the American biochemist who was the first to crystallise an enzyme to show that enzymes were proteins and shared (with Northrop and Stanley) the 1946 Nobel Prize for Chemistry, died in 1955.

13 ***John Ulric Nef***, the Swiss-American chemist whose studies demonstrated that carbon can have a valence of two, e.g. in a quinone, as well as four, died this day 100 years ago.

15 ***Constantin Fahlberg***, the Russian chemist who discovered saccharin, died in 1910.

18 ***Friedrich Strohmeyer***, the German chemist who discovered the element cadmium in 1817, died in 1835.

19 ***Johan Gottlieb Gahn***, the Swedish mineralogist and crystallographer who improved smelting methods and by-product usage, discovered manganese and selenium, and assisted Carl Wilhelm Scheele, was born in 1745. This was the day in 1765 that ***Axel Fredrik Cronstedt***, the Swedish chemist and metallurgist who first isolated nickel, died in1765, and that ***Lothar Meyer***, the German chemist who discovered the Periodic Law independently of Dmitry Mendeleyev and at about the same time, was born in 1830.

20 ***Paul Ehrlich***, the German medical scientist whose pioneering work in chemotherapy included the discovery of Salvarsan (arsphenamine), died this day 100 years ago.

23 Sir ***Henry Tizard***, the English chemist whose work on aircraft fuels ultimately led to the octane rating system, was born in 1885.

25 Sir ***Hans Adolf Krebs***, the German-born British biochemist who received (with Lipmann) the 1953 Nobel Prize for Physiology or Medicine for discovering in living organisms the series of chemical reactions known as the tricarboxylic acid cycle (or the citric acid cycle) better known as the Krebs cycle, was born in 1900.

26 ***Hedley Marston*** was the Australian biochemist who researched the role of cobalt and other trace elements in animal and plant nutrition. He is remembered for announcing at the 1935 ANZAS meeting that a wasting malady of sheep in certain coastal regions was corrected by giving cobalt salt supplements. He was born in 1900. It is the day that ***Johann Friedrich Miescher***, the Swiss biochemist and biologist who studied cell metabolism and discovered the nucleic acids, died in 1895.

27 Gallium was discovered by ***P.E. Lecoq de Boisbaudran*** in 1845.

28 1845 saw the first issue of *Scientific American* published.

30 Sir ***Joseph John Thomson***, the English physicist who discovered the electron, died in 1940, 75 years ago.

September

5 ***Frederick George Donnan***, the British chemist whose research contributed to the development of colloid chemistry and who is remembered for his investigation of the Donnan Effect (1911) that advanced the understanding of the living cell, was born in 1870.

6 ***Phoebus Levene***, the Russian-American chemist who found that the carbohydrate present in nucleic acid from yeast is the pentose sugar ribose, died in 1940, 75 years ago.

7 ***Rodney Porter***, the British biochemist who (with Edelman) was awarded the 1972 Nobel Prize in Physiology or Medicine for discoveries concerning the chemical structure of antibodies, died 30 years ago.

8 ***Hermann Staudinger***, the German who received the 1953 Nobel Prize for Chemistry for discovering of the structure of polymers as long-chain molecules and coined the term *macromolecule*, died 50 years ago, as did ***Willard Frank Libby***, the American chemist who devised carbon-14 (or radiocarbon) dating, the same day in 1980.

9 ***Paul J. Flory***, the American polymer chemist and recipient of the Nobel Prize for Chemistry in 1974 for his synthetic and natural macromolecules studies, died in 1985.

10 ***John Kidd***, the English chemist and physician who obtained and named naphthalene in 1819, was born in 1775.

11 This day in 1940 saw the first demonstration of remote computing by teletype.

16 ***Gordon Gould***, the American physicist who coined the word *laser* from the initial letters of Light Amplification by Stimulated Emission of Radiation, died 10 years ago today.

19 ***John Kenneth Harold Inglis***, Professor of Chemistry at the University of Otago, died on this day in 1935.

22 ***Alice Hamilton***, the American known for providing safer working conditions by investigating mines, mills, and smelters, concentrating on lead, aniline dyes, picric acid, arsenic, carbon monoxide, and other industrial poisons, died in 1970 aged 101.

23 ***Clifford G. Shull***, the American physicist who shared the 1994 Nobel Prize for Physics (with Brockhouse) and developed the neutron diffraction process, was born 100 years ago.

24 ***Severo Ochoa***, the Spanish-American biochemist and recipient of the 1959 Nobel laureate for his discovery of an enzyme in bacteria that enabled him to synthesise ribonucleic acid (RNA), was born in 1905. ***Georges Claude***, the French chemist, engineer and inventor who invented the neon light, was born in 1870, while ***Hans Geiger*** of Geiger counter fame died that day in 1945. ***Hermann Hellriegel***, the German chemist who discovered the fixation of nitrogen by certain legumes, also died on this day, but in 1895.

25 ***William Cumming Rose***, the American biochemist who determined the role of amino acids in nutrition, showed which were essential and calculated the minimum daily requirement for each of them, died in 1985.

28 ***Paul-Urich Villard***, the French physicist and chemist who identified gamma rays, was born in 1860, the day ***Louis Pasteur*** died in 1895.

29 ***Peter Dennis Mitchell***, the British chemist and 1978 Nobel Laureate in Chemistry who clarified how ADP is converted into the energy-carrying ATP, was born in 1920.

30 Sir ***Robert Abbott Hadfield***, the English metallurgist who developed manganese steel died in 1940, 75 years ago, as did ***Charles Richter***, of Richter scale fame, in 1985.

October

2 ***Robert Runnels Williams***, the American chemist and first to synthesise thiamine (vitamin B_1), died in 1965.

3 On this day in 1805, the first US pharmacopoeia was prepared.

4 ***Michael Smith***, the Lancastrian born Canadian biochemist who won (with Mullis) the 1993 Nobel Prize for Chemistry for his development of a technique called oligonucleotide-based site-directed mutagenesis, died in 2000.

6 1790 saw ***Jacob Schweppe*** show his process for making artificial mineral water.

7 1970 saw BP make the first big oil find in the British sector of the North Sea and the day that ***Niels Bohr***, the Danish physicist and first to apply the quantum theory to the problem of atomic and molecular structure, was born in 1885.

8 ***Henry-Louis Le Chatelier***, best known for the principle named after him, was born in 1850.

11 ***Fausto D'Elhuyar***, the Spanish chemist and mineralogist who assisted his older brother Juan José in experiments to separate tungsten from its *wolframite* ore two years after Scheele had discovered it, was born in 1755. It was the day that ***Heinrich Caro***, the German chemist who invented new industrial chemical processes that enabled the German company BASF to become the leading manufacturer, died in 1910.

12 Sir ***Arthur Harden***, the English biochemist who shared (with Euler-Chelpin) the 1929 Nobel Prize for Chemistry for work on the fermentation of sugar and the enzyme action involved that set biochemistry as a separate discipline, was born in 1865, 150 years ago. ***Paul Hermann Müller***, the Swiss chemist who received the 1948 Nobel Prize for Physiology or Medicine for discovering the potent toxic effects on insects of DDT, died this day 50 years ago. ***Franz-Joseph Müller von Reichenstein***, the Austrian mineralogist and mining engineer who discovered tellurium in 1782, was born on July 1, 1740 and died on this day in 1825.

14 ***Friedrich Wilhelm Georg Kohlrausch***, the German physicist who investigated the properties of electrolytes, was born in 1840, while ***Heinrich Kayser***, the German physicist who discovered the presence of helium in the Earth's atmosphere, died the same day in 1940, 75 years ago.

15 ***Konrad Bloch***, the German-born American biochemist who shared the 1964 Nobel Prize for Physiology or Medicine (with Lynen) for their discoveries concerning the natural synthesis of cholesterol and of fatty acids, died in 2000. This is also the day that ***Herbert Henry Dow***, the noted industrialist and pioneer in US chemical industry, died in 1930.

17 ***William Cookworthy***, the English chemist who pioneered the manufacture of porcelain in Britain, died in 1780. This day in 1855 saw the Bessemer steel process patented.

18 In 1955 the discovery of the sub-atomic particle, the negative or antiproton, was reported at UC-Berkeley.

19 Sir ***Charles Wheatstone***, the English physicist who popularised the Wheatstone bridge, died on October 19, 1875.

Conference Calendar

2015 Society of Environmental Toxicology and Chemistry (SETAC) Australasia Conference

The Rutherford Hotel, Trafalgar Square, Nelson, New Zealand

25-28 August 2015

Abstract submissions close 8 May 2015

The conference will provide a great opportunity to showcase your latest research results and discuss with colleagues from other SETAC regions. The ambitious theme is 'System Approach to Environmental Management' and recognises the continuity of environmental processes in space and time, a concept that can enable us to better manage the environment and develop more sustainable solutions. Both novice and experienced presenters are encouraged to submit an abstract for either an oral or poster presentation. The social programme, as with all SETAC conferences, will provides plenty of opportunities for delegates to network with colleagues with various expertise.

To maximise the value of your travel to New Zealand, the conference organisers have coordinated with Ecobiorefinery 2015, which will be held in Rotorua from 30 August - 4 September.

www.setac2015.org.nz

Pacifichem 2015

Honolulu, Hawaii, USA

15-20 December 2015

The theme of Pacifichem 2015 is Chemical Networking: Building Bridges Across the Pacific, emphasizing the collaborative nature of chemistry as a multidisciplinary science and the opportunities to network with Pan-Pacific research groups at the Pacifichem meetings.

The conferences has eleven topic areas:

Core areas: analytical, inorganic, macromolecular, organic, physical, theoretical and computational

Multidisciplinary or cross-disciplinary areas: agrochemistry, environmental, and geochemistry, biological and materials and nanoscience:

Chemistry solutions to global challenges: chemistry of clean energy conversion, storage, and production, bench to bedside: chemistry of health care and connecting chemistry to society

www.pacifichem.org

Chemistry, Chemical engineering and Chemical Process (CCECP 2016)

Hotel Fort Canning, 11 Canning Walk Singapore

18-19 January 2016

Full paper submission by 13 July 2015

The conference aims to foster and conduct collaborative interdisciplinary research in state-of-the-art methodologies and technologies within Chemistry, Chemical Engineering and Chemical Process. The meeting aims to foster attract participants with different backgrounds, to foster cross-pollination between different research fields, and to expose and discuss innovative theories, frameworks, methodologies, tools, and applications.

http://chemistry-conf.org/index.html